A KINETIC STUDY OF THE

TERMINATION AND DECOMPOSITION REACTIONS OF

THE CYCLOHEXADIENYL RADICAL IN THE GAS PHASE

by

ROBERT DAVID SUART

B.Sc., University of British Columbia, 1962

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ABSTRACT

The photolysis of azomethane, di-isopropyl ketone and azoisobutane has been examined briefly in the gas phase and these compounds have been found to be convenient sources of the methyl, isopropyl and tert-butyl radicals respectively.

The photolysis of the mixed vapours of cyclohexadiene-1,4 with each of azomethane, di-isopropyl ketone and azoisobutane has been examined over a series of temperatures. These studies afforded the Arrhenius parameters for the abstraction of the methylenic hydrogen atom from cyclohexadiene-1,4 by the methyl, isopropyl and tert-butyl radicals. There was found no significant difference in the reactivities of these radicals towards the cyclohexadiene-1,4 substrate. The rate constants measured were

$$k_{methyl} = 10^{-12.2 \pm 0.2} \exp \frac{(-5.5 \pm 0.4)}{RT}, \quad k_{isopropyl} = 10^{-11.9 \pm 0.7} \exp \frac{(-6.4 \pm 1.1)}{RT} \text{ and } k_{tert-butyl} = 10^{-12.3 \pm 0.5} \exp \frac{(-5.3 \pm 0.8)}{RT},$$

all in cm.^{3}/molecule sec.

The cyclohexadienyl radical is generated in this metathetical reaction, and the interaction of the cyclohexadienyl radical with the various mentioned initiator radicals was examined kinetically. It was found that the interaction of alkyl radicals with the cyclohexadienyl radical produced either benzene and the hydrocarbon, RH, (disproportionation) or 1-alkylcyclo-hexadiene-2,4 (combination, I) or 1-alkylcyclohexadiene-2,5 (combination, II). The ratio of the rates of formation of the two combination products (I/II) has been found to have the constant value 0.77 ± 0.17 within the experimental error for all the alkyl radicals studied. The ratio of the rate of disproportionation to the combined rates of combination was found to vary systematically over the values 0.27 ± 0.07, 0.52 ± 0.09, and 1.33 ± 0.24 for the methyl, isopropyl and tert-butyl radicals respectively. A previous study of the ethyl radical's reactions with the cyclohexadienyl radical in this laboratory had shown that this ratio for the ethyl radical was 0.38 ± 0.03. The measured values of the termination rate ratios for the various systems are consistent with the expectation that the product of greater entropy should form preferentially and the results are considered to support the

disproportionation transition state model of Bradley and Rabinovitch.

During the photolysis of azomethane-cyclohexadiene-1,4 mixtures at lower intensisties, there was observed the formation of cyclohexene and greater than the expected amount of benzene. This was considered to arise from the decomposition reaction $C_6H_7^{\cdot} \rightarrow C_6H_6 + H^{\cdot}$. Kinetic analysis of this system has afforded an estimate of the heat of formation of the cyclohexadienyl radical, (45 $\pm$ 5 kcal./mole), and consequently of its resonance energy, (24 $\pm$ 5 kcal./mole). This has been considered to be evidence that there is an interaction of the delocalized system across the methylenic carbon bridge, since the resonance energy is substantially greater than that measured in another laboratory for the straight chain pentadienyl radical (15.5 kcal./mole).

The reactions of the isopropyl radical with the cyclohexadiene-1,3 molecule have been studied in the gas phase. The isopropyl radical adds to the unsaturated linkages with a rate constant $k = 10^{-11.9 \pm 0.2}$ exp ($\frac{-5.8 \pm 0.4}{RT}$) cm.^{3}/molec.sec. The abstraction of a methylenic hydrogen atom proceeds with a rate governed by the rate constant $k = 10^{-11.7 \pm 0.4}$ exp ($\frac{-7.1 \pm 0.7}{RT}$). Thus the metathetical reaction proceeds more slowly for the conjugated cyclohexadiene than for the unconjugated system by a factor of 1.9 at 100°. This behavior was also found for the reactions of the ethyl radical with the cyclohexadiene isomers in a previous study, and probably arises from a slightly lower free energy of the cyclohexadiene-1,3 molecule. The ratio of addition to abstraction between isopropyl and cyclohexadiene-1,3 is low, (4.3 at 100°) and degradative chain transfer has been suggested as the reason for the very low tendency of the cyclohexadiene-1,3 molecule to polymerize under homogeneous, free radical conditions.

GRADUATE STUDIES

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PUBLICATIONS

D.G.L. James and R.D. Suart - A Kinetic Study of the
   Cyclohexadienyl Radical. I. Disproportionation and
   Combination with the Isopropyl Radical. J.Am.Chem.
   Soc., <u>86</u>, 5424 (1964).

D.G.L. James and R.D. Suart - The Reactivity of the Cycl
   Polyenes towards Free Radicals. IV. Cyclohexadiene-1,
   3 and the Isopropyl Radical. J.Phys.Chem.,<u>69</u>,2362(19(

D.G.L. James and R.D. Suart - Characteristic Reactions (
   the Cyclohexadienyl Radical Below 200° C. Chem.
   Commun. 484, (1966).

Supervisor: D. G. L. James.

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INTRODUCTION

A. The Cyclohexadienyl Radical and Its Importance in Kinetic Systems

Previous work in this laboratory[1] had indicated that the cyclohexadienyl radical could be generated in the gas phase under conditions where its reactions with various alkyl radicals could be studied. Very little attention has been paid to the possibility of a comprehensive study of the pattern of interaction of a reference radical with a complete sequence of structurally related radicals. Such a study is possible and has been conducted in this work. Furthermore, there is a great paucity of data about the combination and disproportionation reactions of radicals whose free valence is extensively delocalized. Certainly termination reactions are very poorly understood theoretically, and it could be hoped that the results of a study of the termination reactions of a representative series of radicals would offer insight into the fundamental nature of these processes. Finally, the cyclohexadienyl radical is a species that is an important intermediate in a large variety of kinetic systems. This is so since the extensive delocalization of the free valence renders the radical unreactive towards the majority of molecules because of resonance stabilization. The role of the cyclohexadienyl radical in such systems is therefore, to take part in radical termination reactions. Quantitative information on the termination reactions of the cyclohexadienyl radical would be of help in the interpretation of these systems.

Many systems produce the cyclohexadienyl radical as an

intermediate. The mechanism of homolytic arylation involves derivatives of cyclohexadienyl radicals as intermediates. In this technique, radicals are generated in a solution of the aromatic substrate, but the precise mechanism through which these are converted to the ultimate products is unknown[2]. A similar mechanism presumably holds for the methylation of benzene as studied recently by Corbett and Williams[3].

Irradiation of aromatic compounds typically generates substituted cyclohexadienyl radicals[4]. Benzene has been extensively studied; recent experiments by Gaumann[5] and by Eberhardt[6] are in essential agreement, and suggest that the majority of products arise through radical reactions involving the phenyl and cyclohexadienyl radicals. Phenyl and cyclohexadienyl radicals are generated efficiently when benzene vapour is subjected to electrodeless discharge[7]. Recoil tritium atoms apparently generate the cyclohexadienyl radical in gaseous and liquid benzene[8]. Cherniak et al.[9] have shown that hydrogen atoms generally add rapidly to benzene forming cyclohexadienyl radicals.

The radiolysis of cyclohexadiene -1,4[10] also generates cyclohexadienyl radicals, and the distribution of products is generally in agreement with the benzene radiolysis experiments. The above examples indicate that the cyclohexadienyl radical is of considerable importance to a variety of processes.

As indicated above, the role played by the cyclohexadienyl radical is generally accepted to be to remove radicals from the system in radical termination reactions. Very little attention is given to the possibility that the cyclohexadienyl radical may be thermally unstable and expell a hydrogen atom because of the gain of stabilization energy attending aromatization.

$$\text{(cyclohexadienyl radical)} \xrightarrow{\Delta H} \text{(benzene)} + H\cdot \qquad \Delta H = 72 - \Delta H_f^o(C_6H_7\cdot)$$
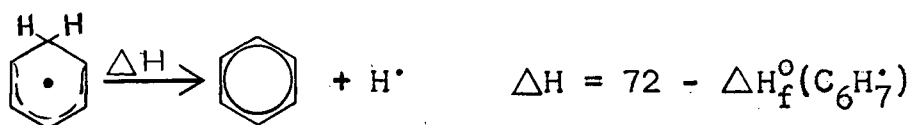
The heat required for this process is 72 kcal./mole less the heat of formation of the cyclohexadienyl radical. Benson[11] has quoted the heat of formation of the cyclohexadienyl radical as 49 kcal./mole, therefore the decomposition of the cyclohexadienyl radical would be only 23 kcal./mole endothermic and could easily be important in some systems where the radicals had a reasonably long lifetime. Such conditions are possible in this work and indeed, evidence for thermal instability of the cyclohexadienyl radical has been obtained. Kinetic study of this reaction offers the means to estimate the resonance stabilization energy of the cyclohexadienyl radical, a quantity of considerable theoretical interest. At present, the resonance energy has been calculated by Fisher[12] to be around 29 - 30 kcal./mole, a value quite high when compared to the very large value of about 37 kcal./mole for the benzene molecule. Benson[13] has recently suggested that the cyclohexadienyl resonance energy will lie between 23 and 25 kcal./mole. An earlier publication[11] listed the bond energy of the methylenic C-H bonds in the cyclohexadiene-1,4 molecule as 74 kcal./mole; this result is consistent with slightly lower resonance energy of 20.5 kcal./mole assuming that without resonance stabilization of the radical, the bond dissociation energy would be 94.5 kcal./mole, the value for the secondary C-H bond in propane.[14]

B. Techniques

Brown[1], working in this laboratory, has previously examined the reactions of the ethyl radical with cyclohexadiene-1,4, and

with the cyclohexadienyl radical thus produced. As this study
typifies much of the work reported here, it will be reviewed to
provide a convenient background.

Ethyl radicals were generated in the gas phase by the
photolysis of diethyl ketone with 3130 $\overset{o}{A}$. radiation. In the
photolysis of the pure diethyl ketone the ethyl radicals thus
generated react by combination or disproportionation, or they
can attack the ketone. The mechanism of photolysis of the pure
ketone has been shown[15-18] to be (in the range of temperatures
from 50 to 250°),

$$h\nu + C_2H_5\overset{O}{\overset{\|}{C}}C_2H_5 \xrightarrow{\text{1}} 2\ C_2H_5^{\cdot} + CO$$

$$2\ C_2H_5^{\cdot} \xrightarrow{\text{2}} C_4H_{10}$$

$$\xrightarrow{\text{3}} C_2H_4 + C_2H_6$$

$$C_2H_5^{\cdot} + (C_2H_5)_2CO \xrightarrow{\text{4}} C_2H_6 + \overset{\cdot}{C}_2H_4\overset{O}{\overset{\|}{C}}C_2H_5$$

$$C_2H_5^{\cdot} + \overset{\cdot}{C}_2H_4\overset{O}{\overset{\|}{C}}C_2H_5 \xrightarrow{\text{5}} C_4H_9\overset{O}{\overset{\|}{C}}C_2H_5$$
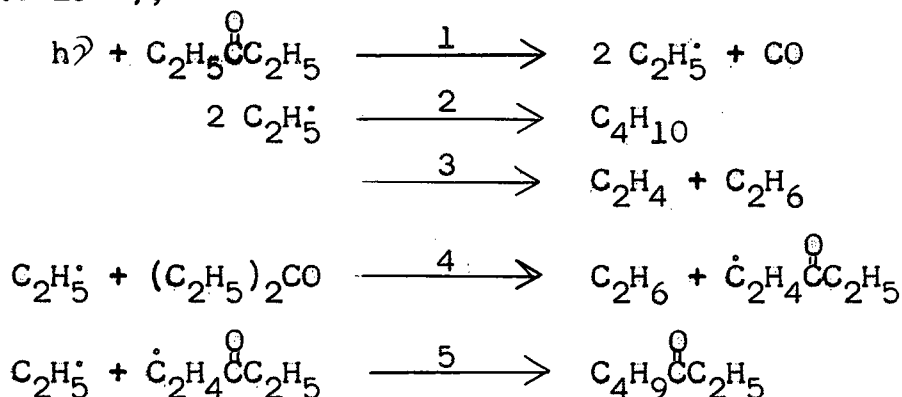
At the higher intensities of light and below 250°, reaction (5)
accounts for all of the pentanonyl radical, $\overset{\cdot}{C}_2H_4\overset{O}{\overset{\|}{C}}C_2H_5$, and a
material balance, M, may be defined as $M = (R_{C_2H_6} + R_{C_4H_{10}})/R_{CO}$,
where R_X is the rate of formation of compound X obtained by
dividing the total yield of X by the duration of the photolysis,
assuming a steady-state regime. Under the experimental condi-
tions, M has the value 0.988 ± 0.02 (Kutschke et al.) and
0.997 ± 0.03 (James and Steacie) indicating that all radicals
are accounted for by the above mechanism.

When this compound is used as a source of ethyl radicals
for experimental study of their metathetical reactions with com-
pounds RH containing labile hydrogen atoms, the ketone can be

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photolyzed in a gaseous mixture with RH. In this case, ethane
is formed in the metathesis from RH as well as from reactions (3)
and (4). The mechanism may be expanded to include this reaction
(6) under the assumption that radicals R· are lost in recombin-
ation processes. Thus:

$$h\nu + C_2H_5\overset{O}{C}C_2H_5 \xrightarrow{1} 2\,C_2H_5\cdot + CO$$

$$2\,C_2H_5\cdot \xrightarrow{2} C_4H_{10}$$

$$\xrightarrow{3} C_2H_4 + C_2H_6$$

$$C_2H_5\cdot + C_2H_5\overset{O}{C}C_2H_5 \xrightarrow{4} C_2H_6 + \dot{C}_2H_4\overset{O}{C}C_2H_5$$

$$C_2H_5\cdot + \dot{C}_2H_4\overset{O}{C}C_2H_5 \xrightarrow{5} C_4H_9\overset{O}{C}C_2H_5$$

$$C_2H_5\cdot + RH \xrightarrow{6} C_2H_6 + R\cdot$$

$$C_2H_5\cdot + R\cdot \xrightarrow{6c} C_2H_5\text{-}R \quad (c = \text{combination})$$

Now,
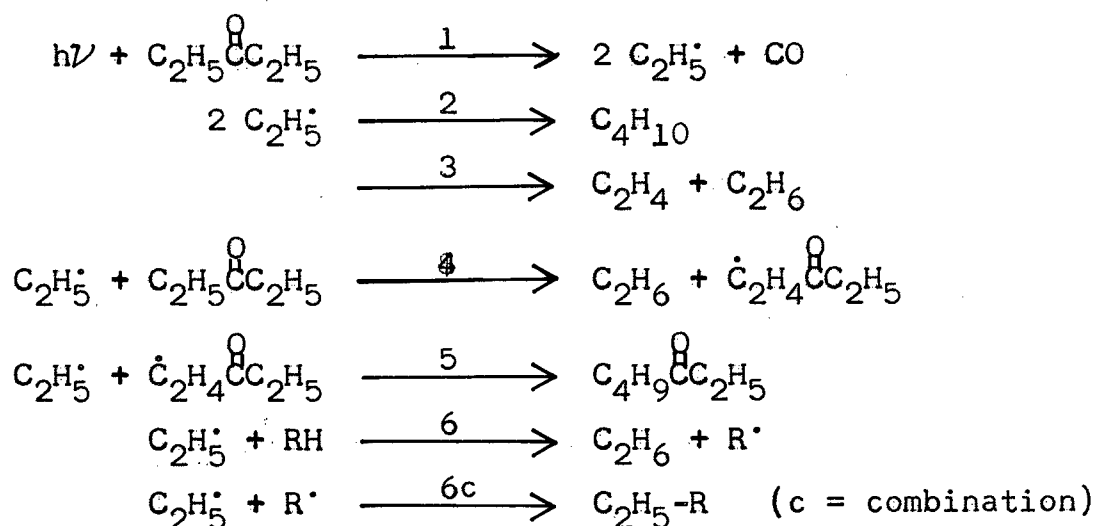
$$[Et]\,k_6\,[RH] = R_6 = R_{C_2H_6} - R_{C_2H_4} - R_4$$

$$= R_{C_2H_6} - R_{C_2H_4} - \frac{k_4}{k_2^{\frac{1}{2}}} R_{C_4H_{10}}^{\frac{1}{2}}[D]$$

where [D] = concentration of diethyl ketone and $[Et] = [C_2H_5\cdot] = R_{C_4H_{10}}^{\frac{1}{2}}/k_2^{\frac{1}{2}}$.

Therefore,

$$\frac{k_6}{k_2^{\frac{1}{2}}} = \frac{R_{C_2H_6} - R_{C_2H_4}}{R_{C_4H_{10}}^{\frac{1}{2}}[RH]} - \frac{k_4}{k_2^{\frac{1}{2}}} \cdot \frac{[D]}{[RH]}$$

Since $k_4/k_2^{\frac{1}{2}}$ is readily available from study of the pure ketone,
values of the rate constant ratio $k_6/k_2^{\frac{1}{2}}$ are available over a
range of temperatures from studies of the photolysis of mixtures
of diethyl ketone with various hydrocarbons. Insofar as measure-
ment of k_2 has been made[19] by Kutschke and Shepp,

$$k_2 = 5.06 \times 10^{-10}\exp(-2000 \pm 1000)/RT \quad (\text{cm}^3/\text{molec.sec.})$$

the values of $k_6/k_2^{1/2}$ measured can be used as a source of absolute rate constants k_6.

In the mechanism above, it has been assumed that all radicals R· are lost in recombination with ethyl radicals. It is well known, however, that radical-radical termination processes frequently involve disproportionation, as well. Thus, in addition to reaction (6c), we may imagine such processes as

$$C_2H_5^· + R^· \xrightarrow{\quad 6d \quad} C_2H_6 + R(-H) \text{ for some olefin } R(-H)$$
$$\text{or } C_2H_5^· + R^· \xrightarrow{\quad 6e \quad} C_2H_4 + RH$$
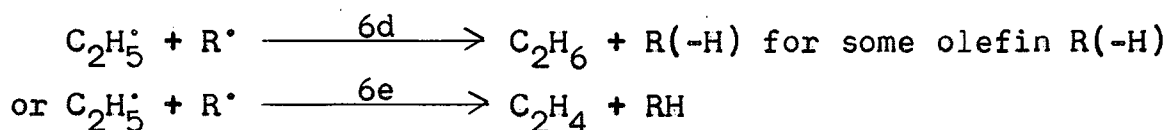
may account for some of the radicals R· formed in reaction (6). Now study of the quantity $R_{C_2H_4}/R_{C_4H_{10}} = k_3/k_2$ for pure diethyl ketone has shown that $k_3/k_2 = 0.136$ independent of temperature[20]. It has been found furthermore[1,20] that when diethyl ketone is photolyzed in mixtures of a variety of hydrocarbons, the quantity $R_{C_2H_4}/R_{C_4H_{10}}$ does not increase significantly which shows that reaction (6e) is not important. This is true of mixtures of diethyl ketone with cyclohexadiene-1,4. No such simple test exists in the case of reaction (6d) however, save actually searching for the olefin R(-H). However, since the main purpose of previous studies with ketone-hydrocarbon mixtures was to measure the activation energies for the abstraction of hydrogen atoms by ethyl radicals, the possible occurrence of reaction (6d) was not important since its effect was probably restricted to a change in the measured A factor. This would be so since probably k_{6c}/k_{6d} is independent (or nearly so) of temperature, in common with most other combination-disproportionation ratios of free radicals. Therefore R_{6d} is a constant proportion of R_6 or $R_{6d} = \emptyset R_6$ and the error incurred in neglecting

reaction (6d) is just a constant, temperature independent factor $1/(1 + \emptyset)$ which will affect only the value of $A_6/A_2^{1/2}$. In the case when RH = cyclohexadiene-1,4, however, R(-H) is the readily measured compound benzene and a means of study of the disproportionation to combination ratio of the ethyl radical with cyclohexadienyl $(C_6H_7^{\bullet})$ radical presents itself. The complete mechanism in this case is

$$(C_2H_5)_2CO + h\nu \xrightarrow{\quad 1 \quad} 2\ C_2H_5^{\bullet} + CO$$

$$2\ C_2H_5^{\bullet} \xrightarrow{\quad 2 \quad} C_4H_{10}$$

$$2\ C_2H_5^{\bullet} \xrightarrow{\quad 3 \quad} C_2H_4 + C_2H_6$$

$$C_2H_5^{\bullet} + (C_2H_5)_2CO \xrightarrow{\quad 4 \quad} C_2H_6 + \overset{\bullet}{C_2H_4}COC_2H_5$$

$$C_2H_5^{\bullet} + \overset{\bullet}{C_2H_4}COC_2H_5 \xrightarrow{\quad 5 \quad} C_4H_9COC_2H_5$$

$$C_2H_5^{\bullet} + C_6H_8\text{-}1,4 \xrightarrow{\quad 6 \quad} C_2H_6 + C_6H_7^{\bullet}$$

$$C_2H_5^{\bullet} + C_6H_7^{\bullet} \xrightarrow{\quad 6c \quad}$$

 I   II

$$C_2H_5^{\bullet} + C_6H_7^{\bullet} \xrightarrow{\quad 6d \quad} C_2H_6 + C_6H_6$$

The reactions (6e),

$$C_2H_5^{\bullet} + C_6H_7^{\bullet} \xrightarrow{\quad 6e \quad} C_2H_4 + C_6H_8\text{-}1,3 \text{ or } C_6H_8\text{-}1,4$$
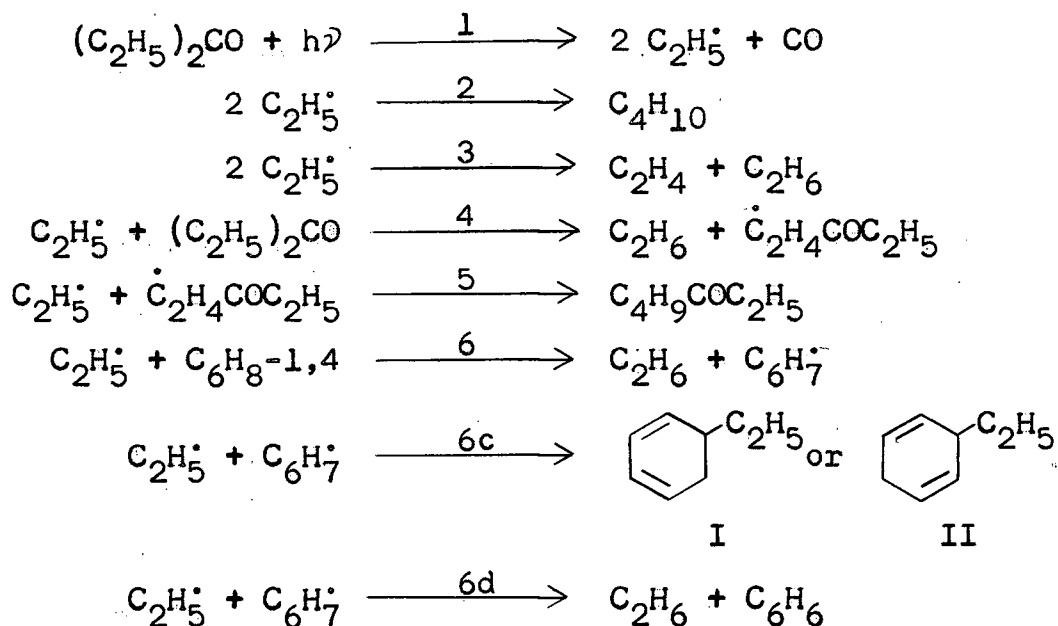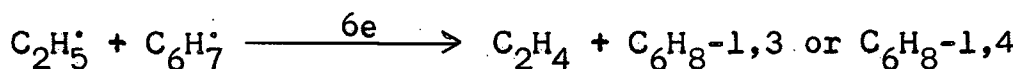
had been quite rigourously ruled out of the mechanism because (a) $R(C_2H_4)/R(C_4H_{10})$ was not significantly enhanced over the normal value 0.136, and (b) no trace of cyclohexadiene-1,3 was produced. Furthermore, in the analoguous study of the photolysis of diethyl ketone-cyclohexadiene-1,3 mixtures, no trace of the 1,4 isomer was produced. From the mechanism

$$R_6 = R_{6c} + R_{6d} = R_{C_2H_6} - R_{C_2H_4} - (k_4/k_2^{1/2})R_{C_4H_{10}}^{1/2}[C_6H_8] - R_{C_6H_6}$$

$$= (k_6/k_2^{1/2})R_{C_4H_{10}}^{1/2}[C_6H_8]$$

whence $\dfrac{k_6}{k_2^{1/2}} = \dfrac{R_{C_2H_6} - R_{C_2H_4} - R_{C_6H_6}}{[C_6H_8] R_{C_4H_{10}}^{1/2}} - \dfrac{k_4}{k_2^{1/2}} \cdot \dfrac{[D]}{[C_6H_8]}$.

and $\quad \dfrac{k_d}{k_c} = \dfrac{R_{C_6H_6}}{R_{C_2H_6} - R_{C_2H_4} - 2\,R_{C_6H_6} - (k_4/k_2^{1/2})\,[D]\,R_{C_4H_{10}}^{1/2}}$

In this way, Brown[1] was able to measure

$13 + \log \dfrac{k_6}{k_2^{1/2}} = (5.7 \pm 0.1) - \dfrac{5.8 \pm 0.1}{2.3\ RT}$ (units of $\dfrac{k_6}{k_2^{1/2}}$, $\dfrac{cm.^3}{molec.\ sec.}$)

and $\dfrac{k_d}{k_c} = 0.38 \pm 0.03$ (independent of temperature), over the

temperature range from 50 to 120°.

In view of the successful application of this analysis to
the photolysis of diethyl ketone with cyclohexadiene-1,4, it was
proposed that similar results would be obtainable from suitable
"clean" sources of other free radicals. Thus, from the photol-
ysis of mixtures of cyclohexadiene-1,4 with azomethane, di-
isopropyl ketone and 2,2'-azoisobutane, it may be possible to
measure k_{6d}/k_{6c} values for $C_6H_7^{\cdot}$ and $CH_3^{\cdot}$, $(CH_3)_2\overset{\cdot}{C}H$, and $(CH_3)_3C^{\cdot}$
radicals as well as $CH_3CH_2^{\cdot}$ radicals as described above. Also,
careful study of the heavy products of the photolyses may allow
isolation, identification, and measurement of the extent of
formation of the combination products from reaction (6c). In
the case of ethyl + $C_6H_7^{\cdot}$ these products are expected to be

I and II
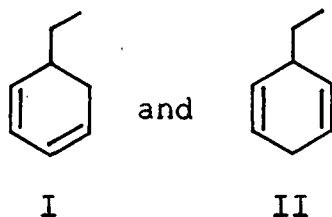
Brown attempted to isolate these products but failed to separ-
ate them using the packed gas chromatography columns available

to him then. He was able to obtain an ultraviolet spectrum of
a mixture of the two, however, and reported this to be similar
to that of cyclohexadiene-1,3. This is what would be expected
from a mixture of I and II. As will be described later, the
use of capillary columns has permitted the measurement of
k_c^I/k_c^{II} for the compounds formed from the methyl, ethyl and iso-
propyl radicals studied in this work.

In this study, the initiator systems employed have been
azomethane, di-isopropyl ketone, 2,2'-azoisobutane as well as
diethyl ketone. Preliminary photochemical experiments performed
on each established their suitability as radical sources and
this will be discussed in appropriate sections. In the ex-
periments with mixed vapours of initiators and cyclohexadiene,
the kinetic analysis follows that given for diethyl ketone with
appropriate variations as will be indicated.

C. Termination Reactions of Free Radicals

Free radicals are the reactive intermediates of a large
number of chemical conversions, particularly those occuring in
the gaseous phase. They are able to attack stable molecules in
addition, metathetical and displacement reactions of very low
activation energy. Particularly important to all such proces-
ses is the fact that free radicals are removed from the system
in an extremely efficient termination process that is bimolecular
in free radicals. Since free radicals are so reactive towards
other radicals and are eliminated in the reaction with free
radicals, the termination process is extremely important in
determining the concentration of radicals in the system.

1. Pressure effects

Intermittent illumination experiments of Roberts and

Kistiakowsky[21] have established the absolute rate constant for methyl recombination. These workers have observed that this rate constant is dependent on pressure in the region below about 10 mm. Hg of acetone. Such an effect is understood in terms of the "hot intermediate" mechanism.

$$2 \ CH_3^\cdot \ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \ C_2H_6^* \ \overset{k_2M}{\longrightarrow} \ C_2H_6 + M^*$$

$$\frac{d[C_2H_6]}{dt} = k_1 [CH_3^\cdot]^2 \left(1 + \frac{k_{-1}}{k_2M}\right)^{-1} = k_1 [CH_3^\cdot]^2 \left(1 + \frac{1}{k_2M\tau}\right)^{-1}$$
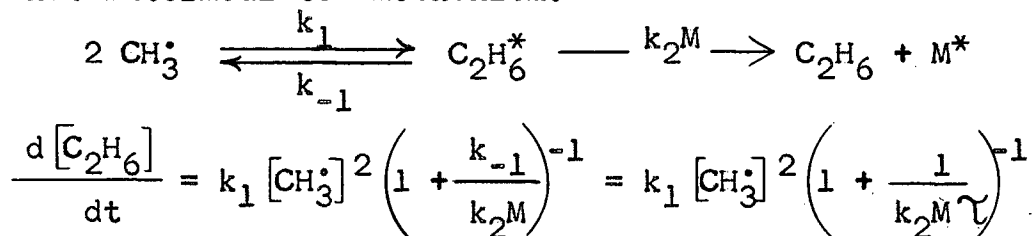
where τ is the natural lifetime of $C_2H_6^*$ with respect to uni-molecular decomposition. Only at high pressures is the assoc-iation rate constant, k_1, measured. In accordance with the simple Kassel expression, the lifetime, τ, will rapidly lengthen as the degree of complexity of the recombining radicals increases. Thus,

$$\frac{1}{\tau} = A \left(1 - \frac{E^*}{E}\right)^{s-1}$$

for a molecule of s oscillators, energized by an energy E greater than E^*, the minimum energy required for decomposition. This requires that the excitation energy, E, be rapidly dis-tributed amongst the oscillators, a position that has received experimental comfirmation recently. Butler[22] has generated excited methylcyclopropane by two routes which both ultimately yield the same distribution of butene products. Harrington et al.[23] has formed excited sec-butyl radicals by addition of hydrogen and deuterium atoms to 2-butene producing the same product distribution. Lee and Rowland[24] find that even in the liquid phase, the product of recoil tritium atom addition to hexene-2 decomposes to ethyl radicals and radio butene. Even the

efficient quenching of the liquid is not rapid enough to halt energy migration to a neighbouring bond to result in decomposition.

Brinton and Steacie[17] have found the termolecular region for ethyl radical recombination is much lower than for methyl recombination. In general, the higher radicals should not display termolecular effects above one or two mm. Hg pressure.

Benson[25] has shown that, in the termolecular region, a temperature dependence may be observed for recombination rate constants of the form

$$k \propto T^{(1-s)}$$

This arises from thermal energy, $(s-1)kT$, resident in the bonds of the radicals before reaction.

2. **Absolute rates of recombination of alkyl radicals in the high pressure limit**

Using the well known rotating sector or intermittent illumination technique, the absolute rate constants for recombination of certain simple alkyl radicals have been measured. The results of these experiments have been compiled in Table I. Certainly, these measurements are subject to error and probably are, at best, accurate to one significant figure. It is evident, however, that all the alkyl radical recombination rate constants are extremely large and reflect collision theory steric factors in the neighbourhood of 0.1.

The rate of recombination of isopropyl radicals[26] has been measured at a series of temperatures and the results do not indicate an activation energy. Kutschke and Shepp[19] claim that their studies of the ethyl radical show an activation energy for recombination and measure the Arrhenius parameters

TABLE I

Absolute Rate Constants of Radical Recombination Reactions

reagents		T ($^{\circ}$C)	ref.	k_2 (cm^3/mole sec.)	
$CH_3^{\cdot}$	$+ \; CH_3^{\cdot}$	125	a	$10^{13.34}$	
		135	b	$10^{13.52}$	
		165	b	$10^{13.90}$	
				$10^{13.5}$ ......(adopted value)	
$CD_3^{\cdot}$	$+ \; CD_3^{\cdot}$	135	b	$10^{13.61}$	
		165	b	$10^{13.41}$	
				$10^{13.5}$ ......(adopted value)	
$CF_3^{\cdot}$	$+ \; CF_3^{\cdot}$	127	d	$10^{13.36}$	
$C_2H_5^{\cdot}$	$+ \; C_2H_5^{\cdot}$	100	c	$10^{13.30}$	
$CH_3^{\cdot}$	$+ \; C_2H_5^{\cdot}$	125	e	$10^{13.62}$	
iso-$C_3H_7^{\cdot}$	$+$ iso-$C_3H_7^{\cdot}$	115	f	$10^{13.88}$ ......independent of temperature	
$^{\cdot}NO_2$	$+ \; ^{\cdot}NO_2$	127	g	$10^{11.7}$	
$CH_3^{\cdot}$	$+ \; ^{\cdot}NO$	25	h	$10^{11.8}$	
		480	i	$10^{11.1}$	may have been measured in termolecular pressure region
		900	i	$10^{11.1}$	

a. A. Shepp, J. Chem. Phys., 24, 939 (1956).
b. E. K. Roberts and G. B. Kistiakowsky, ibid., 21, 1637 (1953).
c. K. O. Kutschke and A. Shepp, ibid., 26, 1020 (1957).
d. P. Ayscough, ibid., 24, 944 (1956).
e. C. A. Heller, ibid., 28, 1255 (1958).
f. E. L. Metcalfe and A. F. Trotman-Dickenson, J. Chem. Soc., 1962, 4620.
g. A. F. Trotman-Dickenson, "Gas Kinetics", Butterworths, London, 1955, pp. 36, 125.
h. W. C. Sleppy and J. G. Calvert, J. Am. Chem. Soc., 81, 769 (1959).
i. W. A. Bryce and K. U. Ingold, J. Chem. Phys., 23, 1968 (1955).

$A = 10^{14.2}$ cm^3/mole sec., $E = 2 \pm 1$ kcal./mole. Their activation energy depends on only three measurements, the lower one being subject to very large error, and is probably not inconsistent with a value of zero for the activation energy. Since Trotman-Dickenson[26] found a zero activation energy for isopropyl radical recombination, it is unlikely that ethyl should have a barrier to recombination.

It is evident from the table of recombination rates that the pre-exponential factors are extremely high. Thus isopropyl reacts either by recombination or disproportionation on almost every collision in the gas phase[26]. Other radicals seem to have steric factors of about 0.1. Such very high frequency factors are consistent only with "loose" transition states where reacting radicals either retain their rotational freedom in the transition state or convert their rotations into very "soft", low frequency vibrations with large partition functions. The transition state theory of reaction rates shows[27] that the steric factors of bimolecular reactions between A + B should be given by the expression,

$$p = \frac{f_{AB}^{\neq}(\text{rot'n})}{q_A(\text{rot'n}) \cdot q_B(\text{rot'n})} \cdot \frac{q_{AB}^{\neq}(\text{vib'n})}{q_A(\text{vib'n}) \cdot q_B(\text{vib'n})} \tag{1}$$

where $\neq$ denotes the activated complex, q(vib'n), q(rot'n) are molecular vibration and rotation partition functions respectively, and f refers to the sum over states of a single degree of freedom. Since, for normal vibrations and rotations f(vib'n)/f(rot'n) $\sim$ 0.1, the steric factor for the association of two, non-linear free radicals will be on the order of 10^{-5} from application of equation (1), realizing that the total

number of degrees of freedom must remain constant and hence rotations will become vibrations. Since measured steric factors are 10^3 to 10^4 times greater than expected, clearly the transition states of radical recombinations are of an exceptional nature.

It has been suggested that the recombining radicals do not lose their rotational freedom in the transition state and rotational entropy is not lost. The steric factor therefore need not fall below unity. Eyring and coworkers[28] have recently calculated the entropies of the hypothetical transition state of hydrocarbon pyrolyses. Their model for the transition state assumed freely rotating radical fragments held together by polarization forces[29] at rather large separation. The entropies thus calculated agreed closely to measured values obtained from intermittent illumination experiments on the recombination of the appropriate radicals. Further, they observe that even small restriction of the rotation would seriously depress the entropies of the transition states. For larger radicals, it is difficult to imagine a freely rotating transition state consistent with the necessity of maintaining the centers of free valence close to-gether[30]; in such cases it seems more reasonable to suggest that the rotations of the free radicals are converted into very low frequency rocking and bending vibrations possessing large partition functions. Recently, Benson[30] has discussed several types of reaction, possessing high pre-exponential factors and suggests that all of these may have loose vibrations in their transition states caused by a strong representation of ionic resonance forms in the electronic description of the transition states. Examining the particular case of the methyl radical

recombination, he calculates from ionization potentials, electron affinities, and polarizabilities of methyl radicals that the transfer of charge from one methyl group to another may be of sufficiently low energy, even in the gas phase that charged structures may be important in the electronic description of recomining methyl radicals. A crude approximation of this energy is given by the equation[30],

$$-\triangle H^{o} = Q_{c} + EA - IP - Q_{d}$$

where Q_{d} = 83 kcal., the C-C bond energy in ethane, IP = ionization potential of methyl radicals, EA = the electron affinity of methyl radicals and Q_{c} is the energy of attraction for two ions separated by a distance r in vacuum.

$$Q_{c} = \frac{\varepsilon^{2}}{r}\left(N_{o} + 1.25\,\frac{\alpha}{r^{3}}\right)$$

In this expression ε is the electron's charge, 4.8×10^{-10} esu., N_{o} is Avogadro's number, and α is the radical's polarizability, in cm^{3}. For r between 2.5 and 2 Å., the ionic energy is sufficiently low that ionic structures may become important.

According to the theory, ionic bonding would be important in lowering the force constants opposing rocking and bending motions of the methyl groups since ionic forces are non-directional. The vibrational partition function ratio of equation (1) would have a large numerator and the loss of rotations would be largely compensated.

Rice[31] has suggested that three-center, hydrogen bonds may provide stability to the transition state even though the radical centers rotate away from each other.

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}\bullet\cdots\bullet\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H \quad \xrightarrow{\text{rotation}} \quad H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H\cdots\bullet\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H$$
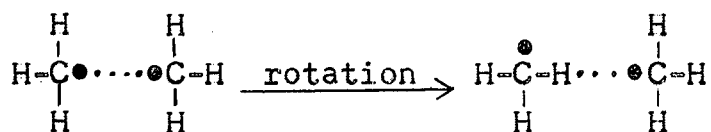
In this way the necessary freedom would remain in the structure, while still being fractionally bound together.

An examination of the rate of disruption of the methyl-allyl bond in chemically activated butene[32] has shown that this process, the reverse of the recombination of methyl and allyl radicals, has a tighter transition state than is observed for C-C bond rupture in alkanes[33]. From the data, a steric factor, $p = 5 \times 10^{-3}$, can be calculated for methyl plus allyl recombination. Rabinovitch[34] believed that such behavior may be general for recombination reactions of delocalized free radicals.

3. Disproportionation

The above discussion of free radical recombination in the high pressure limit makes no mention of disproportionation, an alternative termination process that competes efficiently with recombination when hydrocarbon radicals possess hydrogen atoms $\propto$ to the free valence. In fact, in the case of tert-butyl radicals, disproportionation is much more probable than combination. In Table II, a few of the more important $\triangle$ values have been tabulated, where $\triangle(R,R')$ is defined as k_d/k_c where:

$$R + R' \xrightarrow{k_d} RH + R'(-H)$$

$$R + R' \xrightarrow{k_c} R-R'$$
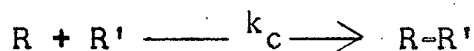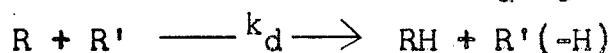
Since we have been required to allow much freedom of recombining radicals in the transition state to account for the high efficiency of this process, we are forced to allow a great deal of freedom in the transition states of disproportionating systems as well. Otherwise the loss of rotational entropy would

TABLE II

Disproportionation to Combination Ratios of Alkyl Radicals

R	$\triangle$(Me,R)	$\triangle$(Et,R)	$\triangle$(iso-Pr,R)	$\triangle$(tert-Bu,R)
Et	0.04 [c]	0.14 [a]	0.19 [c]	0.31 [c]
	0.055 [e]	0.13 [c]	0.065 [d]	1.7 [i]
	0.06 [g]	0.1 [i]	0.3 [i]	
iso-Pr	0.21 [c]	0.43 [c]	0.58 [b]	0.67 [c]
	0.195 [f]	0.21 [k]	0.65 [c]	1.2 [i,m]
	0.17 [j]	0.43 [d]	0.53 [h]	
		0.2	0.5 [i]	
tert-Bu	0.70 [c]	0.48 [c]	0.70 [c]	2.32 [b]
		0.54 [k]	0.5 [i]	3.19 [c]
		0.3 [i]		2.2 [i]
				4.6 [l]

(Preferred values are underlined)

a. D. G. L. James and E. W. R. Steacie, Proc. Roy. Soc., A, 244, 289 (1958).
b. This work.
c. J. A. G. Dominguez, J. A. Kerr and A. F. Trotman-Dickenson, J. Chem. Soc., 3357 (1962).
d. J. C. J. Thynne, Proc. Chem. Soc., 68 (1961).
e. J. C. J. Thynne, Trans. Farad. Soc., 58, 676 (1962).
f. J. C. J. Thynne, Trans. Farad. Soc., 58, 1394 (1962).
g. P. Ausloos and E. W. R. Steacie, Can. J. Chem., 33, 1062 (1955).
h. R. H. Riem and K. O. Kutschke, Can. J. Chem., 38, 2332 (1960).
i. P. J. Boddy and J. C. Robb, Proc. Roy. Soc., A, 249, 547 (1959).
j. C. A. Heller, J. Chem. Phys., 35, 1711 (1961).
k. R. A. Holroyd and G. W. Klein, J. Phys. Chem., 67, 2273 (1963).
l. K. W. Kraus and J. G. Calvert, J. Am. Chem. Soc., 79, 5921 (1957).
m. The greater value has been preferred here because $\triangle$ = 0.67 violates the pattern of the other results.

cause a drop in its pre-exponential factor and the disproportionation process would be unobservable in comparison with the recombination process. We shall discuss the current ideas about such transition states in an appropriate paragraph. A number of pertinent experiments have been performed that shed light on the mechanism of these two termination processes.

The products of the photolysis of diethyl ketone-d_4 have been analyzed by Wijnen and Steacie.[35]

$$CH_3CD_2\overset{O}{\overset{\|}{C}}CD_2CH_3 \xrightarrow{h\nu} 2\ CH_3CD_2^{\cdot} + CO$$

$$2\ CH_3CD_2^{\cdot} \longrightarrow CH_2CD_2 + CH_3CD_2H$$

$$\longrightarrow CH_3CD_2CD_2CH_3$$
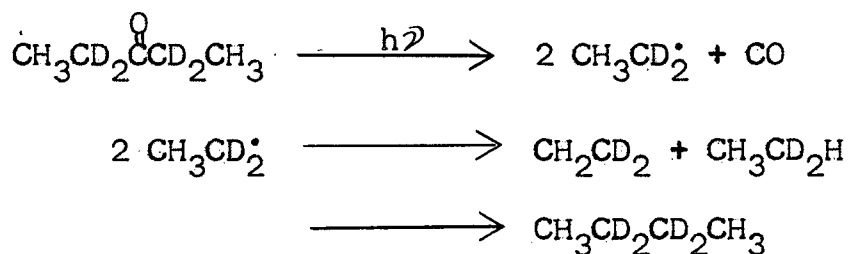
These workers found that all hydrogen atoms transferred in the disproportionation process arose from the β position. That is, no deuterium from the α position was tranferred and the process

$$\begin{array}{ccc} CD_2 & \text{---} & CD_2 \\ | & & | \\ CH_3 & \text{---} & CH_3 \end{array} \qquad\qquad CD_2CD_2 + CH_3CH_3$$

did not occur with any probability. They suggested, on this evidence, that the transition state for disproportionation was likely of the "head-to-tail" variety typical of hydrogen abstraction transition states

$$CH_3\overset{\cdot}{C}D_2\text{---}H\text{---}CH_2\overset{\cdot}{C}D_2$$
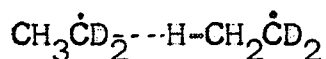
Kraus and Calvert[36] have studied the mutual interaction of the isomeric butyl radicals and found $\triangle(\underline{sec}\text{-Bu}, \underline{sec}\text{-Bu})$, $\triangle(\text{iso-Bu, iso-Bu})$ and $\triangle(\underline{tert}\text{-Bu}, \underline{tert}\text{-Bu})$ to be 2.3, 0.42 and 4.59, respectively. These results were closely in accord with the number of reactive hydrogen atoms available in each system

and tended to substantiate the head-to-tail transition state picture. The recent measurement[37] of $\triangle$(n-Bu, n-Bu) = 0.14, however, does not fit this pattern. Furthermore, Trotman-Dickenson[38] points out that the $\triangle$ values vary systematically when various radicals remove a hydrogen atom from a common donor radical.

In a great many kinetic studies where considerable concentrations of free radicals interact homogeneously in the gas phase, the $\triangle$ values for the radicals have been observed to be sensibly constant with temperature. Considering the experimental accuracy of such studies, the activation energy difference between disproportionation and combination is less than a large calorie. The one instance[39] where marked temperature dependence had been suspected in the $\triangle$(n-Bu, n-Bu) values is probably incorrect because the values measured, around 0.7, are larger than are expected for n-alkyl radicals. Indeed, the most recent redetermination[37] of this ratio has the more reasonable value of 0.14 independent of temperature. At any rate, no reason exists at present to consider it to be temperature dependent.

Much more precise measurements by Szwarc[40,41] have revealed very small but apparently real temperature effects in $\triangle$(Et, Et) measurements in the photolysis of azoethane in the gaseous phase over a wide temperature range from -65° to 40°. The temperature effect observed could be attributed to an activation energy difference E(disp) - E(comb) = -0.3 kcal. Alternatively, the effect could be assigned to the pre-exponential factors, if k(disp)/k(comb) $\propto$ $T^{-0.7}$. Similar results have been found by Klein and co-workers[42] in azoisopropane photolysis where, for

isopropyl radicals E(disp) - E(comb) = -0.26 kcal. The results of these workers extend over the solid as well as the gaseous phase, but from their results, it would appear that the $\triangle E$ observed is real also in the gas phase. Interestingly enough, the larger activation energy (if it is correct to assign the temperature effect to energy differences) belongs to the combination process.

In the work of Dixon et al.,[41] the effects of the solvent cage and changes in phase of the condensed reaction medium have been observed on measurements of $\triangle(C_2H_5^{\cdot}, C_2H_5^{\cdot})$. Such phase change effects are not observed, however, for $CH_3^{\cdot} + C_2H_5^{\cdot}$ generated in the solvent cage.[43] In the solvent cage, a greater temperature dependence of the $\triangle$ values was observed than in the gas phase. It was suggested that specific orientating forces due to the cage may be responsible for such effects, but no concrete conclusions were possible. Furthermore, Watkins and Moser[44] observed that $\triangle(Et, Et)$ is unusually high at 63° for radicals that were required to diffuse into the cage from the bulk solvent, and hence the effect is not due to radicals being formed by azoethane photolysis in the cage bearing an orientation predisposed towards disproportionation. The effect could be caused by difference in the activation volume of the two processes, which they[41] calculate to be $V^{\neq}(disp) - V^{\neq}(comb) = 2.4$ cc./mole, based on internal pressures of the solvents.

In an important study,[40] azoethane has been photolyzed in the gas phase and the effects of added CO_2, up to a total pressure of one atmosphere has been examined. Surprisingly, $\triangle(Et, Et)$ was found to be entirely insensitive to this ad-

mixture, both at -65°, and at 0°. Similarly, H_2O was not effective in altering the efficiency of disproportionation. Such an observation suggests that disproportionation is not a product of unimolecular decomposition of the hot "quasi-molecule" formed on ethyl radical recombination, competing with collisional deactivation. In this regard, certain processes have been observed bearing a superficial resemblance to disproportionation reactions, but which are effectively quenched by added, inert gases. For example, Giles and Whittle[45] and earlier Pritchard and others[46] have reported that fluorinated methyl radicals may exhibit an unusual form of elimination following termination. Thus when $CH_3^\cdot$ and $CF_3^\cdot$ recombine,[45] there may be formed HF and CH_2CF_2 as products, as well as the more normal CH_3CF_3. The yield of $CH_2=CF_2$ is strongly depressed by pressure and surely results from elimination from the excited $CH_3CF_3^*$ quasi-molecule. Such reactivity is analoguous to rupture of the C-C bond following recombination of hydrogen atoms and $C_2H_5^\cdot$ radicals[47] which is also pressure dependent. Many examples of excited radical decompositions are known, particularly from the laboratory of B. S. Rabinovitch,[33] and the results are highly pertinent to unimolecular reaction rate theory. The pressure studies of Szwarc and co-workers[40] demonstrates that disproportionation is a fundamentally different type of reaction.

Primary isotope effects have been measured for the disproportionation to combination ratios of the ethyl radicals. Boddy and Steacie[48] have found $\triangle(C_2H_5, C_2H_5)/\triangle(C_2D_5, C_2D_5) = 1.4$, independent of temperature from 50° to 300°. Similarly, James and Steacie[49] observed the preferential transfer of hydrogen

atoms in the disproportionation of partially deuterated ethyl radicals of the type $CD_jH_{3-j}CD_2^{\cdot}$. Watkins and Moser[44] found tritium atoms 2.3 times and deuterium atoms 1.5 times slower to transfer than hydrogen atoms. These latter measurements are most interesting since they were obtained at $63^\circ K.$, where isotope effects arising from zero point energy differences between the ground and the transition states would be expected to be enormous. Salomon[50] has recently formulated an isotope effect theory based on transition state theory which treats hydrogen abstraction reactions. Based on a transition state involving a linear complex where bending and symmetrical stretching C--H--C frequencies may or may not be involved, he finds exponential expressions of the form

$$k_H/k_D = C \exp(-\triangle(\text{zero point energy})/kT)$$

for the isotope effects. From such an expression, the differences in k_H/k_D observable at room temperature would become very large at $63^\circ K.$ Since Moser's deuterium isotope effect is quite similar to Boddy and Steacie's value at high temperature, the transition state is probably not of the sort used by Salomon in his treatment of isotope effects. Substantial C-H bond breaking apparently has not occurred in the transition state.

4. <u>The Transition State for Disproportionation and Combination</u>

The combination of free radicals had been considered to proceed through a freely rotating transition state,[29] or at least one with very loose, low frequency librational motions about the incipient bond.[30] Since the efficiency of disproportionation is comparable to that of combination (Table II) similar freedom is necessary in the transition state governing this process. The

transition state proposed by Wijnen and Steacie[35] (a head-to-tail structure similar to that of the hydrogen abstraction reactions) has been criticized by Bradley.[136] According to theoretical methods to estimate the partition function of such a structure,[51,52] it would not be of sufficiently high entropy to explain the large pre-exponential factors of the disproportionation process.

Kerr and Trotman-Dickenson[38] proposed a mechanism where both combination and disproportionation proceed through the same, freely rotating transition state forming an excited molecule intermediate. For example, the ethyl radical termination reactions are viewed as passing through the following sequence:

$$CH_3CH_2^{\cdot} + CH_3CH_2^{\cdot} \xrightarrow[\substack{\text{entropy} \\ \text{t.s.}}]{\substack{\text{common,} \\ \text{high}}} CH_3CH_2CH_2CH_3^* \xrightarrow{M} M^* + CH_3CH_2CH_2CH_3$$

$$\longrightarrow CH_3CH_3 + CH_2CH_2$$
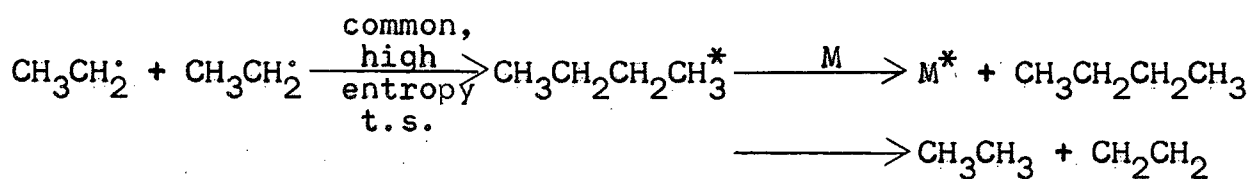
It would be expected, therefore, that combination would be enhanced at high pressures; this in not observed in the ethyl termination case.[40] Benson[30] has further criticized this model as not explaining the isotopic distribution in the pyrolysis of deuterium labelled butane under total inhibition conditions.

A similar, but distinctly different transition state model has been advanced by Bradley and Rabinovitch.[53] These authors consider that both disproportionation and combination have very loosely associated, freely moving transition states, although not necessarily identical for both processes. The system becomes committed to either combination or disproportionation while passing through this state or states, and not as a competitive reaction system of an excited molecule intermediate. This is a very much less detailed view of the process than that of Kerr

and Trotman-Dickenson, but avoids the difficulties encountered in the excited molecule mechanism. One prediction of this proposal is that the ultimate distribution of products will be governed by the entropy differences between them, and that the energy will not be of importance. The system, situated at the transition state, will fall into the most probable, or highest entropy, configurations. Holroyd and Klein[54] have successfully correlated a large number of disproportionation to combination ratios for alkyl radicals by the equation

$$\log_{10}(k_d/k_c) = 0.131 \left[\sum_i {}'S_i^o(disp) - S^o(comb) \right] - 5.47$$

James and Troughton[55] have found that this relationship successfully predicts the $\triangle$(allyl, ethyl) and $\triangle$(ethyl, allyl) values measured in their experiments.

Just as he has argued that extensive representation of charge transfer structures in the combination transition state would effectively increase its entropy, Benson[30] suggests that such a description could be applied to the disproportionation transition state. According to this view, the linear head-to-tail transition state geometry of Wijnen and Steacie may be acceptable if charge transfer resonance forms are important enough to weaken the force constants opposing librational motions. There would be two distinct transition states, one for each termination process, and the product distribution would be determined by the relative ease of forming them. The ionization potentials, electron affinities, and steric characteristics of the reacting radicals all could be important in determining the ultimate product distribution. In this connection, Benson has observed that in the mutual termination of the ethyl, isopropyl,

and tert-butyl radicals, the tendency to disproportionate varies in the opposite sense as the ionization potentials of the reactants, which show a strong, uniform decrease from ethyl to tert-butyl.[56] Indeed, Table II suggests that such trends are quite general for these methyl radical homologues. Unfortunately, steric effects and electron density at the α-carbon atom also vary in a uniform manner over these reactants and firm conclusions are not possible.

D. Aims and Scope of this Investigation

As there is still no definite understanding of what factors influence the probability of disproportionation during the termination reaction of free radicals, it should prove valuable to conduct a study of the distribution of the combination and disproportionation products during the interaction of various radical pairs. The procedure most likely to be instructive is to examine the disproportionation to combination ratios obtained when a reference radical is allowed to react with a representative series of radicals. The work of Dominguez, Kerr and Trotman-Dickenson[57] has provided such series in the case of the interactions of the various members of the homologous series represented by the formulae $^{\cdot}CH_j(CH_3)_{3-j}$ (see Table II). A similar study of the disproportionation ratios of these homologues with the cyclohexadienyl radical is attractive for the following reasons. First, it is of interest to learn if the tendency, observed by Dominguez et al.,[57] for the higher homologues of the series $\overset{\cdot}{C}H_j(CH_3)_{3-j}$ to be more effective in the removal of a hydrogen atom from a given substrate is reproduced for the cyclohexadienyl radical as donor, a system markedly different

from the alkyl donors earlier studied. Secondly, the cyclohexa-
dienyl radical possesses a delocalized free valence and this may
be effective in determining its reactivity. The possibility of
the release of the very great benzene resonance energy in the
formation of the disproportionation products may also influence
the reactivity of the system; the cyclohexadienyl system offers
a unique opportunity to test for the influence of energetics in
these reactions. Finally, there is at present a considerable
body of information available on the properties and the structure
of the cyclohexadienyl radical. For example, Fessenden and
Shuler[58] have prepared the cyclohexadienyl radical in liquid
cyclohexadiene-1,4 and measured its electron spin resonance
spectrum. This spectrum showed that the radical was structur-
ally planar, at least in this environment, and also afforded
estimation of the electron spin densities at the ortho, meta
and para positions to be 0.35, -0.10, and 0.51 respectively.
Harrison et al.[59] have measured the heat of formation of the
cyclohexadienyl cation to 232 ± 3 kcal./mole. From the present
estimate of the heat of formation of the cyclohexadienyl radical
(45 kcal./mole), the ionization potential of the cyclohexadienyl
radical can be estimated as 8.0 ± 0.2 ev.

Beyond the examination of the termination reactions of the
cyclohexadienyl radical, we shall want to search for evidence of
the thermal instability of the species and to obtain thermo-
chemical data on the decomposition reaction. Under the procedure
used to generate the cyclohexadienyl radical, we shall be able
to lower the rate of their formation and therefore to lower the
the rate at which they are lost in mutual termination. These
conditions should favour the decomposition.

EXPERIMENTAL METHODS

A. Description of Apparatus

Measurements of the kinetics of the systems studied in this work were made using conventional high vacuum techniques. As a precaution against the interference of oxygen, and against absorption of materials in grease, mercury cut-offs were employed in place of grease taps in the connecting tubing around the cell, the storage vessels and the analytical line. The general features of the apparatus are illustrated schematically in Figures 1 and 2. The apparatus consists of three essential sections; the preparative line, the reaction cell and optical system, and the analytical train. These will be briefly described.

1. Preparative line

This consists of a manifold connected to the photolysis cell through a mercury cut-off on one end and a large-bore mercury manometer (A, Figure 1) at the other. Materials were stored behind mercury cut-offs in vessels that were connected to this manifold. The cell could be pumped out through the manometer by lowering the mercury thus connecting it to the mercury diffusion pump.

2. Cell and optical system

Photolyses were carried out in a cylindrical, silica cell of 253 cm^3 illuminated volume. This cell was precisely filled with the beam of light from a British Thomson-Houston ME/D 250 W. medium pressure mercury arc lamp which provides intense light from almost a point source. This light was focussed by a quartz lens of focal length 7 cm. into a parallel beam. A front silvered mirror was placed just beyond the cell (N, Figure 2) and served to return the beam of light back through the cell,

increasing the effective intensity of the illumination, and also
reducing the gradient of light intensity within the cell due to
absorption. The beam was then filtered using standard filter
solutions,[60] depending on the initiator being used, to isolate
either the 3130 $\overset{o}{A}$. radiation (ketones) or 3660 $\overset{o}{A}$. radiation
(azo compounds). The lamp was run at 65 volts and 3.6 amps.
developing 234 Watts. No radiation is produced between 2482 and
2752 $\overset{o}{A}$. owing to the reversal of the 2537 $\overset{o}{A}$. resonance line
eliminating the possibility of mercury photosensitization.

For the photolysis of diethyl ketone and di-isopropyl ketone,
an optical filter of 0.5 % potassium hydrogen phthalate 2 cm.
thick was employed. As the ketones do not absorb at longer
wavelengths than 3200 $\overset{o}{A}$. the effective radiation was limited to
the region from 3000 to 3200 $\overset{o}{A}$. Due to photolysis of the
potassium hydrogen phthalate, this solution was renewed for each
photolysis.

For the photolysis of azomethane and 2,2'-azoisobutane the
light from the mercury lamp was filtered through a Pyrex #7380
filter and a 2 cm. thickness of a solution of 250 g. $CuSO_4 \cdot 5H_2O$
per litre of water. This combination passed 65 % of 3660 $\overset{o}{A}$.
radiation and was opaque below 3400 $\overset{o}{A}$. The $CuSO_4$ filter was
effective to remove red and infra-red radiation that may have
contributed to temperature-instability in the cell.

Neutral density filters of aluminum lightly deposited on
silica were useful for attenuating the intensity of illumination.

The cell was housed in an aluminum block electrical resis-
tance furnace. Its temperature was measured by means of three
copper-constantan thermocouples taped to the surface of the cell.
This arrangement was sufficient to maintain the cell temperature

Figure 1. Schematic Diagram of the Vacuum Apparatus
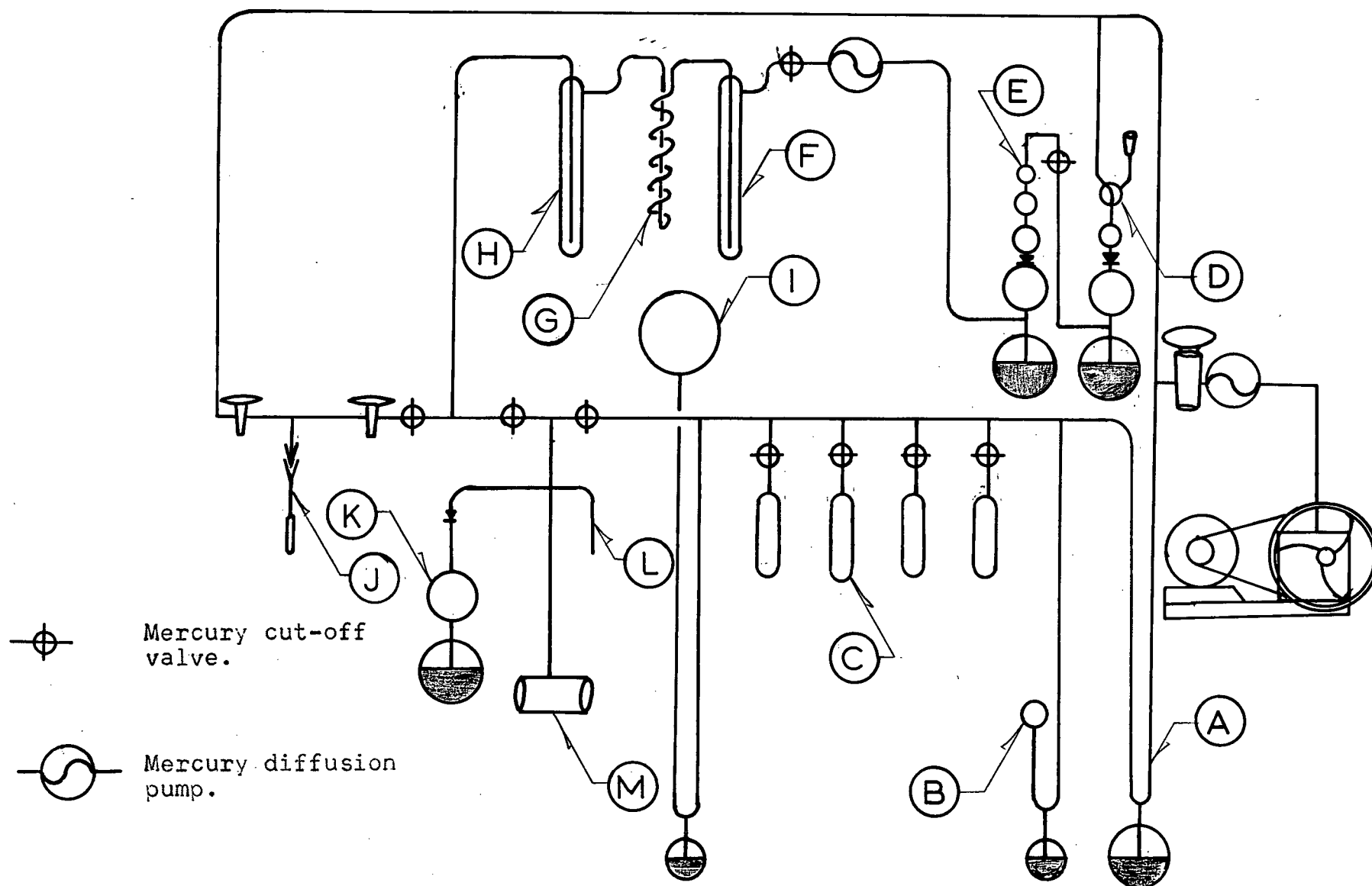
Figure 2. Schematic Diagram of the Optical System

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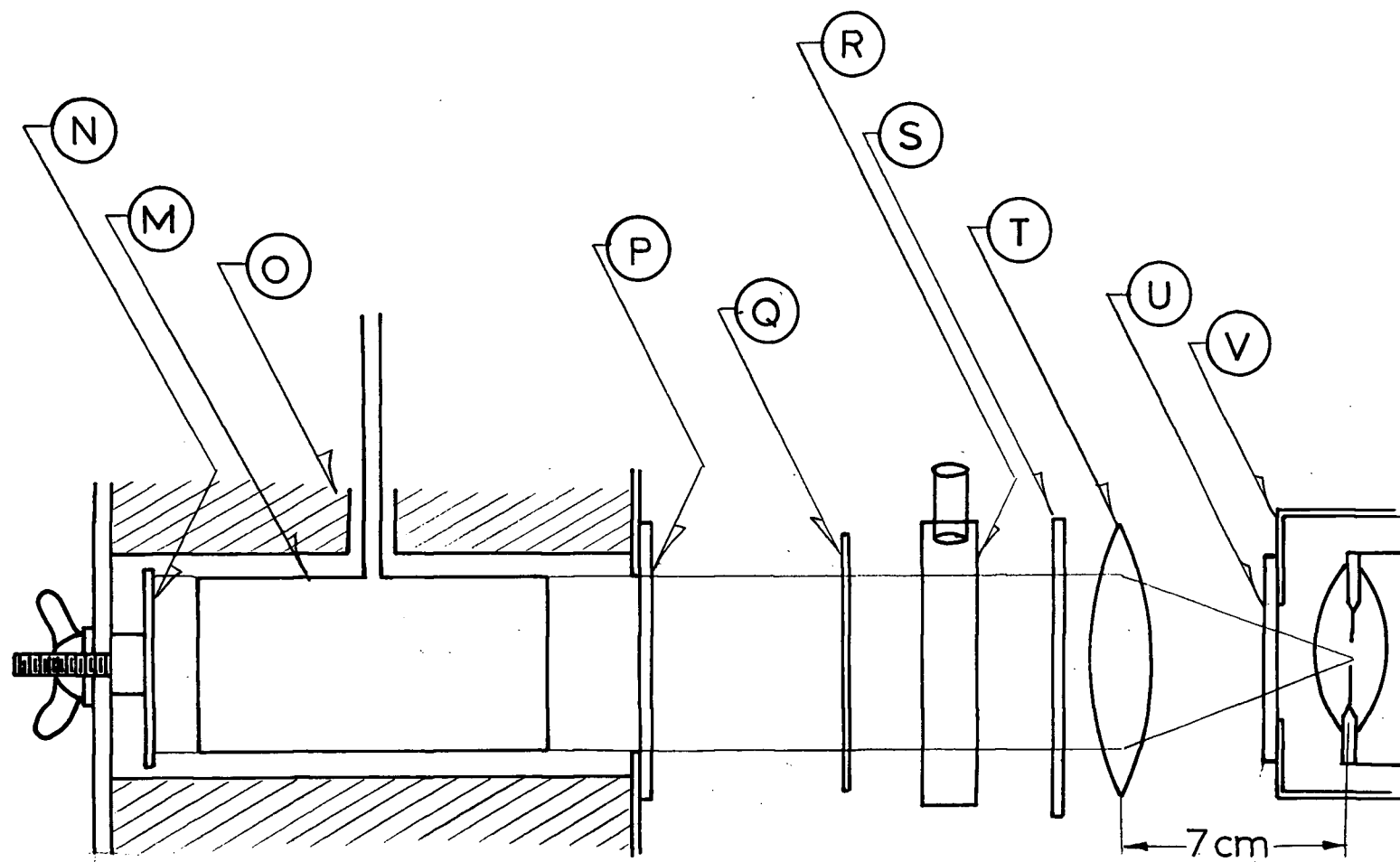
Key to the Labelling of Figures 1 and 2.

A. Wide bore mercury manometer.

B. Standard volume bulb for measuring out gas samples.

C. Liquid reagent storage cells.

D. Toepler pump and three-way grease tap to evacuate the gas burette and gas sample withdrawal.

E. Toepler pump and gas burette.

F. Second variable temperature trap.

G. Spiral trap arranged for solid nitrogen cooling.

H. First variable temperature trap.

I. Five litre gas storage bulb.

J. Cold finger system for removing liquid photolysis residues.

K. Vapour mixer.

L. Cold finger.

M. Silica cell.

N. Front silvered mirror.

O. Electrically heated aluminum block furnace.

P. Corning #774 filter.

Q. Pyrex #7380 filter (for 3660 $\overset{o}{A}$. work only).

R. 2 cm. silica cell for solution filters.

S. Neutral density filters (partially silvered mirrors).

T. Silica lens of 7 cm. focal length.

U. Silica window.

V. British Thompson-Houston ME/D 250 W. medium pressure mercury arc lamp.

constant to within $\pm$ 1° during the course of a kinetic run.

3. The analytical train

The work required that an analytical system of considerable flexibility be employed as a variety of products would be produced from the various initiator systems used. Accordingly, a low temperature fractionating system was used containing two variable temperature traps which were modified Ward stills as proposed by Le Roy[61] capable of maintaining temperatures between liquid nitrogen temperature and room temperature. Also a solid nitrogen spiral trap was used capable of maintaining a temperature of -215° by pumping on liquid nitrogen initially contained in a Dewar flask. The arrangement of these traps is shown in Figure 1. The temperatures used for analysis of each of the compounds will be indicated in an appropriate paragraph.

Briefly, the Le Roy stills consist of a vertically arranged trap fashioned from two concentric tubes about 30 cm. long joined by a ring seal at the top. The outside of the trap is equipped with thermocouples at three places along its length to monitor the temperature. It is then wrapped with lead foil and glass tape over which a heating wire of about 100 ohms is wrapped. The entire trap is placed in a Pyrex jacket capable of being evacuated and surrounded with liquid nitrogen. Temperatures above that of liquid nitrogen are easily arranged by passing a small current (less than one half ampere) through the wire.

Fractions of gaseous products volatile for any particular set of temperatures in the analytical line traps were pumped into a gas burette by a Toepler pump (E, Figure 1) assisted by a mercury diffusion pump. The amount of gas collected was estimated by measuring the pressure required to confine it within a certain

measured volume of the gas burette at the ambient temperature of the room. Provision was made to remove the product fraction by means of another Toepler pump (D, Figure 1) into a bulb to be analyzed by gas chromatography in the case that a fraction may be complex.

As the anaysis of heavier products such as benzene, di-isopropyl and others was necessary for the kinetic studies done, provision was made to remove the residual material after the light products had been removed. The residues were condensed into a small tube and removed from the vacuum system where they were diluted with a convenient solvent and injected immediately onto gas chromatography columns for analysis. A light solvent such as pentane or pentene-1 was used as this material passed quickly and cleanly through the column and did not interfere with analysis of the kinetic products which are retained more strongly. This procedure was checked with synthetic mixtures of benzene, heptane and cyclohexadiene-1,4 and found to give readily reproducible results as long as the sample tube was kept cool by suspending it in a Dewar with liquid N_2 below it, and as long as pre-chilled syringes were used. Mixing was effected by drawing the mixture rapidly up and down in the syringe used for analysis.

Di-isopropyl was not very accurately measured by this technique due to its considerable volatility and alternative procedures were employed in estimation of this compound. This will be indicated in the appropriate place.

4. Chromatographic Analysis

Two types of gas chromatographic analysis were used. For the majority of products the Perkin Elmer Vapour Fractometer 154C

instrument using 2 or 4 meter by ¼ inch I.D. packed columns was
preferred. This system, with a Flame Ionization detector and Leeds
Northrup Model G, 1 mV. recorder offered superior accuracy and
convenience. Gas samples were injected by means of a carrier gas
bypass sampling loop of standard type. For the lightest gases, a
sampling loop with grease taps was adequate, but for analysis of
butane and butene mixtures encountered in the photolysis of azo-
isobutane, a loop was constructed using greaseless taps. Liquid
samples were introduced by a hypodermic syringe through a rubber
septum. Packed column analysis was used for all gaseous samples
and for analysis of the heavy products benzene, cyclohexadiene,
cyclohexene and di-isopropyl. In all cases, products were meas-
ured relative to an internal standard added to the product mixture
prior to removal from the vacuum system. Such internal standards
were either n-heptane or 3-methyl pentane measured out manometric-
ally as vapours in a standard volume (B, Figure 1) bulb on the
vacuum system's preparative line. For all analyses, n-heptane
was used except for those pertaining to the experiments where
azoisobutane was used as initiator as, in this case, n-heptane
was not separated from products. In these experiments 3-methyl-
pentane was used. In measuring out the vapours in the standard
volume bulb, pressures were kept below 2 cm. Hg so that nonideal-
ity corrections were unnecessary.

Nitrogen was used as carrier gas. The flame ionization
detector was operated on H_2 gas flowing at 12 psig. from a tank
through a porous sintered plug into the detector. Similarly,
pure air was passed at 30 psig. through a sintered plug into the
detector. The response of the detector to each component of an

analytic mixture was calibrated by running synthetic mixtures of the compounds and comparing peak areas to the known mole ratios. The measurement of area ratios from chromatographic analysis performed was done using a planimeter. In cases where small peaks required measurement, the average on ten independent determinations of area was used. In this way, the error from measurement of peak areas was maintained on the order of 1 %.

During photolyses at high intensities of cyclohexadiene-1,4 with the various initiators, two products arose from recombination of the cyclohexadienyl radical with the initiator radical. These products consistently elute after the passage of the cyclohexa-diene-1,4 peak in the v.p.c. analyses on polyethylene glycol column. For convenience, these have been assigned the labels products I and II, I being the first to elute. Experiments to be described have shown that these products have the structures:

$$ I = \quad\quad\quad\quad\quad II = $$
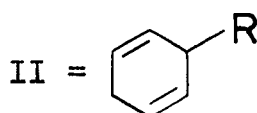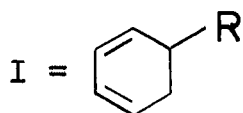
for R = CH_3-, C_2H_5-, iso-C_3H_7- or tert-C_4H_9- depending on the particular initiating radical, R. The packed columns as described above were not capable of separating these peaks but the superior resolving power of Golay capillary columns permitted their separation. Accordingly, two analyses of each kinetic run were performed on the heavy residual products; one on the packed columns using the Perkin Elmer 154C Vapour Fractometer, and a second on a 150 foot, 0.01 inch I.D. capillary column with polyethylene glycol substrate. This second analysis was done on a Perkin Elmer 226 Gas Chromatograph having a temperature program feature of great utility when analyzing products from the

interaction of tert-butyl and isopropyl radicals with the cyclo-
hexadienyl radical. As these compounds were quite involatile,
sampling on the Perkin Elmer 226 was by means of injection of
solutions of sample through a rubber septum as for the packed
column analyses above.

Detection was also by flame ionization using H_2 gas and
pure air introduced through sintered disks under pressure.
Nitrogen was used as carrier gas at 12 psig. pressure. The
column was kept at room temperature until the cyclohexadiene
reagent has passed (about 10 minutes) then the temperature of
the column was rapidly raised to 120° where the heavier products
eluted as sharp peaks. In the case of azomethane-cyclohexa-
diene-1,4 experiments, the heating of the column was not neces-
sary as these products were quite volatile, and in this case
alone the entire capillary column analysis was carried out at
ambient temperature.

B. Reagents

In general the reagents, after purification as described
below, were admitted immediately to the vacuum system and sub-
jected to several degassing cycles of freezing down and pumping.
In the case of initiators, samples of these were photolyzed in
the cell and the products discarded in order to condition the
cell. Otherwise, it was observed that unusual results may be
obtained for initial photolyses. After the purification, a
sample of the purified material was analyzed on several chrom-
atographic columns and spectra were taken. These results are
indicated below.

Azomethane, obtained from Merke, Sharp and Dohme (Canada)

Ltd. was purified by distillation under vacuum from a Le Roy still set at -70°. The vapours passed through a second Le Roy still at -90°. A middle fraction was reserved for use. This compound was stored behind a manometric mercury cut-off in a blackened bulb and kept frozen down with liquid nitrogen. Before use, each sample was degassed by pumping on it when it was held down by liquid nitrogen. This was necessary to remove nitrogen and methane that accumulated regardless of the specified precautions in storage.

<u>Diethyl ketone</u> was used from a sample purified by earlier work[1] in this laboratory. This material was Eastman Kodak White Label grade that had been purified on a Ucon Polar column at 105° using a Beckman Megachrom Preparative Gas Chromatograph. Analysis showed impurities less than 0.1 % and these residual impurities were not affected by photolysis of the sample.

<u>Di-isopropyl ketone</u> was obtained from K and K Laboratories. Substantial impurities were completely removed by passage of the ketone through a 12 foot Apiezon-J column of the Beckman Megachrom at 95° using nitrogen carrier gas at 10 psig. The n.m.r. spectrum of the resulting material was in complete agreement with that expected from di-isopropyl ketone - a heptuplet and a doublet with area ratio 1:6. The heptuplet was centered at 6.72 τ ; the doublet was centered at 8.98 τ .

<u>2,2-Azoisobutane</u> was obtained from Merke, Sharp and Dohme (Canada) Ltd., and found to be virtually pure by analysis on capillary columns using the Perkin Elmer 226 Gas Chromatograph. One impurity could be found which was less than 0.1 % and was not affected by photolysis. The n.m.r. spectrum showed only one, strong peak at 8.89 τ , even under high amplification. It was

degassed and used as is.

Cyclohexadiene-1,4 was obtained from Aldrich Chemical Company. It had an impurity of about 5 % benzene and smaller amounts of cyclohexadiene-1,3 and cyclohexene. This crude material was pas- sed through a 12 foot Apiezon-J column on the Beckman Megachrom Preparative Gas Chromatograph at 75° which effectively removed all umpurities except benzene, which remained to the extent of about 0.1 %. The area ratio of impurity benzene to cyclohexa- diene-1,4 was determined on the polyethylene glycol packed column under the same conditions as were used for the analysis of benzene during kinetic runs. This data was used to correct the rate of formation of benzene as measured in these runs for the impurity benzene. This was always a small correction (less than 10 % of the benzene found after photolysis corresponded to impurity benzene, generally).

The 60 megacycle n.m.r. spectrum revealed two absorptions only. One, due to the methylene protons, was centered at $8.40 \, \mathcal{T}$, and the other due to the olefinic protons, was found at $4.40 \, \mathcal{T}$. Each peak was just perceptibly split into a triplet with a coup- ling constant of about 0.2 c.p.s. This unusually small splitting may be compared to the lack of any splitting between the two classes of protons in cyclobutene.[62]

A further, interesting point is the apparently single ab- sorption of methylene protons. Any great folding of the molecule into a boat shaped structure of C_{2v} symmetry would presumably cause the two protons within a methylene group to be non-equivalent. They then would absorb at different frequencies unless the in- version of the molecule (through the D_{2h} form) occured very

rapidly at room temperature, which would seem likely.
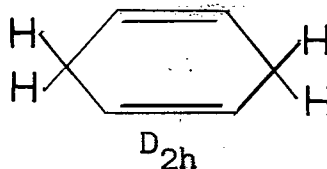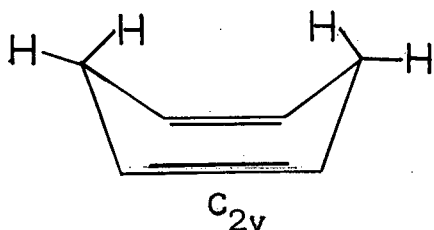
Alternatively, the molecular structure must have very nearly D_{2h} symmetry, a position adopted by Monostori and Weber[63] in recent rotational Raman spectroscopic studies, and by Stidham[64] in vibbrational spectroscopic studies.

Cyclohexadiene-1,3 was obtained from the Columbia Organic Chemical Co. It was purified by passage through the 12 foot Apiezon-J column of the Beckman Megachrom Preparative Gas Chromatograph at 75°. Once again benzene was not completely removed and was present in the final material to the extent of about 1 %. This did not interfere with studies done using this compound, as benzene formation could be determined by an alternative method, and the benzene was not a chemically reactive substance.

PHOTOLYTIC SYSTEMS

In this chapter are presented the detailed experimental pro-
cedures, results and some of the discussion of the photolysis of
the various initiator systems used and of their photolysis in the
presence of substrate vapours.

The purpose of the studies of the photolysis of the mixed
vapours of initiators and cyclohexadiene-1,4 has been to measure
the relative rate constants and Arrhenius parameters for the
attack of methyl, isopropyl and tert-butyl radicals on the diene
molecule. Also, more importantly, the distribution of products
of the interaction of these radicals and of the ethyl radical
with the cyclohexadienyl radical has been sought. These results
are best discussed together, and therefore have been considered
in the General Discussion section.

A. Azomethane as Initiator

1. Pure Azomethane Photolysis

Azomethane is finding increasing use in recent years as a
source of methyl radicals whose reactions with various substrate
molecules may then be studied. It was first examined carefully
in gas phase photolysis by Jones and Steacie[65] and since then,
many workers have studied the photolysis.[66-69] The quantum
yield of nitrogen has been measured as unity[65] and the primary
process is almost entirely a split into methyl radicals and
nitrogen gas. No evidence of excited molecule intermediates has
been obtained. The methyl radicals liberated attack the azo-
methane molecule either abstracting a hydrogen atom[65,66,69] or
attacking the nitrogen-nitrogen double bond in an addition
reaction.[65,70] The rate of this latter reaction has not been
accurately determined.

The gas phase photolysis of azomethane has been re-examined here with special attention to the evaluation of the rate data for methyl radical reactions with the azomethane molecule.

Experimental   The photolysis of azomethane has been studied in sixteen experiments between 24° and 167°.

Azomethane reactant was passed from the storage bulb into the preparative line and reaction cell until the desired pressure was obtained. This material was degassed at liquid nitrogen temperature for at least fifteen minutes, then allowed to vapour-ize and fill the cell. Its pressure was measured using the wide bore manometer (A, Figure 1) with an accurate cathetometer. At the same time the cell temperature was read from the copper-constantan thermocouples with a millivolt potentiometer. The illumination was the 3660 $\overset{o}{A}$.radiation isolated from the B.T.H. medium pressure lamp with the filter combination described above. When the photolysis was started, the temperature in the cell was observed to increase slowly. The mean temperature from a number of readings throughout the run was used. Reactant concentration was, of course, calculated from the initial reading. At the pressure of azomethane used, considering the rather low reactiv-ity of methyl radicals towards azomethane, the reactions could not be measured unless the light was attenuated by a neutral density filter of optical density 1.40. This necessitated a reaction time of about one hour to accumulate sufficient pro-ducts for unequivocal analysis.

After the photolysis was completed the entire reaction mixture was admitted to the analysis line, where the various

traps were maintained at the following temperatures:

1st Variable temperature trap	-135°
Spiral trap	-215°
2nd Variable temperature trap	-175°

The first trap removes the bulk of the azomethane and heavier products. Nitrogen and methane pass through all traps and ethane is held back on the spiral trap. Pumping the volatile fraction into the Toepler pump-gas burette then gives the total yield of nitrogen and methane manometrically. Since the methane alone and not the nitrogen will give a signal on the flame ionization detector, it is possible to estimate the relative concentrations of these two gases in a sample only if a known internal standard can be introduced against which the methane can be measured. The ethane yield from the reaction has served as this standard in the following way. It was demonstrated by chromatographic examination that the ethane pumped into the gas burette when the spiral trap was warmed to room temperature was pure. It could therefore be independently measured manometrically and added thereafter to the N_2-CH_4 fraction. This mixture was then chromatographed on the 4 meter packed silica gel column at 50° with 8 psig. nitrogen as carrier gas. The ratio of CH_4 to C_2H_6 could then be obtained by multiplying by 1.87 the ratio of peak areas. That is

$$\frac{P(CH_4)}{P(C_2H_6)} = 1.87 \frac{Area\ (CH_4)}{Area\ (C_2H_6)}$$

The calibration factor had been obtained in the usual way by comparison of the peak areas of synthetic mixtures of methane and ethane. The methane yield is known then from the ethane yield and the nitrogen can be determined by difference. The

values of the rates of formation of these products have been list-
ed in Table III along with certain derived quantities to be ex-
plained below.

Treatment of Data According to current understanding of the
azomethane photolysis the system can be described in terms of the
following reactions at high intensities and between 20-200°.

$$CH_3NNCH_3 + h\nu \xrightarrow{\quad \phi_r Ia \quad} 2\ CH_3^{\cdot} + N_2$$

$$\xrightarrow{\quad \phi_m Ia \quad} C_2H_6 + N_2$$

$$2\ CH_3^{\cdot} \xrightarrow{\quad 2 \quad} C_2H_6$$

$$CH_3^{\cdot} + CH_3NNCH_3 \xrightarrow{\quad 4m \quad} CH_4 + \dot{C}H_2NNCH_3 \qquad A$$

$$CH_3^{\cdot} + CH_3NNCH_3 \xrightarrow{\quad 4a \quad} (CH_3)_2\dot{N}NCH_3$$

$$CH_3^{\cdot} + \dot{C}H_2NNCH_3 \xrightarrow{\quad 5m \quad} C_2H_5NNCH_3$$

$$CH_3^{\cdot} + CH_3\dot{N}N(CH_3)_2 \xrightarrow{\quad 5a \quad} (CH_3)_2NN(CH_3)_2$$
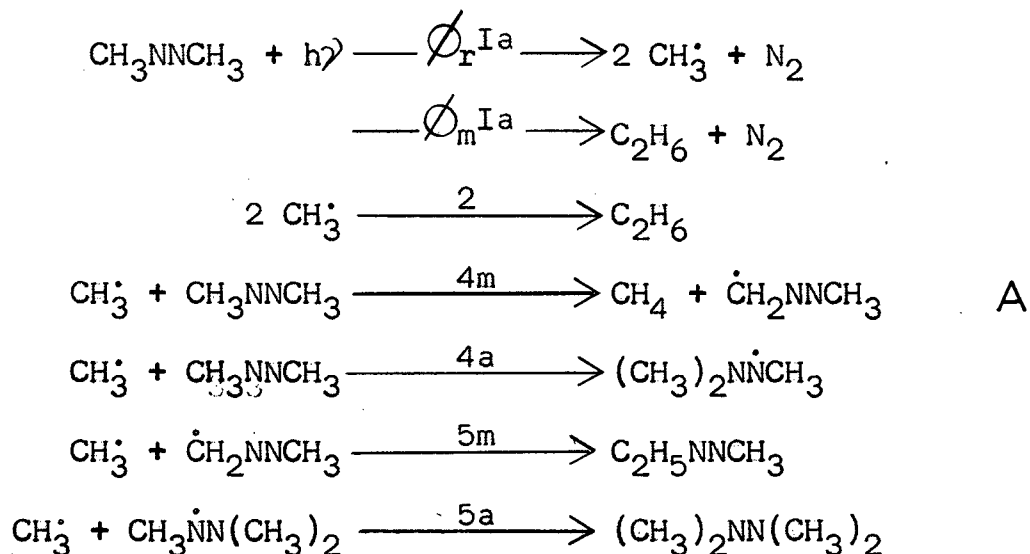
The quantum yield of nitrogen, ϕ_{N_2}, is unity.[65] Therefore
$\phi_r + \phi_m = 1$. The alternative, molecular-ethane, mode of de-
composition has been established by Rebbert and Ausloos.[67,71] It
occurs to a very slight extent ($\phi_m = 0.012$) and represents a
negligible source of ethane in high intensity photolyses where
reaction (2) has a high rate.

During the flash photodecomposition of azomethane, Sleppy
and Calvert[72] did not detect the presence of the possible inter-
mediate species, $CH_3N\dot{N}$, and no interference from this source is
anticipated.

It is under this assumed mechanism, A, that the system has
been analyzed. At the higher intensities of light, it is as-
sumed that all radicals produced from the interaction of methyl
with azomethane are removed by recombination with another methyl

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TABLE III

Addition and Metathesis between the Methyl Radical and Azomethane

($^{\circ}$K)	(sec.)	$10^{12}R(X)$ (molec./cm^3.sec.)				$(cm^3/molec.sec.)^{1/2}$	
						$10^{13}k_{4m}/k_2^{1/2}$	$10^{13}k_{4a}/k_2^{1/2}$
T	t	[A]^a	N_2	CH_4	C_2H_6	M	
297	300	3.06	90.1	0.302	88.3	0.983	-	-
306	3600	3.85	3.65	0.061	3.67	0.936	0.87	3.16
318	3600	2.81	3.11	0.0589	2.86	0.939	1.25	4.01
331	3600	3.58	4.11	0.143	3.53	0.893	2.14	6.59
339	3600	3.57	3.99	0.161	3.32	0.873	2.49	7.81
351	3600	3.66	3.92	0.260	3.11	0.860	4.03	8.50
359	1800	2.02	11.01	0.428	9.90	0.938	6.76	10.7
374	1800	2.70	16.97	0.821	14.20	0.885	8.12	19.1
380	1800	2.90	17.09	0.993	13.84	0.868	9.24	21.0
381	1800	2.44	14.67	0.850	11.96	0.873	10.2	22.2
386	1800	3.39	20.05	1.13	15.86	0.847	(8.37)^b	22.7
391	1800	1.83	11.89	0.964	9.57	0.886	17.1	24.1
411	1800	3.34	21.70	2.97	13.67	0.767	24.1	40.9
423	300	2.54	19.32	3.28	12.70	0.826	36.3	37.3
430	1800	2.03	13.61	2.86	8.06	0.802	50.2	48.1
440	1800	1.72	11.91	2.64	6.45	0.763	61.0	65.4

^{a} 10^{17} [A] = Concentration of azomethane (molecules/cm^3).

^{b} Value excluded on statistical grounds.

radicals. If this mechanism holds true, one molecule of nitrogen should represent either the formation of one molecule of CH_4, one molecule of C_2H_6 or the consumption of two $CH_3^{\cdot}$ radicals in an addition reaction followed by termination of the adduct radical. We may define the following "material balance quotient", M, where

$$M = (R_{CH_4} + R_{C_2H_6})/R_{N_2} \qquad (2)$$

When the value of M falls below unity, it indicates the occurence of the addition reaction (4a). In order to assess the accuracy of the analytical technique, a photolysis was done using extremely high light intensity, where radical recombinations are favoured, and little addition, comparatively, would be anticipated. The first run entered into Table III corresponds to this experiment which was done at room temperature to further discourage addition to azomethane. As can be seen, the measured material balance is very close to unity, confirming the analytical accuracy.

It is easily shown, from the above mechanism, using the usual steady-state treatment for methyl radicals, that

$$\frac{k_{4a}}{k_2^{\frac{1}{2}}} = \frac{R_{N_2}(1 - M)}{[\text{Azomethane}] R_{C_2H_6}^{\frac{1}{2}r}} \qquad (3)$$

where R(X) means the rate of formation of compound X. In this expression, $R_{C_2H_6}^r$ refers actually to the ethane formed in bimolecular recombination of methyl radicals, and not to that formed in the molecular elimination process. $R_{C_2H_6}^r$ is equal to $R_{C_2H_6} - 0.012\,R_{N_2}$ where the factor 0.012 has been measured in the low intensity photolysis experiments to be considered in another section. Since molecular elimination as measured in this work, and also by Thynne,[73] Szwarc et al.[74] and Rebbert and Ausloos[67,71]

is approximately one percent of R_{N_2}, the difference is insignif-
icant.

Similarly, the steady-state treatment yields the expression:

$$\frac{k_{4m}}{k_2^{1/2}} = \frac{R_{CH_4}}{[\text{Azomethane}] R_{C_2H_6}^{1/2} r} \tag{4}$$

These rate ratios along with computed values of the material
balance have been tabulated for each run in Table III. Arrhenius
plots of the rate ratios are given in Figure 3 and Figure 4. From
a least mean squares treatment of the Arrhenius data, we obtain
the following values for the Arrhenius parameters:

$$10^{13} \frac{k_{4m}}{k_2^{1/2}} = 10^{(6.0 \pm 0.3)} \exp\left(-\frac{8.5 \pm 0.5}{RT}\right) \left(\frac{cm.^3}{molec.\ sec.}\right)^{1/2}$$

$$10^{13} \frac{k_{4a}}{k_2^{1/2}} = 10^{(4.7 \pm 0.2)} \exp\left(-\frac{5.9 \pm 0.4}{RT}\right)$$

The errors have been expressed at the 5 % probability level.

Toby and Weiss[75] have obtained evidence that the recombination
of methyl radicals during azomethane photolysis may be pressure
dependent at azomethane concentrations below 4×10^{17} molec./cm.^{3}
Increases in the function $R_{CH_4}/[A] R_{C_2H_6}^{1/2} r$ of 10 - 20 % were de-
tected as the azomethane concentration fell to 1.7×10^{17}, the
lowest concentration used in the present study. It is suspected,
therefore, that the Arrhenius parameters measured here are
slightly in error because of this pressure effect. We may replace
the rate equation (2) of Scheme A by the more detailed sequence

$$2\ CH_3^{\cdot} \xrightarrow{\ k_2\ } C_2H_6^{*}$$

$$C_2H_6^{*} \xrightarrow{\ k_b\ } 2\ CH_3^{\cdot}$$

$$C_2H_6^{*} + CH_3N_2CH_3 \xrightarrow{\ k_c\ } C_2H_6 + CH_3N_2CH_3^{*}$$
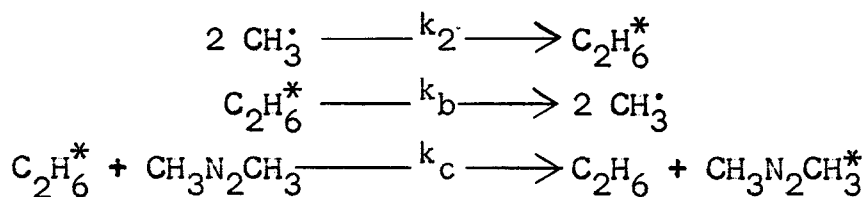
Figure 3. Addition of the Methyl Radical to Azomethane
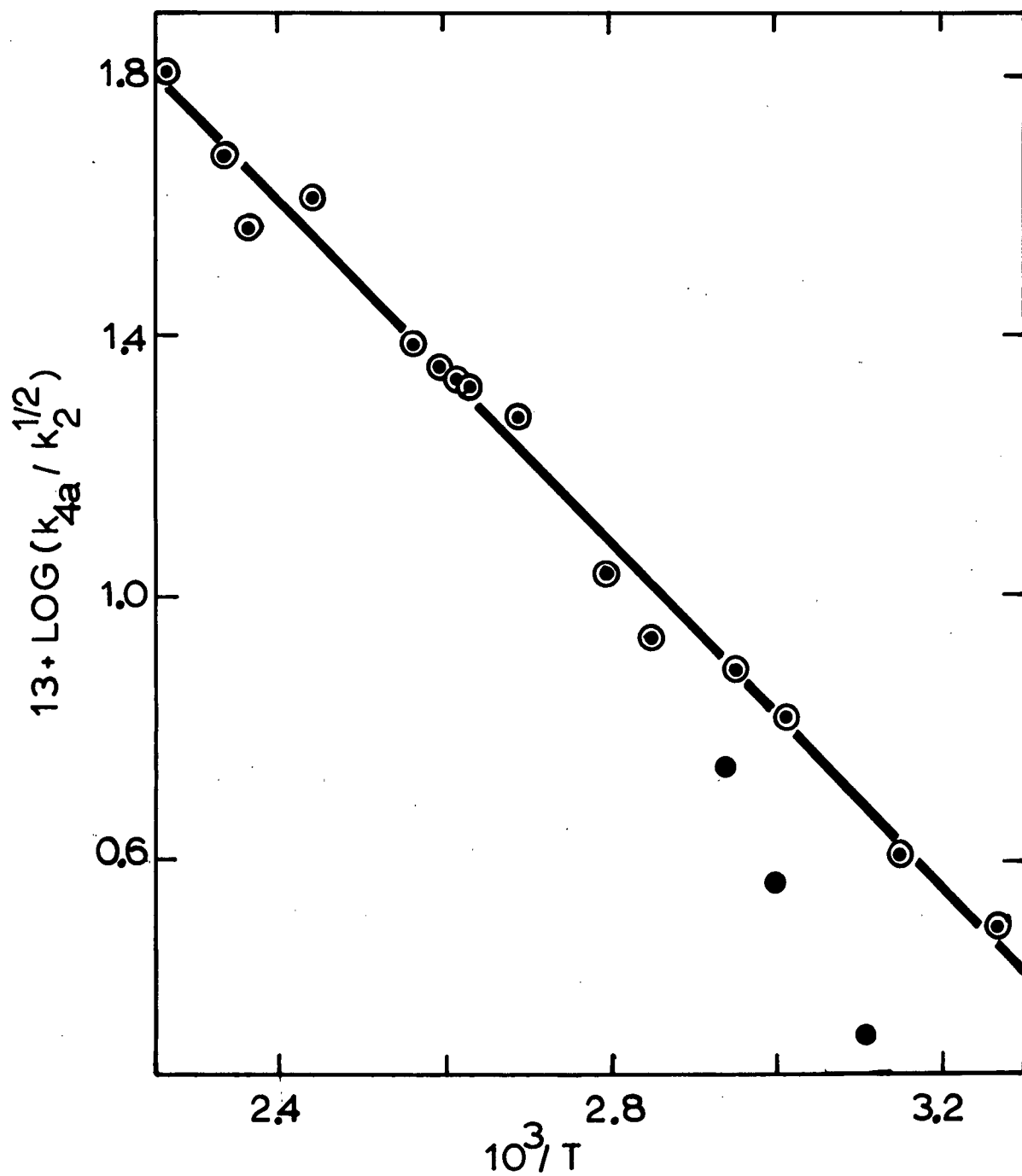
● Experiments done with the variable temperature
   trap at -160°

Figure 4. Metathesis between the Methyl Radical and Azomethane
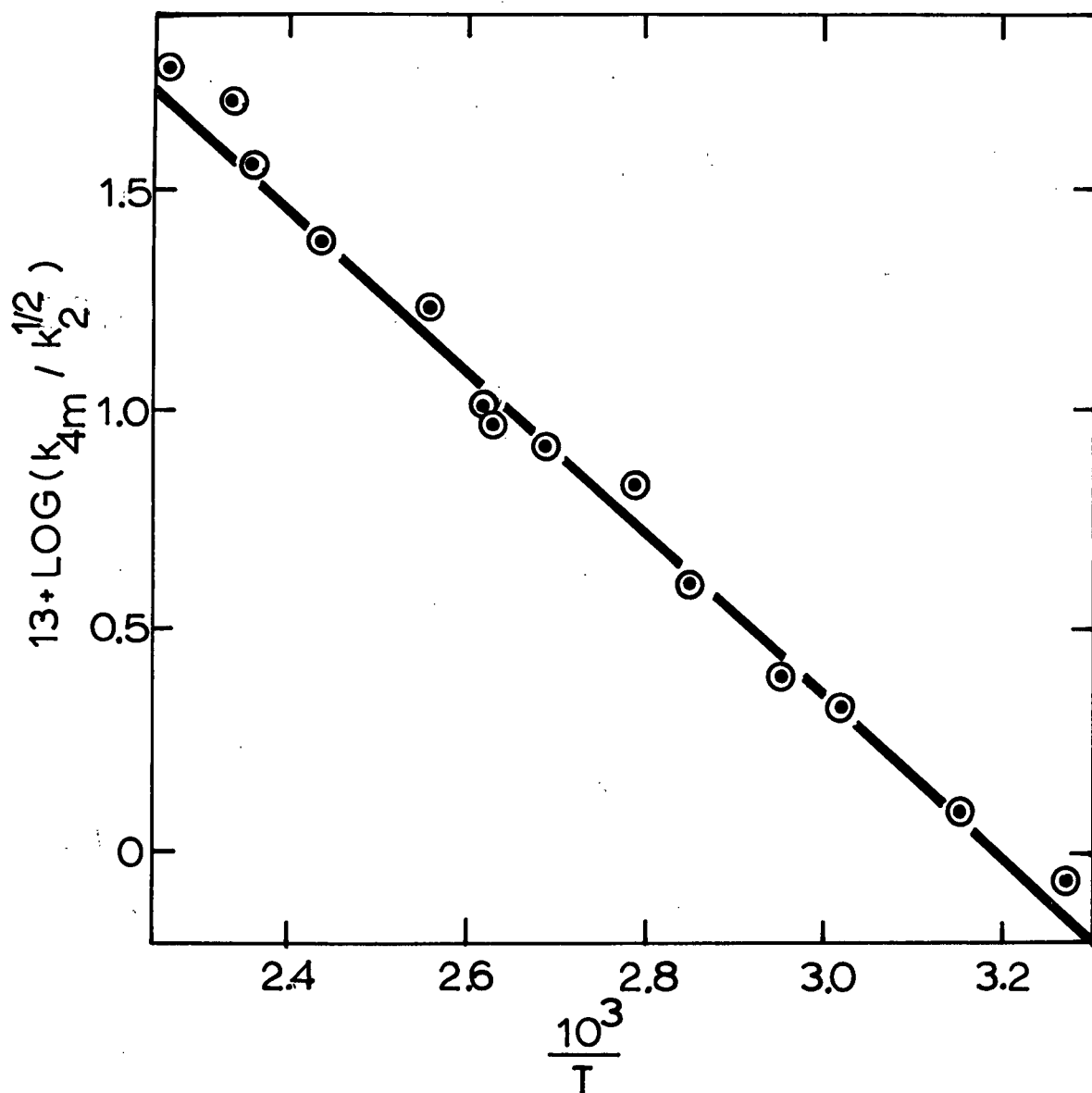
Applying a steady-state treatment to $[C_2H_6^*]$, we readily show that

$$\frac{k_{4m}}{k_2^{1/2}} = \frac{R_{CH_4}}{R_{C_2H_6}^{1/2}[A]}\left(1 + \frac{k_b}{k_c[A]}\right)^{-1/2}$$

$$\frac{k_{4a}}{k_2^{1/2}} = \frac{R_{N_2}(1-M)}{R_{C_2H_6}^{1/2}[A]}\left(1 + \frac{k_b}{k_c[A]}\right)^{-1/2}$$

where $[A] = [Azomethane]$. Therefore, each result of Table III can be corrected for pressure effects if we can evaluate the function $(1 + k_b/k_c[A])$. Unfortunately, Toby and Weiss' results do not provide an accurate assessment of k_b/k_c. However, for purposes of making a small correction, this ratio has been estimated as $\log_{10}k_b/k_c = 18.2 - 0.44 \cdot 10^3/T$ in molecules/cm.^{3}, which is consistent with their results. Recalculation of $k_{4m}/k_2^{1/2}$ and of $k_{4a}/k_2^{1/2}$ using this correction provides the Arrhenius expressions

$$\frac{k_{4m}}{k_2^{1/2}} = 10^{(5.7 \pm 0.2)}\exp\frac{-(8.2 \pm 0.4)}{RT}$$

$$\frac{k_{4a}}{k_2^{1/2}} = 10^{(4.4 \pm 0.3)}\exp\frac{-(5.6 \pm 0.4)}{RT} \left(\frac{cm.^3}{molec.\ sec.}\right)^{1/2}$$

This slight change is barely significant at the 5 % level of error. In view of the tentative nature of the values of the pressure dependent rate constants for methyl recombination, we shall prefer the uncorrected results; if more precise pressure dependence studies are available in the future, these can be recorrected in the manner indicated above.

An interesting effect was noticed in the photolysis experiments that may perhaps deserve further investigation. Results quoted above were measured with the second variable temperature

trap set at -175° when measuring ethane. Preliminary work was done on this system using -160° for the setting of this variable temperature trap. At this higher temperature it was observed that the ethane fraction did not come over pure, but contained small but kinetically important amounts of another unidentified product, the effect of which was to cause a depression of the measured value of k_{4a}. This is undoubtedly due to the fact that M values measured would be very sensitive to such spurious materials that would artificially enhance the value of $R_{C_2H_6}$. The effect dies out at about 85°. The earlier measurements are indicated on Figure 3. The presence of such an effect implies that the simple mechanism presented above for azomethane photoysis may not hold exactly.

Discussion Of chief interest in the results of the azomethane photolysis is the value of the addition rate constants. This has been measured previously by Jones and Steacie[65] and more recently by Kerr and Calvert[70] and the results of these workers have been shown on Figure 5 along with values from this work. Clearly, agreement is poor among the three determinations, although the points of Jones and Steacie are in reasonable agreement with this work, except for a persistent lowering by about 20 % above 50°. The Arrhenius parameters reported in each study are listed in the following table:

	(kcal.) $E_{4a} - \frac{1}{2}E_2$	$(cm^3/molec. sec)^{\frac{1}{2}}$ $\log(A_{4a}/A_2^{\frac{1}{2}}) + 13$
Present work	5.9 ± 0.4	4.7 ± 0.2
Jones and Steacie (1952)	6.4	not quoted
Kerr and Calvert (1965)	7.1	5.7

Figure 5. Addition of the Methyl Radical to Azomethane;
Comparison with Previous Determinations.
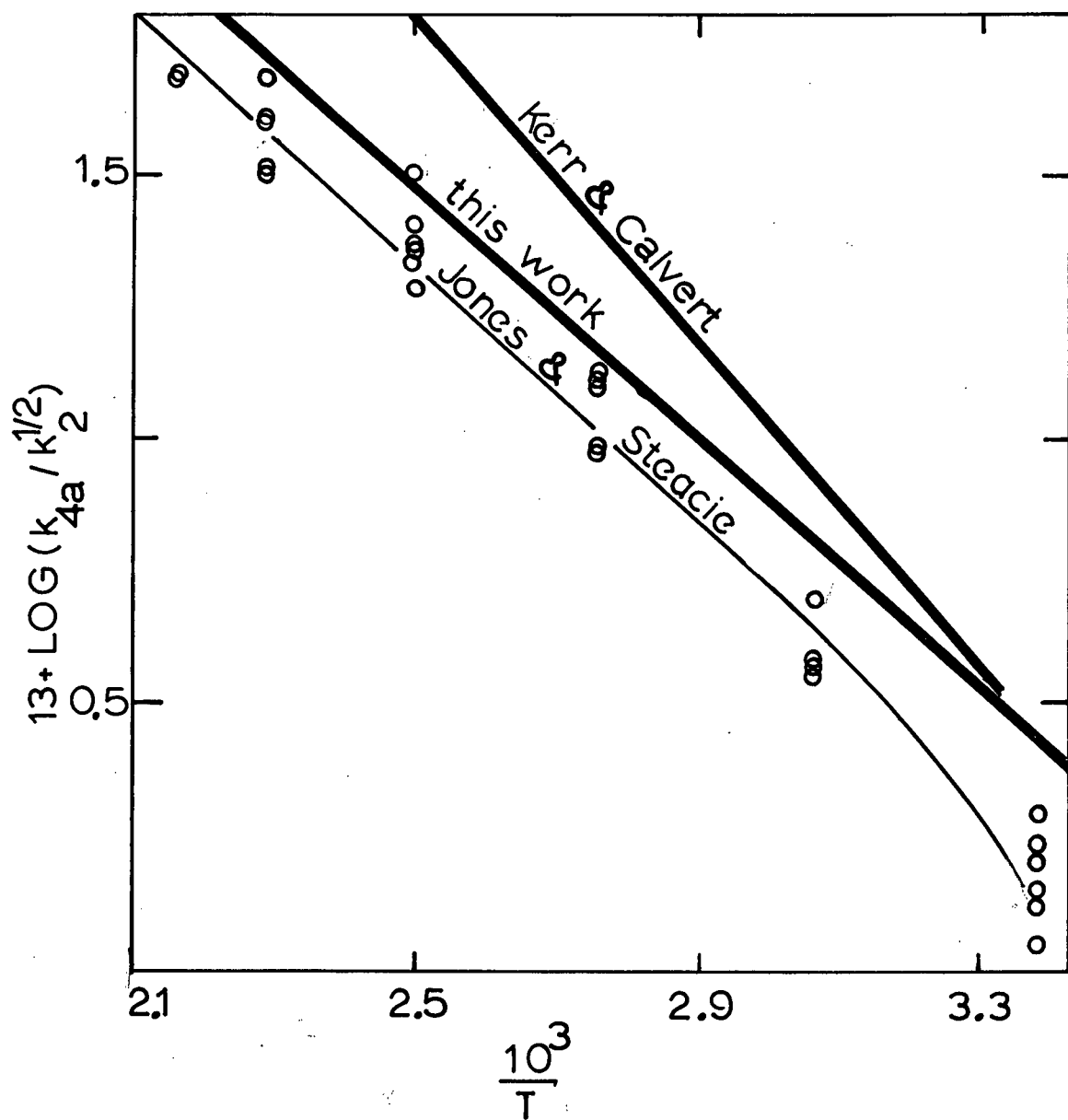
O Experimental points of Jones and Steacie.

The results of Jones and Steacie have been calculated using the same assumptions as in this work, that is, that the radicals formed during the addition reaction are all removed from the system by termination with a methyl radical. However, calculation of M values from their data according to the corresponding expression (2) shows that their methyl radical flux was not sufficiently high to support their assumption. Thus, above 90° their M values are consistently less than 0.5, indicating such a high rate of formation of adduct radicals that mutual termination must be effective. Furthermore, the scatter of their experimental results indicates insufficiencies in their assumptions. They have also measured the addition activation energy by mass spectrometric determination of the product tetramethylhydrazine, $(CH_3)_2NN(CH_3)_2$, and found essential agreement with their activation energy of 6.4 kcal. However, as other fates must exist for the adduct radical than to form tetramethylhydrazine, the same objections apply to this result as apply to their material balance technique. The present experiments have been carried out with a rate of nitrogen generation (or methyl generation) about 5-10 times greater than that of Jones and Steacie, resulting in M values never less than 0.75. Under these conditions, the material balance technique is much more secure.

The limiting case, when the rate of initiation falls very low would result in conditions where the material balance quotient is correctly formulated as:

$$M' = (\tfrac{1}{2} R_{CH_4} + R_{C_2H_6})/R_{N_2} \qquad (5)$$

Such conditions probably exist at the highest temperatures studied by Jones and Steacie where their M values are less than

0.5. If we calculate their high temperature points according to this assumption of mutual termination of adduct radicals, we find that their results are very close to those of this work.

A further difficulty with Jones and Steacie's results is that they have measured their ethane yield using a trap at -160°. As it is now found that these conditions result in an artificial fall off of $k_{4a}/k_2^{\frac{1}{2}}$ below 80°, and as their lowest temperature results (24°) seem to be rather depressed (Figure 5), it is possible that their measurements of $E_{4a} - \frac{1}{2} E_2$ are increased by this source of error. It is also easily shown that the mutual termination of adduct radicals would cause a compensating decrease in the measured activation energy, although probably not a very great decrease.

The values measured by Kerr and Calvert[70] differ more seriously from those of this work, having a larger activation energy and pre-exponential factor. They have measured the addition reaction in a rather complex system. Azomethane was photolyzed in the presence of acetaldehyde and the product, $(CH_3)_2NNHCH_3$ was observed. This was imagined to be formed in the following steps:

$$CH_3NNCH_3 + h\nu \xrightarrow{\phi_r \text{Ia}} 2 \ ^\cdot CH_3 + N_2$$

$$^\cdot CH_3 + CH_3NNCH_3 \xrightarrow{k_{4a}} (CH_3)_2N\overset{\cdot}{N}CH_3 \qquad B$$

$$CH_3CHO + (CH_3)_2N\overset{\cdot}{N}CH_3 \xrightarrow{k_s} CH_3\overset{\cdot}{C}O + (CH_3)_2NNHCH_3$$
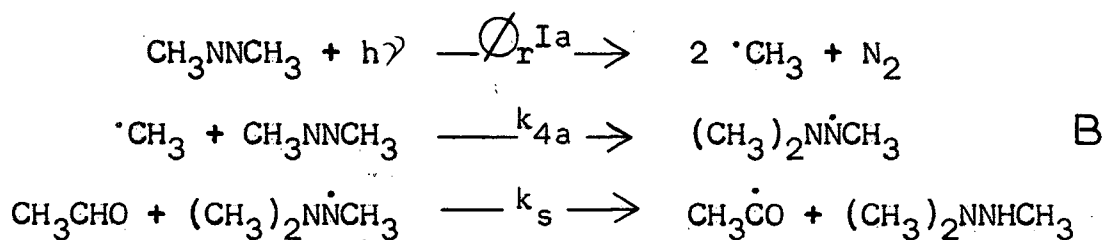
This product, $(CH_3)_2NNHCH_3$ was measured and taken as an index of the rate of addition of methyl to azomethane. Such a procedure can only be valid if all $(CH_3)_2N\overset{\cdot}{N}CH_3$ are efficiently scavenged by CH_3CHO, otherwise the activation energy of the scavenging step will be a component of the addition activation energy measured. As they report the presence of tetramethyl-

hydrazine, their activation energy can be considered only an upper limit.

The activation energy of 5.9 kcal. measured in this work for methyl addition to azomethane may be compared with 6.0 kcal. measured by Cerfontain and Kutschke[76] for the addition of ethyl radicals to azoethane. It is quite unlikely that the addition of methyl radicals should have a higher activation energy than addition of ethyl radicals, therefore the 5.9 kcal. result is preferrable to that of Kerr and Calvert.

The activation energy determined here is lower than Kerr and Calvert's value and goes in hand with a low steric factor. If we assume the diameters of methyl and of azomethane to be 3.5 and 5.5 $\overset{o}{A}$. respectively, then the steric factor becomes 7.1×10^{-5} if $k_2 = 10^{10.5}$ litre/mole sec. From these assumptions, Kerr and Calvert's steric factor becomes 6.7×10^{-4}, ten times greater and in accord with steric factors observed[77] for ethyl radical addition to terminal olefins. As we shall see, there is reason to believe that non-terminal olefins have much lower steric factors and hence the smaller value may be in accord with experience.

It is difficult to find methyl addition rate constants in the literature with which to compare the azomethane results. Of particular interest would be the rate of methyl attack on 2-butene in the gaseous phase. Virtually all work has been done in the laboratory of M. Szwarc in iso-octane solution and solvent effects may well cloud the picture. However, accurate results are available[77] for ethyl radical addition to terminal and non-terminal olefins and may be used for comparison. Also available is work by Mandelcorn and Steacie[78] concerning the addition of methyl radicals to ethylene and propylene. James and Steacie

have found that ethyl addition to non-terminal olefins, eg. trans-octene-2 and cyclohexene is at least ten times lower than that for terminal mono-olefins and were not able to measure addition to these compounds. Results for terminal olefins indicated that substitution of alkyl groups lowers the activation energy for radical addition. Similarly, Mandelcorn and Steacie[78] found a lower activation energy (6 kcal./mole) for methyl radical addition to propylene than to ethylene (7 kcal./mole). It is likely that the low reactivity of non-terminal mono-olefins is the result of a steric effect. Since azomethane is a non-terminal site of unsaturation, a low steric factor may well be expected and, indeed the value 7.1×10^{-5} is rather small and would seem more reasonable than the value of Kerr and Calvert.

The activation energy found for methyl addition to azomethane is lower than that found by Kerr and Calvert and lower than for typical alkyl radical addition to the C=C double bond, although the disubstituted mono-olefins appear to show a comparable activation energy towards ethyl attack. In view of the facts that (a) The N=N double bond is likely to be weak compared to the C=C double bond because of the lower catenating power of nitrogen. (b) The C-N bond is only slightly weaker than the C-C bond, and (c) The azomethane molecule may be somewhat activated by the methyl groups attached to it, a low activation energy may be expected for methyl attack on the N=N double bond.

The results for the abstraction reaction are more in accord with other work. The activation energy of 8.6 ± 0.5 kcal. is in good agreement with that measured by Kutschke and Toby[79] (E = 8.4 kcal.) and by Gray et al.[80] (E = 8.2 kcal.) who have measured the reaction over the same temperature range as in this work.

Toby[66] has pointed out that the various values measured for the activation energy of this process tend to drift with temperature, the lower values being measured at lower temperatures. His experiments suggested a component of the reaction may occur on the vessel walls with a lower activation energy. The sensitive analytical method employed in this investigation for the determination of methane has allowed the measurement of the reaction at very high intensities where the quantum yield of methane is very low, particularly at lower temperatures. This higher methyl radical concentration would tend to disfavour any heterogeneous reaction, and therefore the measured temperature dependence of the rate constant lies at the upper bound of those measured previously, which may have suffered from this interference.

On the other hand, a recent redetermination[75] of E_{4m} has given the lower result, $E_{4m} = 7.5 \pm 0.3$ kcal./mole, where all the mechanistic details have been taken into account. Inspection of their data shows that the low activation energy depends strongly on one experimental result at 25°, and that, neglecting this, the remaining four points are not inconsistent with $E_{4m} = 8.5$, if reasonable errors are assigned.

Another complication arises when lower radical fluxes are used in measurements of the metathetical reaction. As mentioned under Treatment of the Data, the rate constants for each run are determined from experimental data from relation (4), where the ethane rate has been corrected for ethane arising from molecular elimination. Now at the lowest intensity and highest temperatures, the overall quantum yield of ethane can fall quite low because many radicals are consumed in reactions with azomethane.

Neglect of the correction for the ethane generated by molecular elimination in azomethane photolysis may produce substantial errors when the quantum yield of ethane falls below 0.1. This can occur when low intensities are employed or when the azomethane concentration is great, and nearly all methyl radicals form methane, or are lost in addition. In the present work, the ethane quantum yield is always greater than 0.54 and the molecular elimination ethane is a negligibly small correction. The pressure dependence of rate constants measured by Jones and Steacie[65] derives from this cause.

It is interesting to compare the results for hydrogen abstraction from azomethane by methyl radicals to similar results obtained for the isoelectronic molecules butene-2[81] and acetone[82] compiled in the following table.

abstraction	$10^3 p$ [d]	(kcal.) E_a
$CH_3^{\cdot} + CH_3COCH_3$ [a]	1.2	9.7
$CH_3^{\cdot} + CH_3N{=}NCH_3$ [b]	1.4	8.6
$CH_3^{\cdot} + CH_3CH{=}CHCH_3$ [c]	1.71	7.7

[a] Trotman-Dickenson and Steacie.[81]
[b] This work.
[c] Knox and Trotman-Dickenson.[82]
[d] Using $\sigma(CH_3^{\cdot}) = 3.5$ Å.; $\sigma(\text{substrate}) = 5.5$ Å.

The activation energy for abstraction from acetone is typical of the values found for primary hydrogen atom abstraction from alkanes, which lie around 10 kcal. The lower value for abstraction from butene-2 surely arises from the fact that the allyl resonance energy is partially released in the transition state, thus lowering the activation energy. The measured activation

energy for abstraction from azomethane lies between the other two, and it is tempting to suppose that the extent of activation of the various hydrogen abstraction reactions lies in the same order as the degree of resonance stabilization of the incipient allylic moieties. Thus it is proposed that the resonance energies of these groups lie in the order:

$$CH_2 \doteq CH \doteq CH_2(CH_3) > CH_2 \doteq N \doteq N(CH_3) > CH_2 \doteq C \doteq O$$
$$\underset{CH_3}{|}$$
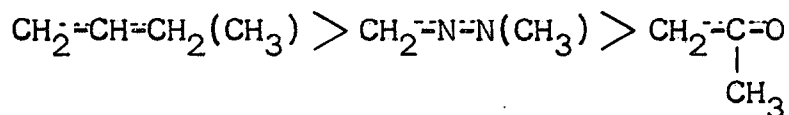
2. <u>Azomethane-cyclohexadiene-1,4 mixtures- high intensity photolysis</u>

As azomethane appears to be a good source of methyl radicals when used under appropriate conditions, it has been photolyzed in the presence of cyclohexadiene-1,4. The objectives were (a) to generate cyclohexadienyl radicals under conditions where their reactions with methyl radicals could be examined, (b) to gather data on the abstraction of hydrogen atoms from cyclohexadiene-1,4 by methyl radicals, and (c) to determine if any addition of methyl radicals to the double bonds of cyclohexadiene-1,4 could be found. Because of the very great reactivity of cyclohexadiene-1,4 towards methyl radicals, a very high rate of photolysis was necessary to ensure consumption of cyclohexadienyl radicals by reactions with methyl radicals. To secure this, the full intensity of the B.T.H. mercury lamp at 3660 $\overset{o}{A}$. was employed.

<u>Experimental</u> The system has been examined in sixteen experiments between 24° and 117°.

Azomethane was measured out into the reaction cell in the same way as described for the pure azomethane experiments, thoroughly degassing each sample prior to measurement. This measured

sample was then temporarily kept in a storage cell while a sample of cyclohexadiene-1,4 was similarly measured into the photolysis cell. Both vapours were then frozen into a cold finger attached to the cell and the mercury cut-off closed. The mixed vapours were then allowed to volatilize and were thoroughly mixed by raising and lowering the mercury in the mixer bulb (K, Figure 1) twenty times.

After mixing, the sample was irradiated with the maximum intensity of illumination available at 3660 $\overset{o}{A}$. from the B.T.H. medium pressure lamp using the same filters as for pure azomethane photolysis. With the concentrations of reactants and temperatures used as tabulated in Table IV, this light was sufficient to generate nitrogen at approximately 10^{14} molecules/cm^3 sec., or about 10-20 times faster than for pure azomethane. As cyclohexadiene-1,4 is very reactive towards methyl, rather small concentrations were employed and even at the short reaction times employed (typically 300 seconds, see Table IV) a significant amount of the cyclohexadiene (up to 25 %) was consumed. A correction was applied as explained under Treatment of the Data and values of [B] listed in Table IV are corrected values, where B is the effective concentration of cyclohexadiene-1,4.

After photolysis was completed, the reagents were refrozen into the cold finger, and then allowed to vapourize into the analytical line where the three traps (Figure 1) were set at the following temperatures:

1st Variable temperature trap	-135°
Spiral trap	-215°
2nd Variable temperature trap	-175°

TABLE IV

Metathesis between the Methyl Radical and Cyclohexadiene-1,4

(°K)	(sec.)			$10^{-12}R(X)$ (molec./cm^3 sec.)					$\left(\dfrac{cm^3}{mol.sec.}\right)^{1/2}$			
T	t	$[A]^a$	$[B]^a$	N_2	CH_4	C_2H_6	C_6H_6	M*	$10^{13}k_6/k_2^{1/2}$	$\triangle(1)$	$\triangle(2)$	$k_{\delta c}^{I}/k_{\delta c}^{II}$
296	120	6.24	0.98	131.2	8.25	118.3	1.66	0.970	59	0.358	0.302	0.698
304	600	3.14	1.35	74.1	10.57	64.6	2.84	0.976	70	(0.594)	(0.432)	0.804
305	1200	2.91	1.28	56.0	9.86	48.3	1.20	1.020	96	(0.162)	0.274	0.719
321	120	7.46	1.49	182.4	31.87	155.3	5.05	0.999	138	0.233	(0.379)	0.659
321	300	2.91	1.49	74.6	19.87	66.5	3.24	1.160	135	0.248	0.239	0.631
323	600	4.01	0.90	98.7	14.55	83.4	2.00	0.971	146	0.201	0.230	0.780
325	300	5.11	0.78	119.2	13.94	102.9	2.47	0.960	142	0.302	0.239	0.846
334	300	3.25	0.80	83.3	17.33	69.6	2.86	1.010	208	0.261	0.295	0.722
347	300	6.98	0.51	191.2	23.95	163.9	4.10	0.961	251	0.265	0.251	0.778
355	120	9.18	0.94	219.7	47.67	164.4	7.70	0.930	284	0.292	0.248	0.697
356	300	10.46	0.27	262.1	22.59	217.5	2.65	0.918	298	0.292	0.242	0.800
357	300	5.77	1.65	158.8	71.28	98.0	12.18	0.989	344	0.278	0.305	0.841

TABLE IV (continued)

$(^{\circ}K)$	(sec.)			\multicolumn{4}{c}{$10^{-12}R(X)$ (molec./cm^3 sec.)}		$\dfrac{cm^3}{mol.sec}^{\frac{1}{2}}$			
T	t	$[A]^a$	$[B]^a$	N_2	CH_4	C_2H_6	C_6H_6	M^*	$10^{13}k_6/k_2^{\frac{1}{2}}$	$\triangle(1)$	$\triangle(2)$	k_{6c}^I/k_{6c}^{II}
363	600	8.48	0.74	187.8	44.33	131.1	7.19	0.896	364	0.306	0.319	0.880
368	120	9.98	0.96	240.0	62.62	155.5	11.06	0.863	354	0.356	(0.404)	0.683
376	300	8.45	0.76	223.8	64.45	144.4	10.07	0.888	492	0.293	0.311	0.800
390	300	8.65	0.74	223.0	79.32	124.9	15.10	0.848	610	(0.435)	(0.413)	0.824
Mean value, excluding entries in parentheses										0.283	0.271	0.871
Limits of error at 5% probability level										±0.097	±0.076	±0.159

a $10^{17}[A]$ = Concentration of azomethane (molecules/cm^3)
  $10^{17}[B]$ = Concentration of cyclohexadiene-1,4 (molecules/cm^3)

b $\triangle(1)$ = $R_{C_6H_6}/(R_{CH_4} - 2\,R_{C_6H_6} - \dfrac{k_{4m}}{k_2^{\frac{1}{2}}}[A]R_{C_2H_6}^{\frac{1}{2}}r)$

c $\triangle(2)$ = R_{6d}/R_{6c} Calculated as described in text, page 70.

These are the same temperatures as used for pure azomethane studies.
The first trap stops the bulk of the azomethane, all of the cyclo-
hexadiene and heavy products. The methane, ethane and nitrogen
yields were determined using exactly the same procedure as was
employed for pure azomethane. The purity of the gaseous product
fractions was checked for some runs by analysis on an Associated
Electrical Industries M.S.9 mass spectrometer. The mass peaks
observed were precisely what would have been expected from a mix-
ture of ethane, methane and nitrogen and confirmed the results of
the routinely used v.p.c. analysis for the ethane to methane ratio.
The analytical method for gaseous products was judged, therefore,
to be sufficient.

After the gaseous products had been removed, azomethane was
stripped from the residues by pumping them through a trap at -78°
and the remaining material was mixed with a measured amount of
n-heptane as a chromatographic internal standard and then frozen
into a sample tube and removed from the vacuum line. Two analyses
were performed, each on a separate portion of the sample.

(1) About 5 μl. of the mixture was injected onto a 2 meter,
packed, polyethylene glycol column "R", using a Perkin Elmer
Vapour Fractometer 154C with flame ionization detection. Care
was taken to ensure that the injection port temperature never
rose above 100° to guard against possible pyrolysis of the sam-
ples. When nitrogen gas at 12 psig. was passed through the column,
the materials were eluted in the order: pentene-1 (solvent),
n-heptane (internal standard), benzene, cyclohexadiene-1,4, and
a final peak due to product II. A typical chromatographic record
is reproduced in Figure 6. No other products were observed even
when alternative columns were employed to search for them. The

Figure 6. Packed Column Analysis of the Products of the High Intensity Photolysis of Azomethane-Cyclohexadiene-1,4 Mixtures.
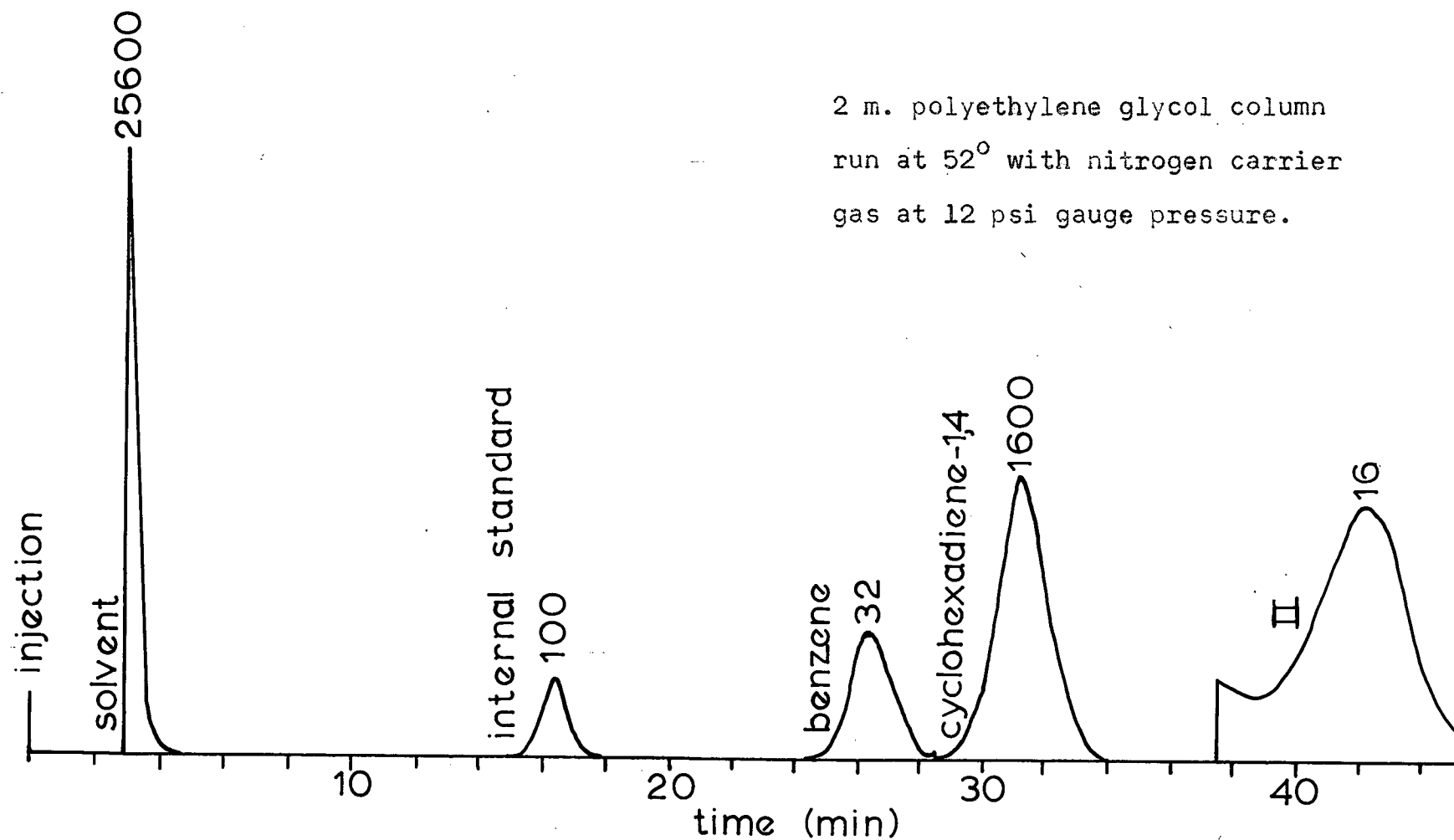
ratio of areas, benzene to cyclohexadiene-1,4 was used to make a small correction to the benzene yield due to the presence of a small amount of benzene in the cyclohexadiene-1,4 starting material. This correction was always less than 10 % of the total benzene peak area. The residual area was converted to moles of benzene by comparison with the area of the n-heptane peak using the calibration:

$$\frac{\text{moles (benzene)}}{\text{moles (n-heptane)}} = 1.095 \frac{\text{Area (benzene)}}{\text{Area (n-heptane)}}$$

The calibration factor 1.095 was determined from measurements of synthetic benzene-n-heptane mixtures.

(2) A second analysis was done on the residues in order to measure the long retention time peaks I and II (see Figure 7A) which are better resolved on a capillary column than on the packed columns used for benzene analysis. (I is not separated from the tail of the cyclohexadiene-1,4 peak on the packed column.) About 5 μl. of the product mixture was injected into the stream splitting injection block on a Perkin Elmer Model 226 gas chromatograph using a capillary polyethylene glycol column "R", as described under Experimental Methods. When the column was maintained at room temperature the products were eluted as shown schematically in Figure 7A. Peak areas for compounds I and II, benzene and cylohexadiene-1,4, were measured with a planimeter. Special care was taken while running this analysis to check for the presence of cyclohexadiene-1,3 and other products. None were observed. Specifically, $R_{C_6H_8-1,3} < 0.01 \ R_{C_6H_6}$

<u>Treatment of the Data</u> Analytical examination of the photolysis of azomethane-cyclohexadiene-1,4 mixtures at high intensities has revealed the following products: nitrogen, methane, ethane,

Figure 7. Capillary Column Analysis of the Products of the High Intensity Photolysis of Azomethane-Cyclohexadiene-1,4 Mixtures.

A. Reproduction of a typical analysis.

B. Reproduction of the analysis of the products of the hydrogenation experiment.
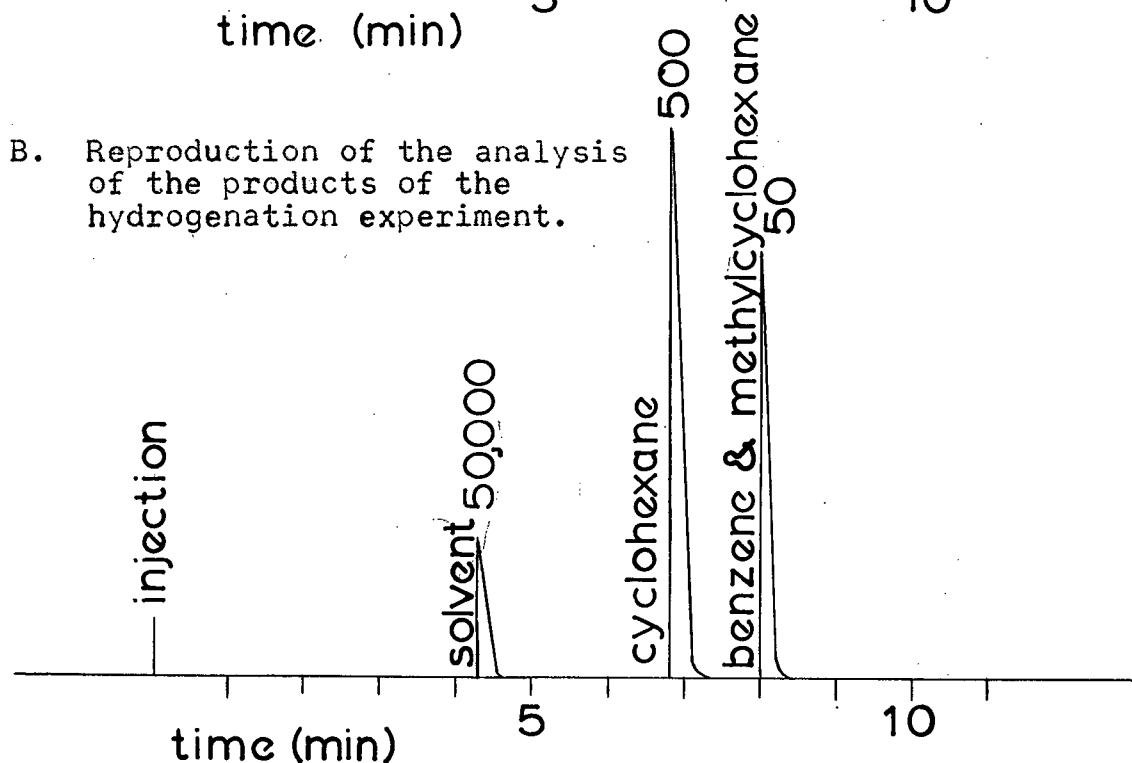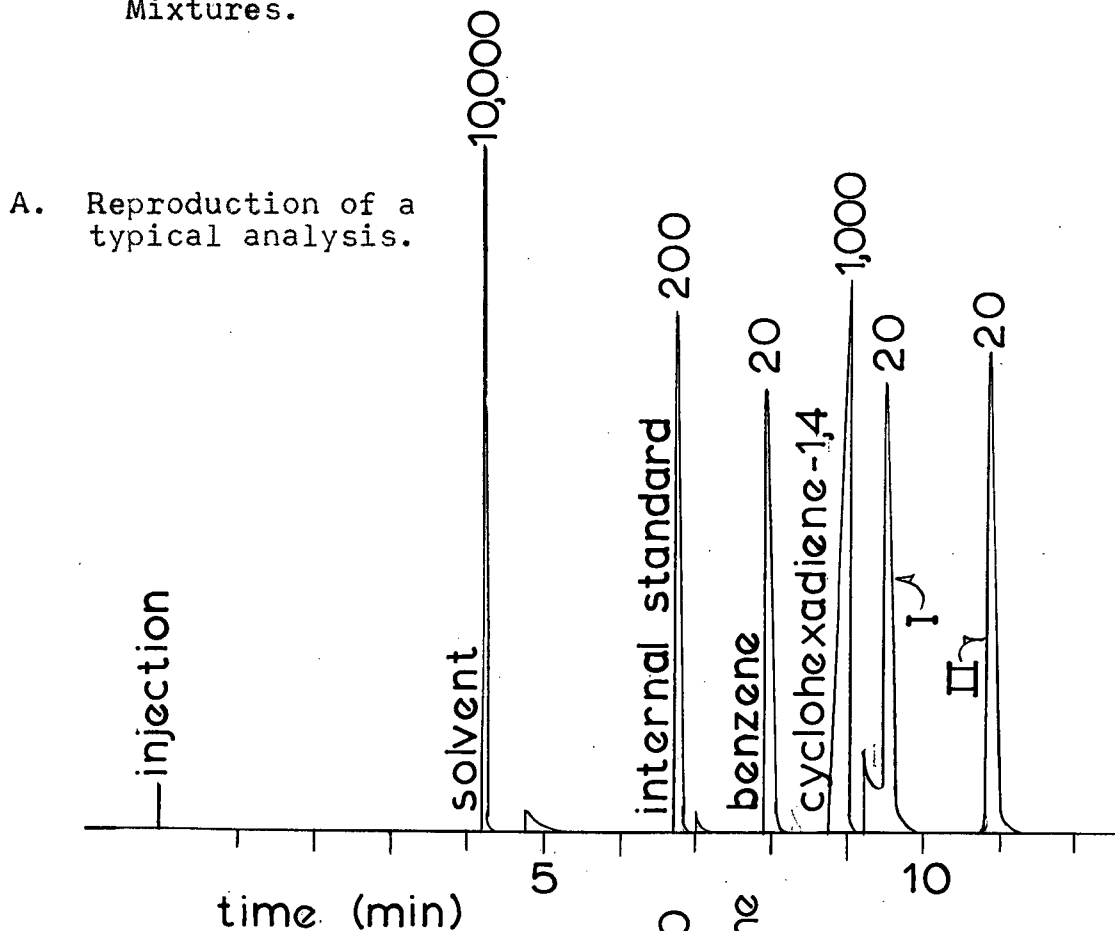
benzene and two heavy products designated I and II which will be shown to be the two products of recombination expected in the reaction of methyl and cyclohexadienyl radicals.
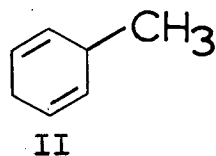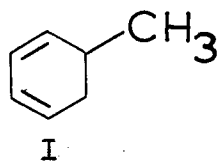
The accessible analytical data and certain other derived quantities to be discussed have been presented in Table IV.

The reaction scheme C has been proposed to account for the experimental observations. This scheme is very similar to that found to be adequate in many other investigations of this type. At the high intensities employed it is supposed that all secondary radicals resulting from methyl attack on a substrate molecule react with another methyl radical. At the moderate temperatures of the photolysis, such an assumption in reasonable. The disproportionation step, 6d, is necessary to account for the significant benzene yields found.

$$CH_3N_2CH_3 + h\nu \quad -^{I_a\emptyset_r} \rightarrow 2\ CH_3^{\cdot} + N_2$$
$$-^{I_a\emptyset_m} \rightarrow C_2H_6 + N_2$$
$$2\ CH_3^{\cdot} \xrightarrow{\ 2\ } C_2H_6$$
$$CH_3^{\cdot} + CH_3NNCH_3 \xrightarrow{\ 4m\ } CH_4 + \dot{C}H_2NNCH_3$$
$$CH_3^{\cdot} + \dot{C}H_2NNCH_3 \xrightarrow{\ 5m\ } C_2H_5NNCH_3$$
$$CH_3^{\cdot} + CH_3NNCH_3 \xrightarrow{\ 4a\ } (CH_3)_2N\dot{N}CH_3$$
$$CH_3^{\cdot} + (CH_3)_2N\dot{N}CH_3 \xrightarrow{\ 5a\ } (CH_3)_2NN(CH_3)_2$$
$$CH_3^{\cdot} + C_6H_8\text{-}1,4 \xrightarrow{\ 6\ } CH_4 + C_6H_7^{\cdot}$$
$$CH_3^{\cdot} + C_6H_7^{\cdot} \xrightarrow{\ 6_c^{I}\ } I$$
$$\xrightarrow{\ 6_c^{II}\ } II$$
$$\xrightarrow{\ 6d\ } CH_4 + C_6H_6$$

C
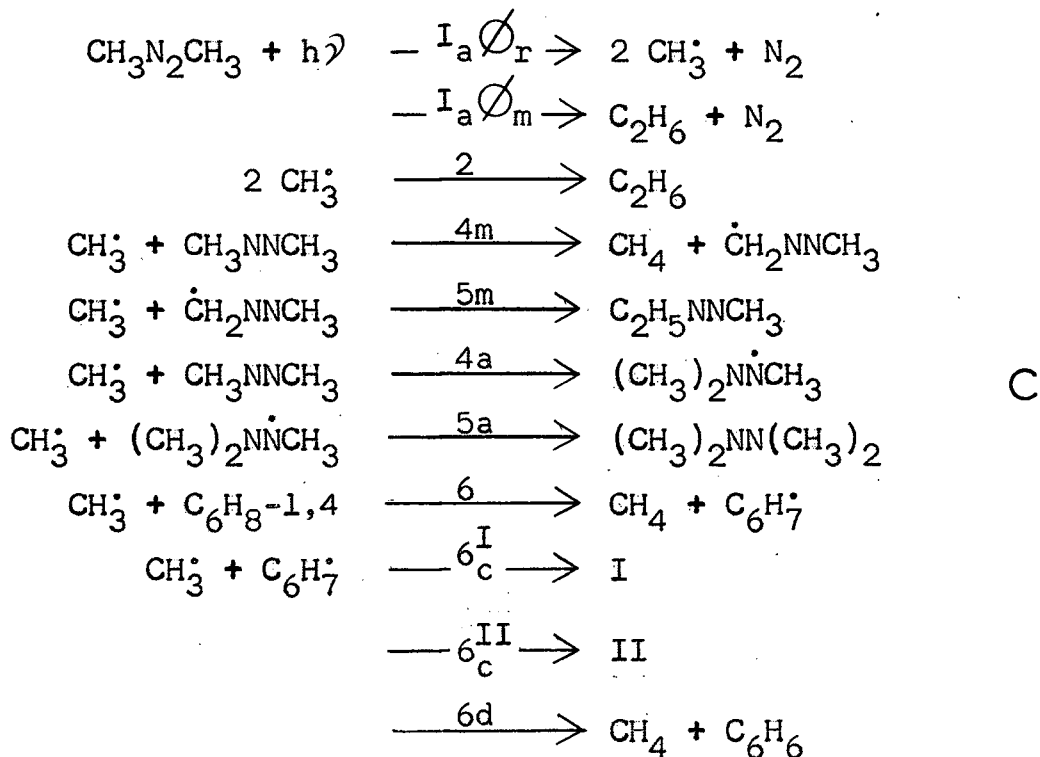
The above scheme leads to the following relationships when analyzed according to the usual steady-state treatment:

$$\frac{k_6}{k_2^{\frac{1}{2}}} = \frac{R_{CH_4} - R_{C_6H_6}}{[B] \; R_{C_2H_6}^{\frac{1}{2}r}} - \frac{[A] \; k_{4m}}{[B] \; k_2^{\frac{1}{2}}} \tag{6}$$

where $[A]$ = concentration of azomethane; $[B]$ = concentration of cyclohexadiene-1,4. As $CH_3^{\cdot}$ reacts very rapidly with cyclohexadiene-1,4, small reactant pressures and high intensities of illumination are required. These conditions cause a significant consumption of cyclohexadiene in the course of the run by the time enough products have accumulated for unequivocal analysis. The values of $[B]$ in Table IV have been corrected for this consumption by the following method:

$$[B]_{eff} = [B]_{in} - \frac{R_6 t}{2}$$

$$= [B]_{in} - \frac{t}{2}\left[R_{CH_4} - R_{C_6H_6} - \frac{k_4}{k_2^{\frac{1}{2}}}[A]R_{C_2H_6}^{\frac{1}{2}r}\right]$$

where t = the reaction time. Once again, the correction for ethane formed in the molecular elimination process at the rate $\emptyset_m R_{N_2} = 0.012 R_{N_2}$ is not sigificant due to the large overall yields of ethane. In these experiments $\emptyset_{C_2H_6} \geqslant 0.55$.

Values of $10^{13} k_6/k_2^{\frac{1}{2}}$ have been compiled for each experiment in Table IV and their logarithms are plotted as a function of $10^3/T$ in Figure 8. The least mean squares treatment of the data yields the Arrhenius expression:

$$10^{13} \frac{k_6}{k_2^{\frac{1}{2}}} = 10^{(5.9 \pm 0.2)} \exp - \frac{(5.52 \pm 0.35)}{RT}$$

As in the case of the photolysis of pure azomethane, a tentative correction for the pressure dependence of the recombination

Figure 8. Metathesis between the Methyl Radical and Cyclohexa-
diene-1,4.
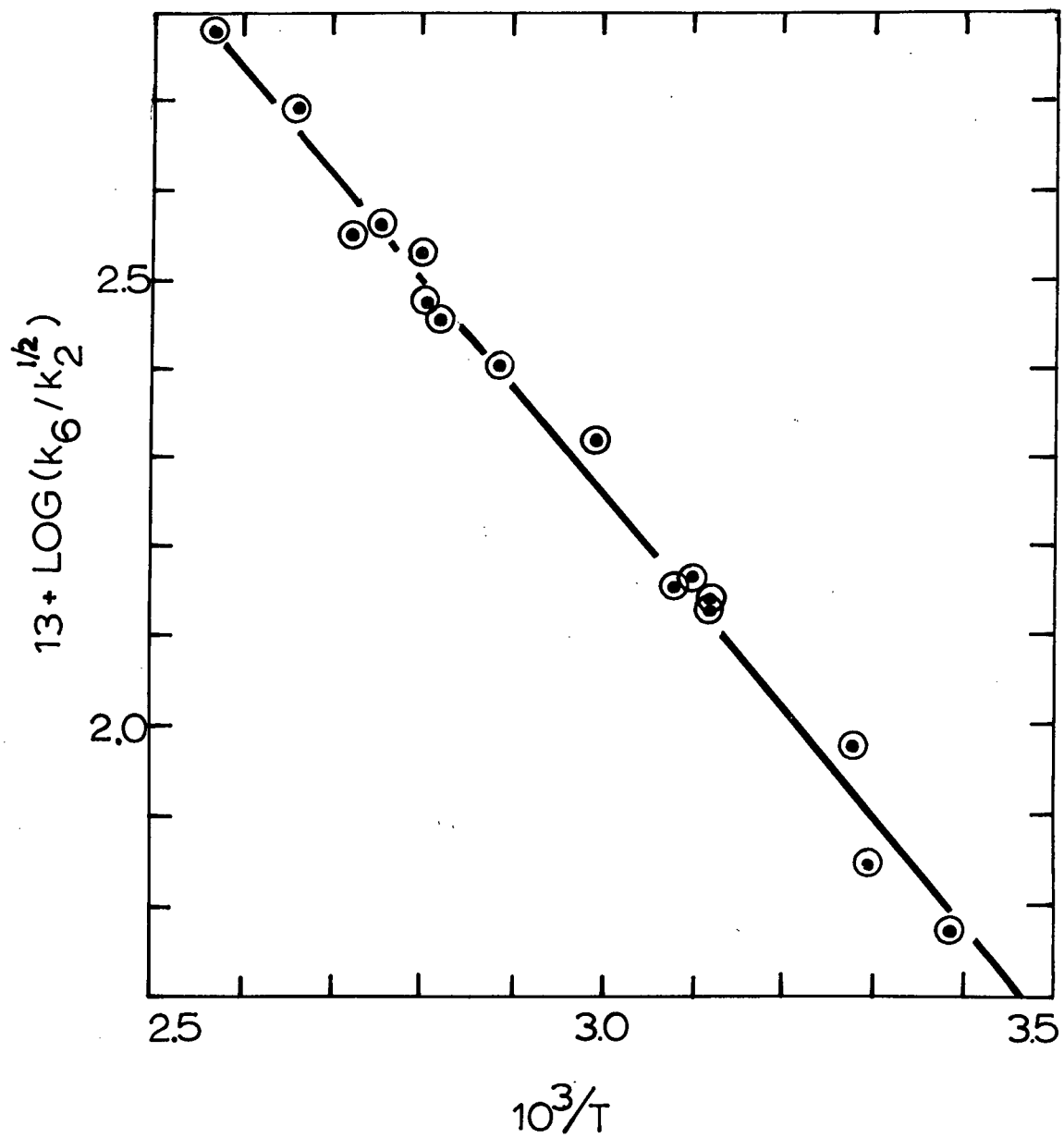
of methyl radicals can be made using the data of Toby and Wiess.[75]
Replacing reaction (2) with the system of reactions

$$2 \; CH_3^\cdot \xrightarrow{\; 2 \;} C_2H_6^*$$

$$C_2H_6^* \xrightarrow{\; b \;} 2 \; CH_3^\cdot$$

$$C_2H_6^* + CH_3NNCH_3 \xrightarrow{\; c \;} CH_3NNCH_3^* + C_2H_6$$

it is readily shown that each run in Table IV must be multiplied
by a correction factor,

$$\left[1 + \frac{k_b}{k_c(\, [A] + [B] \,)} \right]^{-\frac{1}{2}}$$
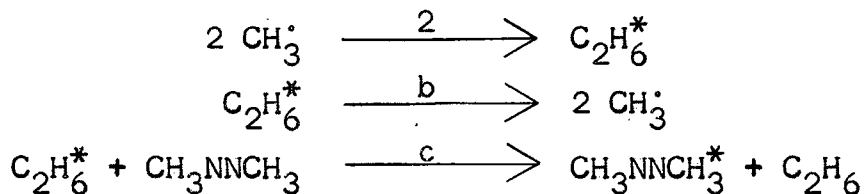
where we estimate k_b/k_c from Toby and Weiss' data using the ap-
proximate relation $\log(k_b/k_c) = 18.2 - 0.44(10^3/T)$. When the
runs are corrected in this fashion there is obtained the new
Arrhenius expression

$$10^{13} \frac{k_6}{k_2^{\frac{1}{2}}} = 10^{(5.9 \, \pm \, 0.2)} \exp - \frac{(5.55 \pm 0.32)}{RT}$$

This result is not different from the uncorrected one.

The disproportionation to combination ratio of methyl and
cyclohexadienyl radicals can be calculated from the relationship:

$$\triangle(CH_3^\cdot, C_6H_7^\cdot) = \frac{k_{6d}}{k_{6c}^I + k_{6c}^{II}} = \frac{R_{C_6H_6}}{R_6 - R_{C_6H_6}}$$

$$= \frac{R_{C_6H_6}}{(R_{CH_4} - \frac{k_4}{k_2^{\frac{1}{2}}}[A]R_{C_2H_6}^{\frac{1}{2}} - 2 \, R_{C_6H_6})} \tag{7}$$

Values of this expression have been presented in Table IV under
the heading $\triangle(1)$ for each kinetic run. This method of determin-
ation of $\triangle(CH_3^\cdot, C_6H_7^\cdot)$ does not make use of the experimentally
available chromatographic peak areas of compounds I and II obtained
from the capillary column analysis. Presumably, the ratio of the

areas of the benzene peak to the sum of the areas of peaks I and
II, multiplied by the appropriate calibration factor would give
$\triangle(CH_3^\cdot, C_6H_7^\cdot)$ directly. The lack of authentic samples of the
combination products makes calibration of the detector impossible,
so an independent determination of $\triangle(CH_3^\cdot, C_6H_7^\cdot)$ by this method
is precluded. The area ratios from the capillary column analysis
have a lower statistical standard deviation than the values from
equation (7) and clearly arise from more direct experimental
procedures. Accordingly, values of $\triangle(2)$ are presented in Table IV
which have been found from these area ratios using a calibration
factor calculated from $\triangle(1)$ values in the following way.

The values of the area quotient Q, where

$$Q = \frac{Area(I) + Area\ (II)}{Area(C_6H_6)}$$

were found from the capillary column analyses for each run. Q
was found to have the value 2.92 $\pm$ 0.81, independent of temperature.
Each value of $\triangle(1)$ from equation (7) was then multiplied by the
Q value for each experiment to give the quotient P = 0.793 $\pm$ 0.172
for sixteen runs whose median value lies between 0.762 and 0.834.
The mean value, $\overline{P}$, was used as a calibration factor to recalculate
values for $\triangle(2) = \overline{P}/Q$ for each run. In this way we are able to
utilize the more accurate capillary column analytical data, but,
of course, the actual measured value of $\triangle(2)$ reflects the re-
sults obtained by use of equation (7). The mean value of $\triangle(1)$
differs slightly from the mean value of $\triangle(2)$ because different
data have been ommitted on statistical grounds from the final
averaging but this difference is not significant in view of the
overall errors.

The ratio of the areas of peaks I and II has been used directly to calculate the values for k_c^I/k_c^{II} listed in Table IV. This is reasonable insofar as it is unlikely that the response of the detector would be much different towards such similar compounds as these two isomeric recombination products.

The logarithms of the values of $\triangle(2)$ and of k_c^I/k_c^{II} have been presented as funtions of $10^3/T$ in Figure 9. As can be seen, no significant temperature trend is evident in these plots.

The value $k_c^I/k_c^{II} = 0.76 \pm 0.16$ can be compared to the similar ratio found by Eberhardt et al.[10] in radiolysis experiments of cyclohexadiene-1,4-$^{14}CH_3I$ solutions. In these liquid phase experiments $k_c^I/k_c^{II} = 0.59 \pm 0.13$ at room temperature in reasonable agreement with present measurements, and substantiating the observed preference for the non-conjugated combination product.

Since fairly rapid addition of methyl radicals to azomethane occurs, and causes a depression of the material balance, $M^* = (R_{CH_4} + R_{C_2H_6} - R_{C_6H_6})/R_{N_2}$, it is difficult to check for methyl addition to cyclohexadiene-1,4 on a material balance basis. We can rule this reaction out however, on the following grounds.

(1) The reaction sequence:
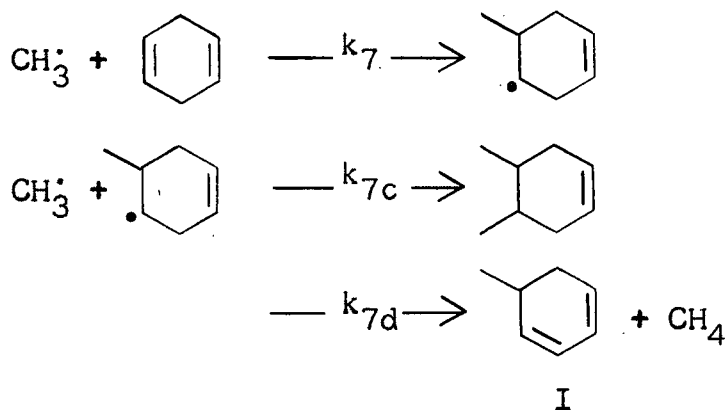
(a) would cause an increase in k_c^I/k_c^{II}. In fact, this ratio is lower for the methyl radical than for other radicals studied

Figure 9. Combination and Disproportionation of the Methyl Radical with the Cyclohexadienyl Radical.
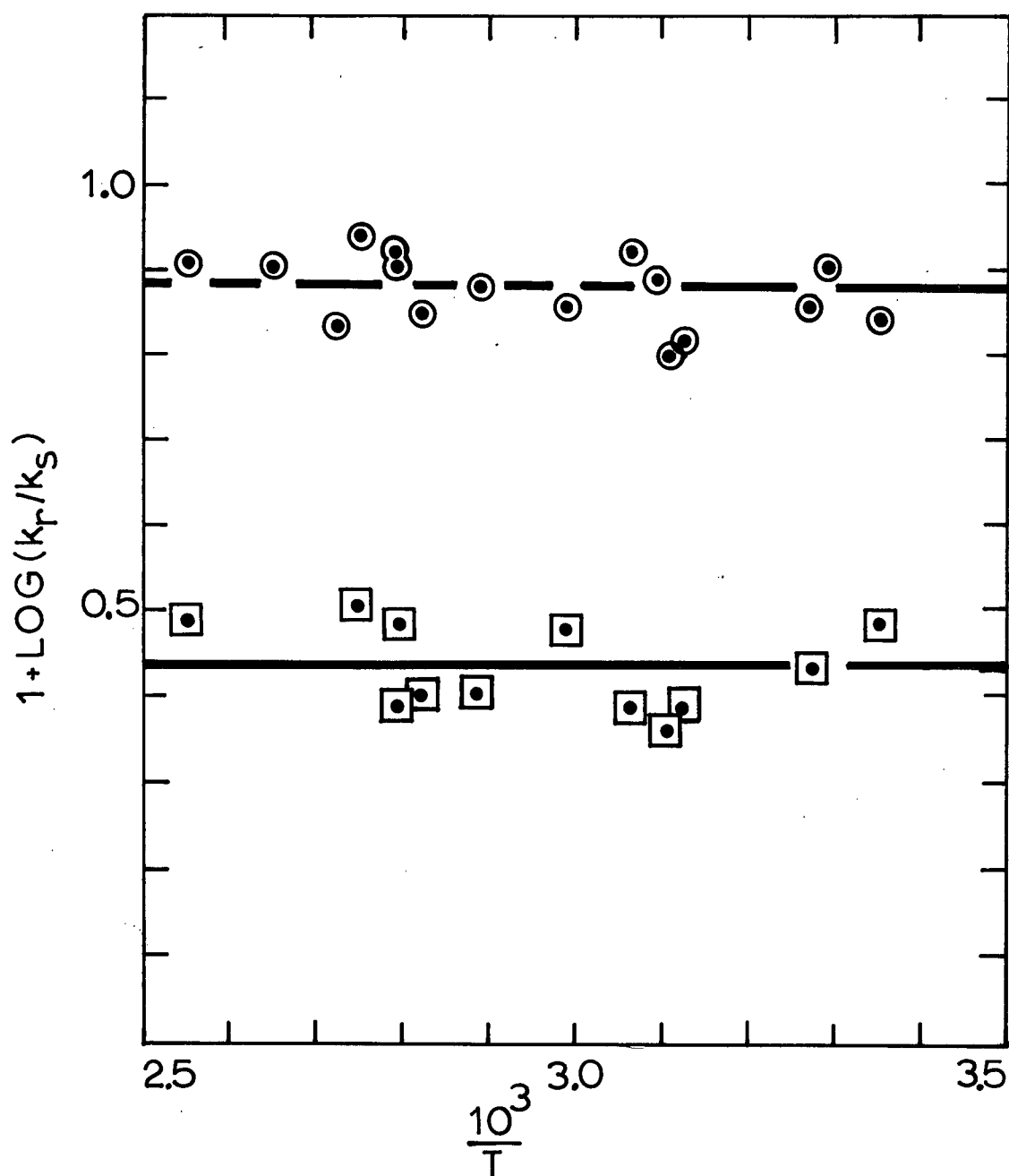
$\odot \quad k_r/k_s = k_{6c}^{I}/k_{6c}^{II}$

$\boxdot \quad k_r/k_s = k_{6d}/(k_{6c}^{I} + k_{6c}^{II})$

here where addition does not occur. (See General Discussion)
(b) would certainly lead to the product 4,5-dimethylcyclohexene which is readily detectable on the capillary chromatography column, but was not found.

(2) Dominguez and Trotman-Dickenson[83] have examined the methyl, ethyl, isopropyl and _tert_-butyl addition reactions to acetylene, and found the methyl radical to be no more reactive than the isopropyl radical, which has been found not to add to cyclohexadiene-1,4.

The detection of minute amounts of cyclohexadiene-1,3 in the reaction products could be easily accomplished from the capillary column analysis, but was not, in fact, observed. This indicates that there is no mutual termination of the cyclohexadienyl radicals since later work (See Low Intensity Photolysis of Azomethane-Cyclohexadiene-1,4 Mixtures) has shown that the 1,3-diene is a product of such reactions, ie:
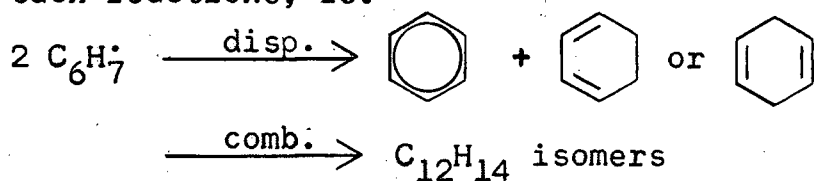
$$2\ C_6H_7^{\bullet} \xrightarrow{\text{disp.}} \text{\bigcirc} + \text{\hexagon} \text{ or } \text{\hexagon}$$

$$\xrightarrow{\text{comb.}} C_{12}H_{14} \text{ isomers}$$

This knowledge adds support to the use of equation (7). Another indication from the low intensity work is that $C_6H_7^{\bullet}$ radicals decompose into hydrogen atoms and benzene above ca. 136°. As the work done here does not extend beyond 117°, and as efficient removal of $C_6H_7^{\bullet}$ radicals by methyl termination will cause this species to have very short lifetimes in this system, interference from decomposition is not anticipated.

Special experiments made on Azomethane-Cyclohexadiene-1,4 system to identify Products I and II In all the experiments made at high radical concentration on the abstraction of hydrogen atoms from cyclohexadiene-1,4, two heavy products appear in the

capillary column chromatograms for all initiator radicals except

tert-butyl. In the case of methyl radicals, these elute rapidly,

and are widely separated. As one proceeds towards tert-butyl rad-

icals the two products are retained to longer retention times and

are less widely separated, until, for tert-butyl experiments,

they are no longer resolved on the column. Of course, we suspect

these compounds to be the representatives of the homologous series:

 and for R = CH_3-, C_2H_5-, $C_3H_7^i-$, and $C_4H_9^t-$

I   II
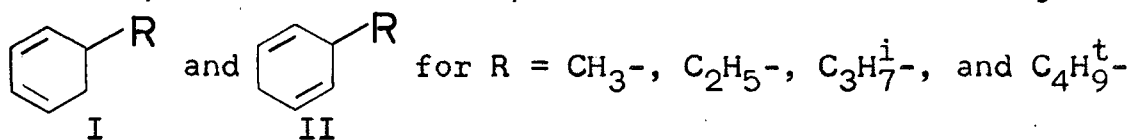
In the methyl case, a hydrogenation experiment has shown that

these products have the skelatal structure of methylcyclohexane.

(1) Hydrogenation of the heavy products. 16 mm. of azo-

methane and 4 mm. of cyclohexadiene were photolyzed at room

temperature (23°) for 30 minutes. Following this treatment the

light products and azomethane were pumped off through a dry ice-

acetone trap and the remaining materials were frozen into 1 ml.

n-pentane and removed from the vacuum system. Chromatographic

analysis of this mixture showed the typical distribution of pro-

ducts, plus cyclohexadiene-1,4 as shown in Figure 7A (no heptane,

of course, was present in this sample.)

The remaining solution was shaken for 30 minutes under a

pressure of one atmosphere of hydrogen in the presence of 10 mg.

of Adam's hydrogenation catalyst, (PtO_2) at 0°. 100 μl. of the

product of this treatment injected onto the capillary column

gave the chromatogram shown schematically in Figure 7B where

the cyclohexadiene-1,4 has given rise to the strong cyclohexane

peak and the previous benzene peak has been much enlarged. Run-

ning the sample again using a capillary column with a hydrocarbon

grease substrate demonstrated that this latter peak contained both benzene and methylcyclohexane. Thus the compounds I and II were observed to be hydrogenated to methylcyclohexane. It was concluded, therefore that I and II are unsaturated derivatives of methylcyclohexane.

(2) Chromatographic retention times of I and II on the capillary column are 9.5 and 10.9 min. respectively (Figure 7A). This represents a shift of 1.8min. between cyclohexadiene-1,3 and I and 2.0 min. between cyclohexadiene-1,4 and II. Since both products I and II have the methylcyclohexane carbon skeleton and their v.p.c. retention times are consistent with methylated cyclohexadiene-1,3 and cyclohexadiene-1,4 respectively, there is little doubt that they have the structures
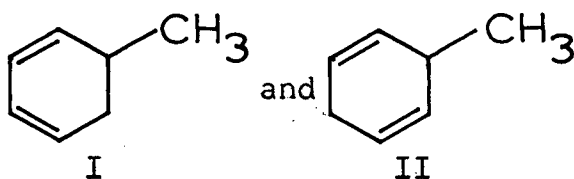
It will be assumed that the higher homologues are analogously formed in the cases of more complex initiating radicals.

3. _Azomethane-cyclohexadiene-1,4 mixtures - low intensity photolysis_

The very high reactivity of cyclohexadiene-1,4 towards the methyl radical qualifies it as an efficient scavenger if it is present in sufficient concentration and if the rate of photolysis of azomethane is sufficiently slow. Under these conditions all radicals in the system will be replaced by the cyclohexadienyl radical. This has been used here as a means of producing the cyclohexadienyl radical to study its mutual interactions and to seek evidence for its unimolecular decomposition at higher _temperature_.

Some evidence for the reaction, $C_6H_7^. \longrightarrow H^. + C_6H_6$, has been found, and Arrhenius parameters have been estimated for this reaction, although it is clear that the mechanism of the process taking place is quite complex.

Experimental Photolysis of azomethane-cyclohexadiene-1,4 mixtures was done in the same way as for the previous high intensity studies, except that much larger pressures of the diene and lower pressures of azomethane were used. These conditions are indicated in Table V. Neutral density filters of optical densities 1.88 and 1.4 were used to attenuate the 3660 $\overset{o}{A}$. illumination isolated from the mercury arc lamp.

After photolysis, analysis proceded generally as for the high intensity experiments. All products volatile at -175° were pumped into the gas burette. These comprised methane, nitrogen and ethane. Also, minute traces of ethylene (quantum yield, $\emptyset$(ethylene), from about 0.0001 to 0.0005) were consistently found. This is of unknown origin and is so small that it has not been considered in the mechanism. Ethylene likely arises as a low probability decomposition of photo-excited azomethane. The ethane-methane ratio was determined by chromatographic analysis, then the total product distribution could be calculated from the relation $R_{N_2} = \frac{1}{2} R_{CH_4} + R_{C_2H_6}$. This relation uses the observation of the high intensity studies that methyl radicals do not add significantly to the cyclohexadiene-1,4 molecule.

Three mass spectrometric analyses (Table V) had sufficiently strong N_2 peaks to give accurate results in spite of the natural nitrogen background. The ratio of the (corrected) peak heights at m/e = 16 and at m/e = 28 is representative of the

TABLE V

The Unimolecular Decomposition of the Cyclohexadienyl Radical

T (°C)	t (min.)	$[A]^b$	$[B]^b$	$R_X \times 10^{-12}$ (molecules/cm^3 sec.)							10^{-4}(mol/cm^3 sec.)$^{1/2}$	
				N_2	CH_4	R_6	C_2H_6	C_6H_{10}	C_6H_8-1,3	C_6H_6	$k_8/k_7^{1/2}$	$k_8/k_{7d'}^{1/2}$
63	1080	0.380	10.1	0.107	0.210	0.210	0.0016	0	0.0116	0.0306	-	-
73	1020	0.528	10.5	0.160	0.316	0.315	0.0019	0	0.00671	0.0493	-	-
80	1200	0.435	7.49	0.120	0.238	0.238	0.0012	0	0.0135	0.0403	-	-
89	420	0.229	7.36	0.0974	0.193	0.193	0.0009	0	0.0101	0.0290	-	-
101	1110	0.363	7.025	0.111	0.219	0.218	0.0019	0	0.0122	0.0405	-	-
118	240	0.470	5.86	0.388	0.751	0.749	0.0122	0	0.0499	0.150	-	-
123	180	1.13	3.79	0.847	1.658	1.646	0.0185	0	0.0664	0.358	-	-
136[a]	1200	0.444	8.55	0.145	0.289	0.288	0.0006	0.0093	0.0174	0.0983	1.73	4.98
145[a]	1080	0.340	8.25	0.105	0.208	0.208	0.0012	0.0248	0.0159	0.0946	5.45	13.9
151[a]	1080	0.618	7.90	0.172	0.338	0.337	0.0028	0.0384	0.0244	0.179	6.60	17.4
157	1170	0.408	5.78	0.154	0.305	0.305	0.0012	0.0576	0.0226	0.178	10.5	27.2
162	420	0.514	8.93	0.380	0.752	0.751	0.0041	0.250	0.0861	0.575	28.8	60.2

TABLE V (continued)

($^{\circ}$C)	(min.)			$R_X \times 10^{-12}$ (molecules/cm^3 sec.)							10^{-4} (mol/cm^3 sec.)$^{1/2}$	
T	t	$[A]^b$	$[B]^b$	N_2	CH_4	R_6	C_2H_6	C_6H_{10}	C_6H_8-1,3	C_6H_6	$k_8/k_7^{1/2}$	$k_8/k_{7d'}^{1/2}$
163	1200	1.258	8.93	0.383	0.761	0.757	0.0027	0.216	0.066	0.550	24.8	59.5
164	210	0.281	6.79	0.230	0.455	0.454	0.0022	0.134	0.0366	0.242	19.9	49.5
165	1260	0.357	2.19	0.121	0.241	0.239	0.0007	0.108	0.0146	0.207	22.1	63.3
166	1140	0.434	2.97	0.160	0.316	0.315	0.0018	0.145	0.0245	0.259	25.8	65.0
166^a	1020	0.429	7.88	0.0972	0.189	0.189	0.0028	0.179	0.0247	0.275	41.1	80.0
166	180	1.046	7.806	0.780	1.537	1.529	0.0134	0.295	0.131	1.005	23.9	57.7
172^a	1170	0.446	7.40	0.139	0.277	0.276	0.0010	0.268	0.0298	0.366	51.0	110.
186	1080	0.355	6.30	0.173	0.341	0.340	0.0020	0.580	0.0201	0.600	99.5	290.

^{a} Product analysis checked by mass spectrometry.

^{b} $[A] = 10^{-17}$ Concentration of azomethane (molecules/cm^3.)
$[B] = 10^{-17}$ Concentration of cyclohexadiene-1,4 (molecules/cm^3.)

ratio of the pressures of methane and nitrogen. The mass spectro-
meter was calibrated by examination of mass spectra taken during
the high intensity photolysis experiments of azomethane and cyclo-
hexadiene-1,4, where the relative pressures of methane and nitro-
gen were accurately determined analytically. This indicated that
the ratio of peak heights, h(16)/h(28), could be multiplied by
1.528 to obtain relative pressures. The three determinations
gave the following results:

T	R_{CH_4}/R_{N_2}	
(°C)	Mass Spectrometry	Normal Analysis
136	1.94	1.99
151	2.00	1.97
172	2.04	1.99

Independent analysis confirms, therefore, the adopted analytical
method up to the high temperature region.

The liquid residues were analyzed on the packed, polyethylene
glycol column at 50°, in the usual way, providing measurements
for cyclohexene, cyclohexadiene-1,3, benzene and finally the
starting material, cyclohexadiene-1,4. Yields of these products
have been presented in Table V.

It is possible to monitor the efficiency of the scavenging
of the methyl radical by measuring the rate of formation of
1-methylcyclohexadiene-2,5 (II) whose chromatographic peak is not
too seriously interfered with by the tail of the cyclohexadiene-1,4
peak in the capillary column analysis. It can be calculated from
the disproportionation ratios measured in this section that if
$R_{C_6H_8-1,3}$ is twelve times greater than R_{II}, then the rate of loss
of methyl radicals in recombination with the cyclohexadienyl
radical is less than one percent of the total methyl radicals

introduced. Traces of II are found in most runs; those in which its chromatographic area is greater than one twelfth that of cyclohexadiene-1,3 have been rejected.

<u>Treatment of the data</u> At 123° and below, there is produced no cyclohexene, and the ratio of benzene to cyclohexadiene-1,3 production becomes constant, Under these conditions, the system is likely described by Scheme D, where efficient scavenging of methyl radicals and ultimate termination by cyclohexadienyl radicals is considered.

At the reactant pressures used, attack of $CH_3^\cdot$ on azomethane is quite negligible, amounting to well under 1 % of all methyl radicals produced. Values of R_6 in Table V have been calculated from R_{CH_4} by subtracting the methane that arises from attack of methyl radicals upon the azomethane molecule. This is readily done from the measured values of $k_{4m}/k_2^{1/2}$ and $k_6/k_2^{1/2}$ listed in Table XV.

$$CH_3N{=}NCH_3 + h\nu \xrightarrow{\phi_r I_a} 2\ CH_3^\cdot + N_2$$

$$\xrightarrow{\phi_m I_a} C_2H_6 + N_2$$

$$CH_3^\cdot + C_6H_8{-}1,4 \xrightarrow{\quad 6 \quad} CH_4 + C_6H_7^\cdot$$

$$2\ C_6H_7^\cdot \xrightarrow{\quad 7d' \quad} \text{⬡} + \text{⬡} \quad (11 \pm 2\ \%)$$

$$\xrightarrow{\quad 7d'' \quad} \text{⬡} + \text{⬡} \quad (20 \pm 8\ \%)$$

$$\xrightarrow{\quad 7c \quad} C_{12}H_{14}\ \text{isomers}\ (69 \pm 6\ \%)$$
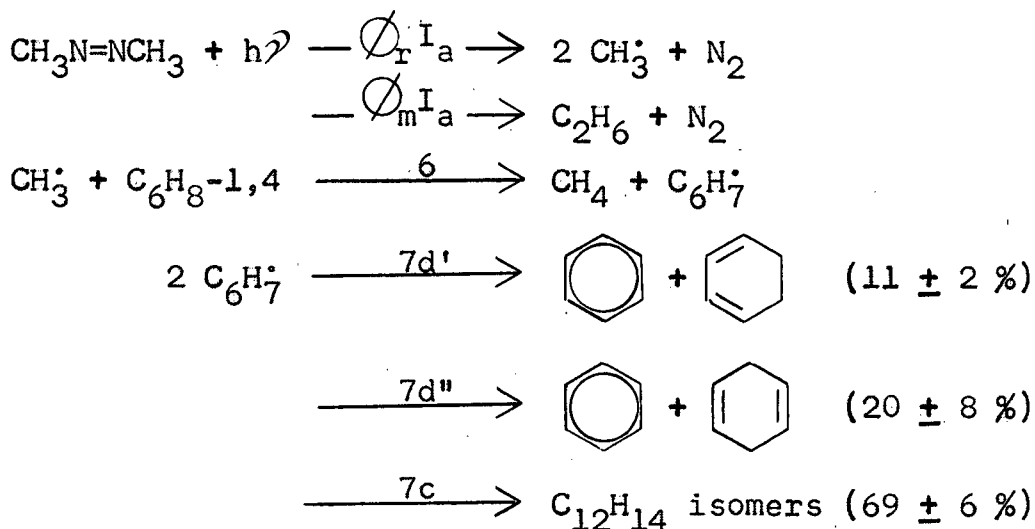
D

The ethane produced arises from the molecular elimination process previously described, and a quantitative estimate (or at least an upper limit, if bimolecular recombination of $CH_3^\cdot$ is not completely quenched) is available. If the overall quantum yield of nitrogen is unity, then the quantum yield of molecular

elimination is given by the equation:

$$\log \emptyset_m = \log(R_{C_2H_6}/R_{N_2}) = \overline{2}.08 \pm 0.4$$

independent of temperature, where the estimate is obtained by the statistical analysis of 20 experiments at reactions temperatures from 63 to 186°. These results are given as an Arrhenius plot in Figure 10B, and are in good agreement with independent estimates based upon the use of oxygen,[71] sulphur dioxide[73] and cyclohexadiene-1,4[74] as scavengers, and upon the kinetic analysis of the photolysis of a mixture of azomethane and azomethane-$\underline{d}_6$.[67] The mean value of 0.012 is clearly in general agreement with the results of the other studies, and the greater scope of this investigation increases the weight of the evidence that the quantum yield of the molecular elimination process is independent of temperature between 25 and 186°. Since temperature apparently neither quenches nor enhances the molecular elimination process, it probably arises through a highly excited, upper electronic state where thermal energy is of little significance. This is consistent with the fact that the overall quantum yield, $\emptyset(N_2)$, is unity over a range of temperatures in the vapour.[65]

Since $R_{C_6H_6}/R_6$ is less than one-half, it is apparent that recombination occurs and accounts for an appreciable fraction of the $C_6H_7^{\cdot}$ radicals. Statistical treatment of the low temperature results yields $(k_{7d'} + k_{7d''})/k_{7c} = 0.45 \pm 0.12$ and $k_{7d'}/(k_{7d'}+k_{7d''})= 0.36 \pm 0.08$ at the 5 % probability level of error. With the data at the head of the following page, and from the relation,

$$\frac{(k_{7d'} + k_{7d''})}{k_{7c}} = \frac{2(R_{C_6H_6}/R_6)}{1 - 2(R_{C_6H_6}/R_6)}$$

we find $(k_{7d'} + k_{7d''})/k_{7c} = 0.45 \pm 0.12$. This result has not been

previously reported.

T($^\circ$C)	$R_{C_6H_6}/R_6$	$R_{C_6H_8-1,3}/R_6$
63.1	0.1445	0.0552
72.5	0.1562	(0.0214)
79.8	0.1691	0.0567
89.2	0.1507	0.0525
100.9	(0.1853)	0.0558
Avg. =	0.155 ± 0.029	0.0551 ± 0.0078

We can evaluate $\dfrac{k_{7d'}}{k_{7d'} + k_{7d''}} = \dfrac{(R_{C_6H_8-1,3}/R_6)}{(R_{C_6H_6}/R_6)} = 0.356$

Assessment of the error proceedes as follows:

$$d\left(\frac{k_{7d'}}{k_{7d''}}\right) = \frac{R_{C_6H_8-1,3}/R_6}{(R_{C_6H_6}/R_6)^2} \, d\left(\frac{R_{C_6H_6}}{R_6}\right) + \frac{d(R_{C_6H_8-1,3}/R_6)}{R_{C_6H_6}/R_6}$$
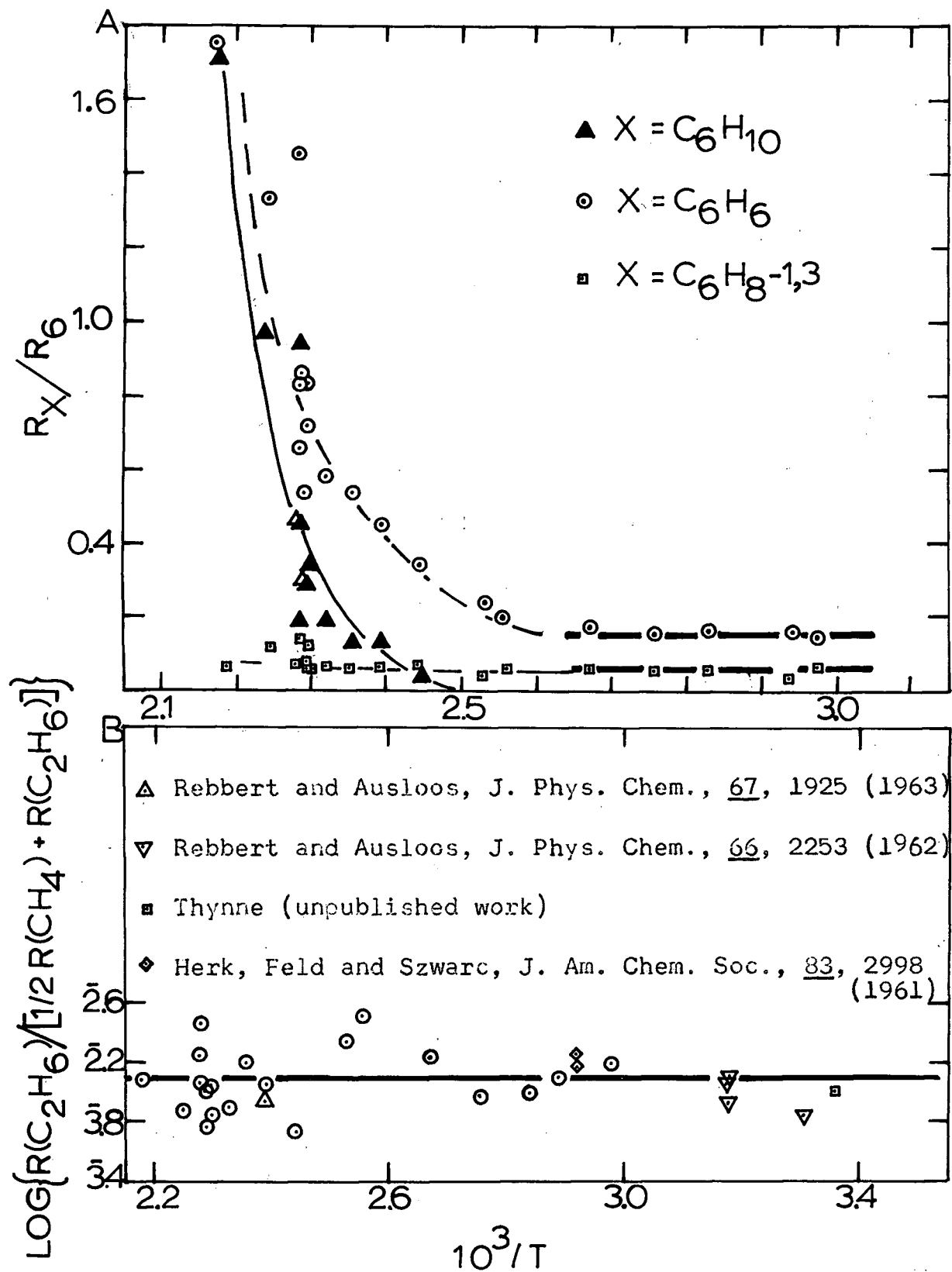
$$= 0.166 \text{ at } 0.25 \text{ % level}$$

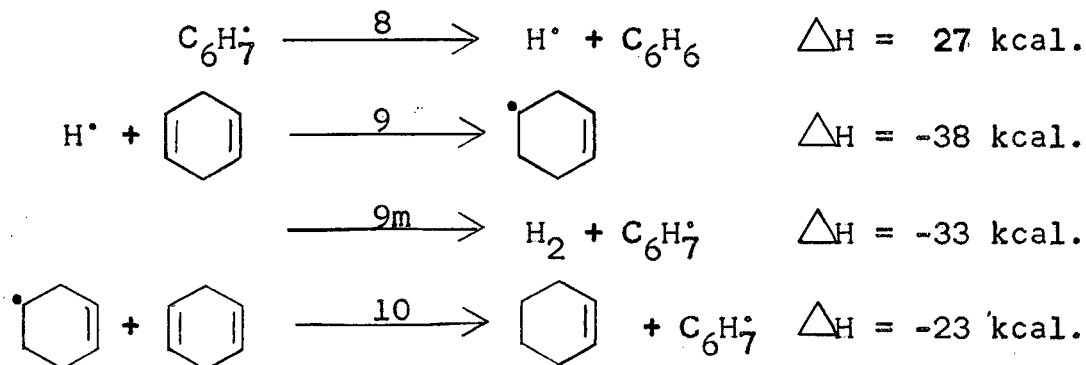$$= 0.075 \text{ at } 5 \text{ % level.}$$

The result, 0.36 ± 0.08, can be compared to Eberhardt's re-sult of 0.27 ± 0.04 from radiolysis of liquid cyclohexadiene-1,4.[10] Agreement is reasonable, although the condensed phase apparently yields less of the 1,3-diene.

As the temperature rises above 120° (Figure 10A), the yield of benzene increases with respect to methane, and we begin to de-tect cyclohexene. As the cyclohexadienyl radical is highly act-ivated towards thermal decomposition, the observed behavior may be caused by the extra reactions given in Scheme E. This se-quence is part of the mechanism proposed for the radiolysis of liquid cyclohexadiene-1,4,[10] and reactions (9) and (10) have been shown to be rapid in that system, where hydrogen atoms are generated

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Figure 10. Temperature dependence of the yields of the products

radiolytically.

$$C_6H_7^\cdot \xrightarrow{\ 8\ } H^\cdot + C_6H_6 \qquad \triangle H = 27 \text{ kcal.}$$

$$H^\cdot + \text{(benzene)} \xrightarrow{\ 9\ } \text{(cyclohexadienyl radical)} \qquad \triangle H = -38 \text{ kcal.}$$

E

$$\xrightarrow{\ 9m\ } H_2 + C_6H_7^\cdot \qquad \triangle H = -33 \text{ kcal.}$$

$$\text{(cyclohexadienyl radical)} + \text{(benzene)} \xrightarrow{\ 10\ } \text{(cyclohexadiene)} + C_6H_7^\cdot \qquad \triangle H = -23 \text{ kcal.}$$

The thermochemical values quoted have been calculated from standard values and the following data.

X	$H_f^0(X)$	Source
(cyclohexadienyl radical)	45	Measured in this work.
(benzene)	26	Cox, Tetrahedron, 19, 1175 (1963).
(cyclohexadiene)	27	$\triangle H_f^0$(cyclohexane) - 2 H_{hyd}(cyclohexene) Harrison et al., J. ACS, 87, 5099 (1965).
(cyclohexadienyl radical)	41	Assumes H + (cyclohexadiene) ⟶ (radical) to be 38 kcal./mole exothermic.

Examination of the gaseous products of several representative runs (indicated in Table V) by mass spectrometry showed that the rate of molecular hydrogen production was less than one percent of the methane rate. Reaction (9m) does not appear to be very important, therefore, and it shall be assumed that it does not occur at all. We ultimately wish to calculate Arrhenius parameters for reaction (8). It will then be shown that the neglect of (9m) causes no significant error as long as hydrogen production is below one percent of the methane production.

The olefinic linkages of cyclohexadiene-1,4 are apparently much more reactive towards hydrogen addition than the methylenic

hydrogen atoms are towards metathesis. In view of the very low
activation energies of hydrogen atom addition to olefins,[84] this
conclusion is not unreasonable. A similar pattern of reactivity
is shown by the interaction of the hydrogen atom with propene;
the rate constants for metathesis and addition stand in the ratio
of 0.04 at 25° and less than 0.08 at 240°.[85-87] The predominance
of the addition process with propylene is probably due to the
favourably low activation energy of 2.2 kcal./mole.[84] The pre-
dominance of the addition process with cyclohexadiene-1,4 may be
due to a favourable difference in the activation energies,
$E_{9m} - E_9 = 3$ kcal./mole. The activation energies for the metathe-
sis of the methyl, ethyl, isopropyl and tert-butyl radicals with
cyclohexadiene-1,4 are indistinguishable at 5.5 $\pm$ 0.3, 5.8 $\pm$ 0.1,
6.5 $\pm$ 1.0 and 5.3 $\pm$ 0.8 kcal./mole respectively (See Table XV),
indicating that the strength of the incipient bond has little
influence on the value of the activation energy. Let us tentative-
ly assign the values: $E_9 = 2$ kcal./mole, $E_{9m} = 5$ kcal./mole and
$A_9 = A_{9m}$; we then obtain the ratio $k_{9m}/k_9 = 0.03$ at 164°, in
qualitative agreement with the observed behavior. Reaction (9),
therefore, accounts for all of the hydrogen atoms released, form-
ing a secondary radical, unstabilized by resonance. Slaugh[88] has
found this species not susceptible to structural isomerization.
The cyclohexen-4-yl radical is structurally related to the iso-
propyl radical which has been found (Table XV) to have similar
reactivity towards C_6H_8-1,4 as the methyl radical. Inspection of
the liquid products by capillary column chromatography shows that
the products, $CH_3-C_6H_7$, (both isomers I and II) are inhibited
strongly by the C_6H_8-1,4 scavenger, therefore no reason exists

to believe the cyclohexen-4-yl radical should interact with the cyclohexadienyl radical in this system. Thus all termination is by reactions (7c) and (7d), as is expected in the presence of an efficient scavenger.

The reactions of Scheme E are the propagation steps of a chain reaction. That a chain is involved is indicated by the fact that $R_{C_6H_{10}}/R_6$ becomes greater than unity at 186°.

Some possible, alternative reactions can be shown to be unlikely. It is not easy to vary the pressure of cyclohexadiene-1,4 over a very wide range, therefore experimental evidence is lacking to disprove the bimolecular process,

 $\Delta H = -11$ kcal.
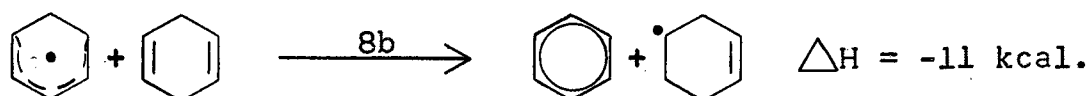
which yields the same products as reaction(8). Hydrogen atoms are not generated in this process, so that the formation of molecular hydrogen need not arise. The value of E_{8b} obtained by a kinetic analysis based upon the complete suppression of reaction (8) by reaction (8b) would not differ significantly from the value for E_8 of 31 ± 5 kcal./mole that we shall see characterizes the formation of cyclohexene. Using a mean value of 5×10^{17} molec./cm^3 for the concentration of cyclohexadiene-1,4, we can calculate that an absurdly high value of 10^{17} litre/mole sec. would be necessary for A_{8b} in order for this reaction to have the observed rate. Should reaction (8b) compete at all, it must be at most a minor process.

The reaction

 $\Delta H = -1$ kcal.
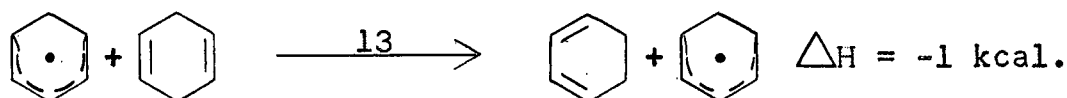
may contribute to the observed increase in $R_{C_6H_8-1,3}/R_6$, (Figure 10A).
It is unlikely that E_{13} is less than the value of about 5.5
kcal./mole observed for the reactions R· + ⬡ ⟶ RH + $C_6H_7^.$
where R· is an alkyl radical; methyl, ethyl, isopropyl or
tert-butyl, and may be much greater. We would expect a much
sharper rise in the ratio $R_{C_6H_8-1,3}/R_{CH_4}$ than is observed, hence
reaction (13) is not a likely explanation for this effect.

The direct pyrolysis of cyclohexadiene-1,4 has been reported
by Frey.[89] The reaction, $C_6H_8-1,4 \longrightarrow C_6H_6 + H_2$ was found to
have the rate constant k = $10^{12.02} exp(-42,690/RT)$ sec^{-1}. At
500°K. and assuming $C_6H_8-1,4$ = 5 x 10^{17} molec./cm^3, the rate
of this reaction would be 0.017 x 10^{12} molec./cm^{3}sec., about
one hundred times less than the benzene yield from other sources.
Pyrolysis experiments were done in this work to determine thermal
sensitivity of the reactant, and none was found.

The molecular hydrogen elimination

⬡ $\xrightarrow{8a}$ H_2 + ⬡· $\triangle H$ = 26 kcal.
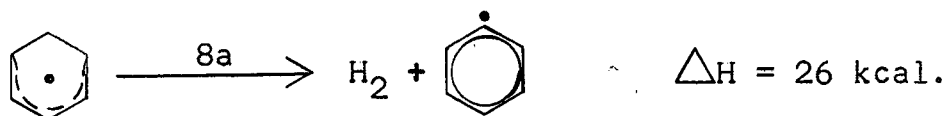
is not important as H_2 is not detected in the gaseous products.

Several runs have been performed at 164 ± 1.7°, where the
rate of initiation has been varied over as wide a range as is
convenient without breaking down the assumption of total scaveng-
ing. Figure 11 shows that the benzene arising from dispropor-
tionation, ie., $R_{C_6H_6} - R_{C_6H_{10}}$, and the cyclohexadiene-1,3 are
generated at a rate proportional to the rate of initiation, R_6.
This is consistent with the assumption that they form in a reac-
tion bimolecular in the cyclohexadienyl radical. We conclude that
$R_{C_6H_8-1,3}$ and $R_{C_6H_6} - R_{C_6H_{10}}$ are reliable measures of the square
of the concentration of $C_6H_7^.$. Figure 12 shows that cyclohexene

Figure 11. Kinetic Order of Cyclohexadiene-1,3 and Benzene Production.

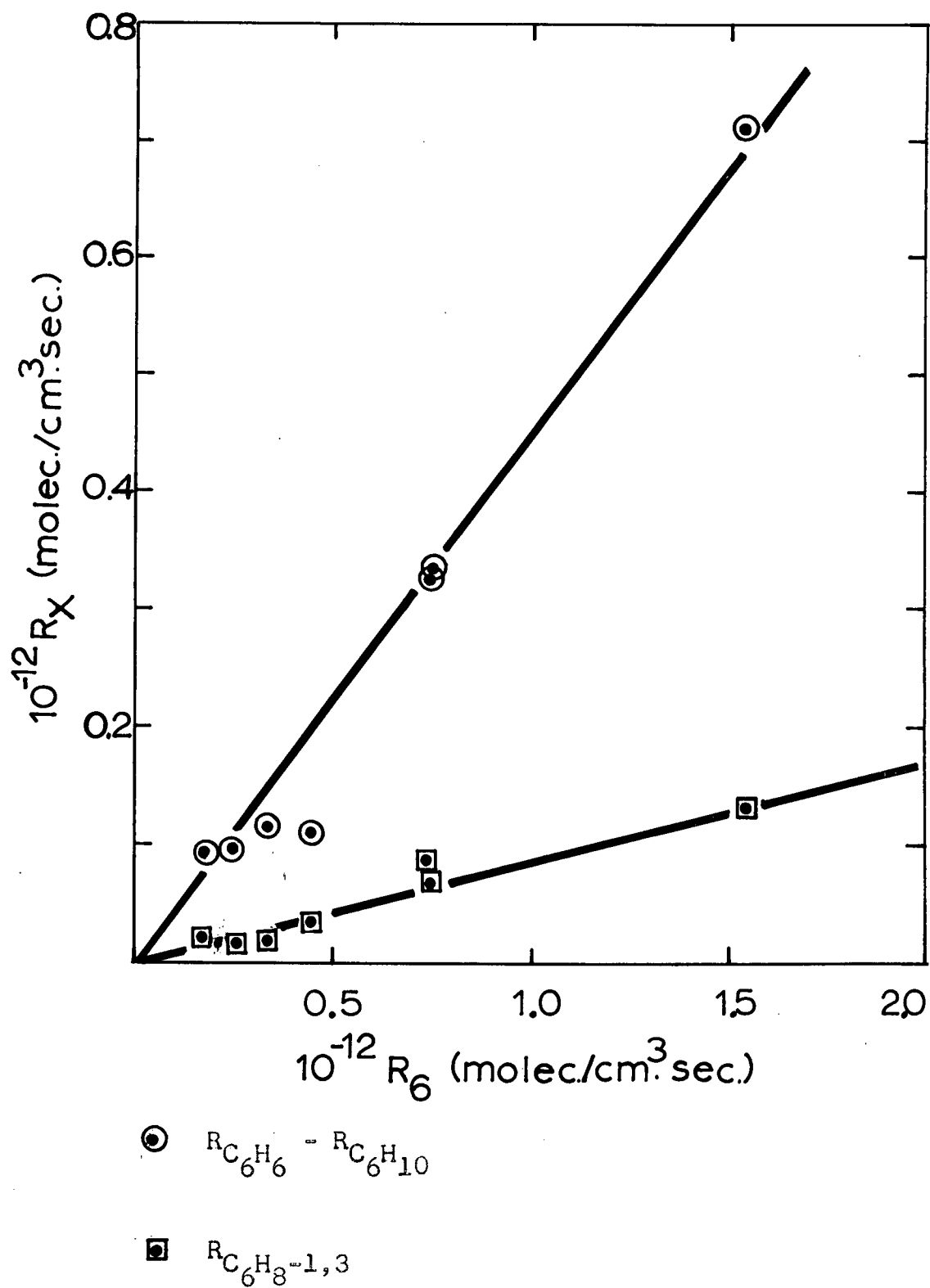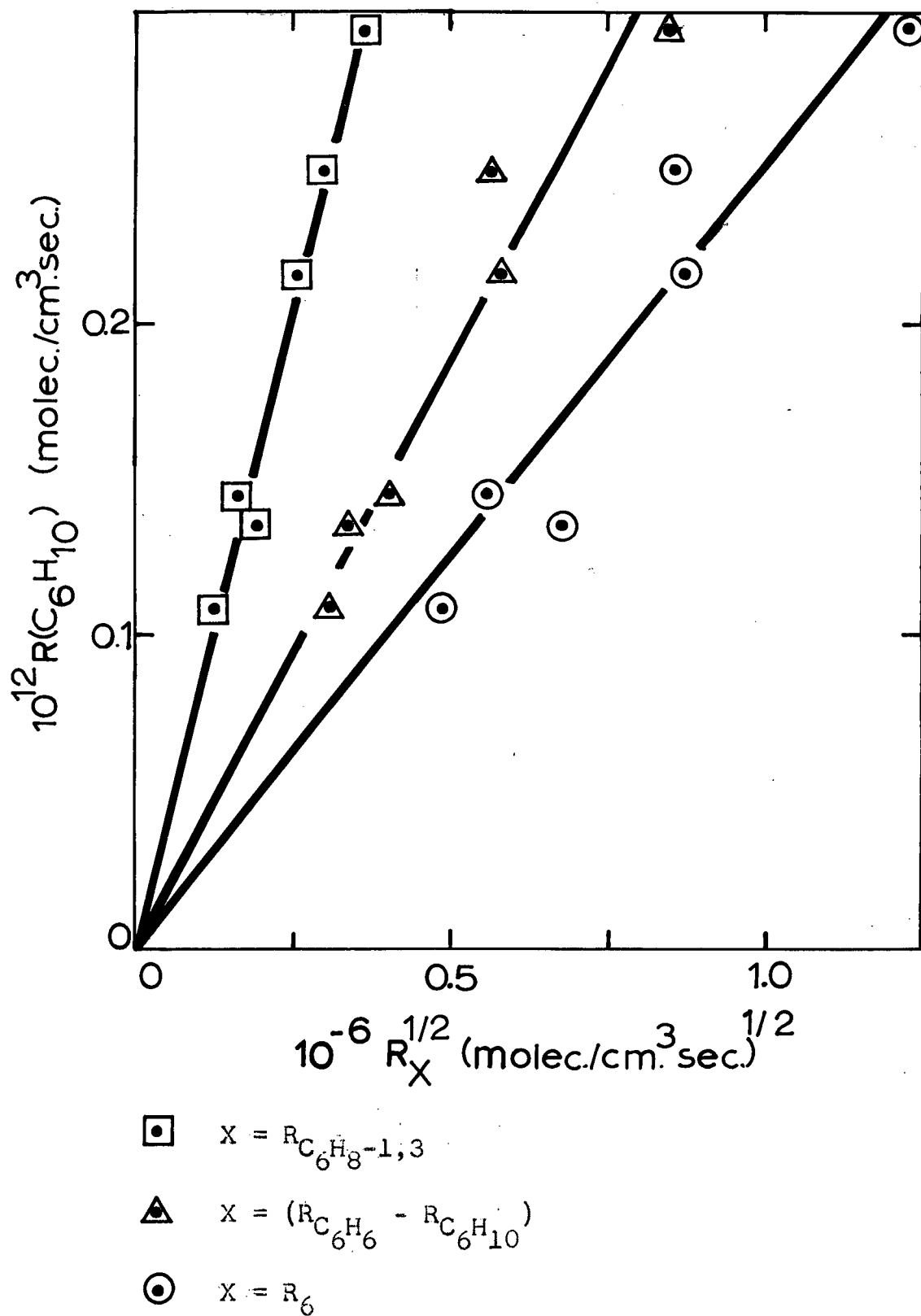
$\odot$ $R_{C_6H_6} - R_{C_6H_{10}}$

$\boxdot$ $R_{C_6H_8-1,3}$

Figure 12. Kinetic Order of Cyclohexene Production.

Legend:

$\boxdot$ $X = R_{C_6H_8-1,3}$

$\blacktriangle$ $X = (R_{C_6H_6} - R_{C_6H_{10}})$

$\odot$ $X = R_6$

is produced at a rate proportional to the square root of the rates of production of cyclohexadiene-1,3, of the benzene from disproportionation and the rate of initiation. This indicates that the rate controlling process in cyclohexene production is first order in the cyclohexadienyl radical concentration. To this extent, the experiments at 164° substantiate the mechanism of Schemes D and E.

Inspection of the slope of the benzene plot of Figure 11 indicates that $R_{7d}/R_6 = (k_{7d'} + k_{7d''})/(k_{7d'} + k_{7d''} + k_{7c}) = 0.90$, which is consistent with $(k_{7d'} + k_{7d''})/k_{7c} = 9.1$. Below 101°, this ratio was found to be $(k_{7d'} + k_{7d''})/k_{7c} = 0.45 \pm 0.12$; it is not likely that such a strong temperature coefficient exists for this disproportionation ratio. In Figure 13A and 13B the logarithms of the disproportionation ratios assuming Schemes D and E have been plotted against $10^3/T$. There is a strong increase in the disproportionation products with rising temperature. Evidently, Schemes D and E do not cover all of the processes of the mechanism.

A number of modifications could be made to account for the increasing k_{7d}/k_{7c} ratios. The combination products $C_{12}H_{14}$ might be unstable, leading back to benzene and cyclohexadienes. Two possibilities for this include a unimolecular conversion,
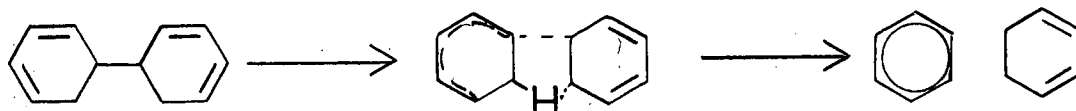
with similar reactions for other $C_{12}H_{14}$ isomers. A simpler scheme would require only the reversal of (7c).

$$C_{12}H_{14} \xrightarrow{-7c} 2\ C_6H_7^{\cdot}$$
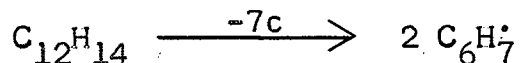
Such a reverse reaction would cause the observed rise in benzene with concomitant rise in C_6H_8-1,3.

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Figure 13. Temperature Dependence of the Disproportionation Ratios.
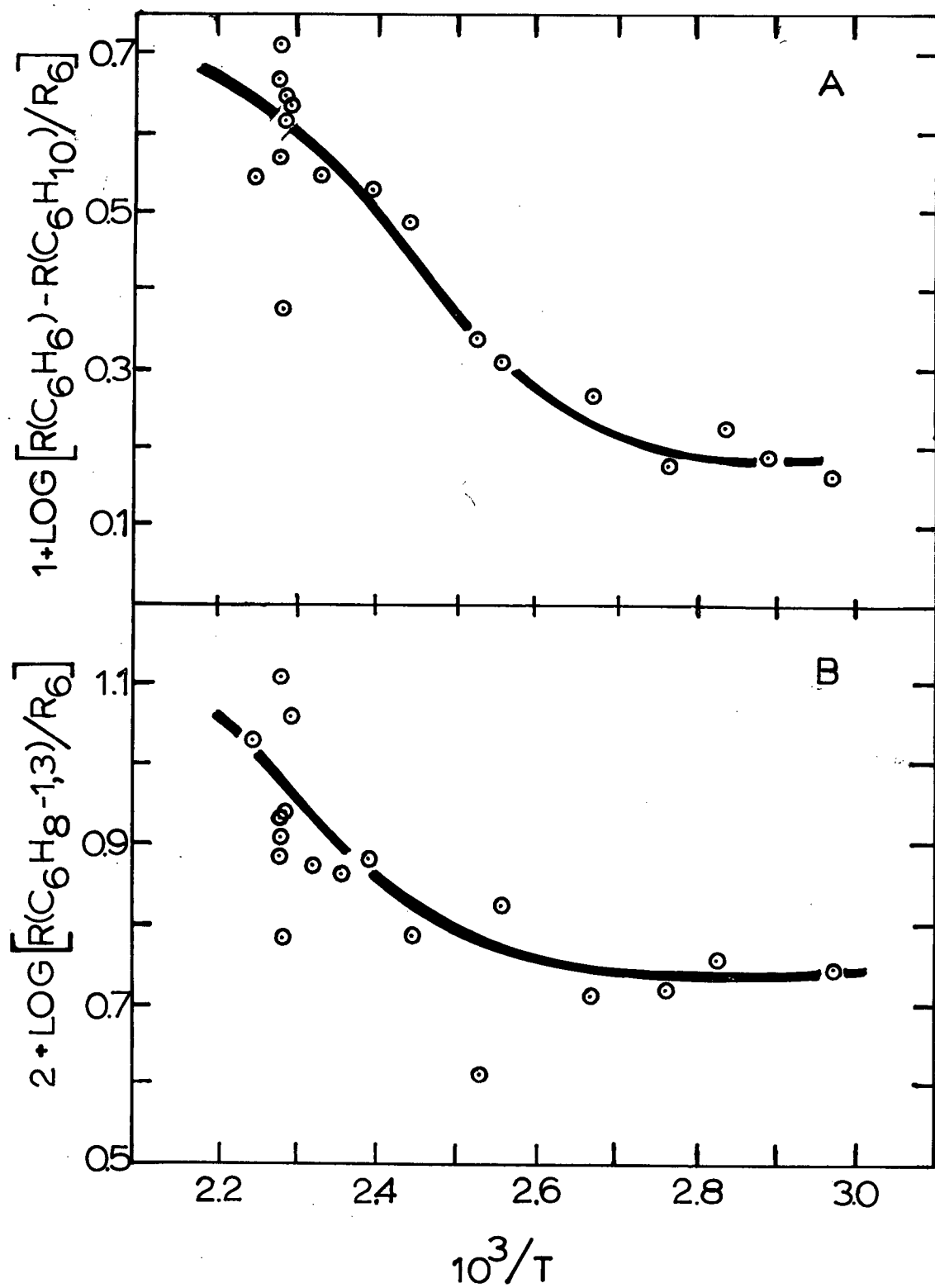
To have a half-life of 10 hours at 434°K., the activation energy of reaction (-7c) must be 35 kcal./mole, assuming $A_{-7c} = 10^{13}$ sec.$^{-1}$ This would correspond to a weakening of the inter-annular C-C bond by about 45 kcal. due to the development of the cyclohexadienyl resonance energy in each of the $C_6H_7^{\cdot}$ fragments. As we shall see, this is consistent with the estimate of 24 kcal./mole resonance energy obtained from measurement of the activation energy of reaction (8).

Pyrolysis of the dimers at 160° was confirmed by a simple experiment. A gaseous mixture of azomethane (0.824×10^{17} molecules/cm^3) and cyclohexadiene-1,4 (7.50×10^{17} molecules/cm^3) were photolyzed at 59° for 18.0 hours to accumulate the dimers; experience indicated that no cyclohexene should form under these conditions. The volatile products and azomethane were removed by fractionation at -78° and methane, ethane and nitrogen were measured. The residue, including dimers, was heated in the dark at 160° for 23 hours. Cyclohexene was subsequently detected in the products and the ratios of total yields of products were $C_6H_{10}/CH_4 = 0.27$, $(C_6H_6-C_6H_{10})/CH_4 = 0.15$. This is consistent with thermal decomposition of dimers to cyclohexadienyl radical which, being at low concentration, yielded cyclohexene and benzene by the sequence of reactions (8), (9), (10). A similar experiment with post-irradiative heating at 174° gave $C_6H_{10}/CH_4 = 0.125$, and $(C_6H_6 - C_6H_{10})/CH_4 = 0.31$, suggesting that the decomposition may be more complex at higher temperatures. Of course, under these conditions, wall reactions and similar complications render the quantitative interpretation of the experiments uncertain, but the pyrolysis, (-7c), does seem to be implicated.

To eliminate side effects caused by this pyrolysis, a recirculatory system might be useful, where the accumulating $C_{12}H_{14}$ dimers could be trapped out of the system before they caused interference. Alternatively, an independent study of the pyrolytic reaction, (-7c), could provide data needed for the kinetic analysis. Indeed, pyrolysis of these compounds is interesting in its own right, since the bond dissociation energy of the interannular C-C bond can be related to the cyclohexadienyl resonance energy. A possible synthetic route to the dimers has been found.[90] Without the results of a study of this pyrolysis, quantitative treatment of the system is very difficult because pyrolysis of the dimeric products makes the steady-state assumption invalid. As recombination products accumulate, they become an increasingly important source of $C_6H_7^{\cdot}$ radicals until finally, a new steady-state exists when $R_{7c} = R_{-7c}$. The initial and steady-state concentrations of $C_6H_7^{\cdot}$ are then, respectively

$$\left[C_6H_7^{\cdot}\right]_{in} = R_6^{1/2}/(k_{7c} + k_{7d'} + k_{7d''})^{1/2}$$

$$\left[C_6H_7^{\cdot}\right]_{ss} = R_6^{1/2}/(k_{7d'} + k_{7d''})^{1/2}$$

Therefore, since $(k_{7d'} + k_{7d''})/k_{7c} = 0.45$, the $C_6H_7^{\cdot}$ concentration increases by about 80 % under the worst conditions.

$$\frac{\left[C_6H_7^{\cdot}\right]_{ss}}{\left[C_6H_7^{\cdot}\right]_{in}} = \left(\frac{k_{7c} + k_{7d'} + k_{7d''}}{k_{7d'} + k_{7d''}}\right)^{1/2} = 1.8$$

The fact that, at 164°,(Figure 11), the disproportionation reactions (7d) account for 90 % of the injected $C_6H_7^{\cdot}$ radicals indicates that the equilibrium between $C_6H_7^{\cdot}$ and $C_{12}H_{14}$ is nearly established, and a new steady-state regime exists. If so, $R_{C_6H_8-1,3}$ is again a reliable index of $\left[C_6H_7^{\cdot}\right]^2$.

The values presented in Table V for R_X, the rates of form-

ation of the various products, are actually calculated by dividing the total product yield by the reaction time. As such, then, they represent mean rates averaged over the reaction period. In this way, the rate of cyclohexene production as measured is properly written $R_{C_6H_{10}} = k_8 \langle [C_6H_7^{\cdot}] \rangle$, and the rate ratio $k_8/k_{7d'}$ becomes $k_8/k_{7d'} = (R_{C_6H_{10}}/R_{C_6H_8-1,3}^{1/2}) \left(\langle [C_6H_7^{\cdot}]^2 \rangle^{1/2} / \langle [C_6H_7^{\cdot}] \rangle \right)$. For a slowly changing radical concentration such as we have here, the correction ratio of the mean radical concentration to the root-mean-square radical concentration is not likely to be of importance.

Neglecting for the moment the pyrolysis reaction, -7c, and analyzing the system of Schemes D and E according to a steady-state treatment leads to the following simple relationships:

$$k_8/k_{7d'}^{1/2} = R_{C_6H_{10}}/\sqrt{2} \, R_{C_6H_8-1,3}^{1/2} \tag{8}$$

$$k_8/k_7^{1/2} = R_{C_6H_{10}}/R_6^{1/2} \tag{9}$$

$$k_8/k_{7d}^{1/2} = R_{C_6H_{10}}/\sqrt{2} \left(R_{C_6H_6} - R_{C_6H_{10}} \right)^{1/2} \tag{10}$$

where $k_{7d} = k_{7d'} + k_{7d''}$ and $k_7 = k_{7d'} + k_{7d''} + k_{7c}$. It can be shown that equations (8) and (10) should be multiplied on the right by a factor $\langle [C_6H_7^{\cdot}]^2 \rangle^{1/2} / \langle [C_6H_7^{\cdot}] \rangle$ to correct for the pyrolysis of the dimers. Equation (9) requires the more complex correction factor,

$$\langle [C_6H_7^{\cdot}]^2 \rangle^{1/2} / \langle [C_6H_7^{\cdot}] \rangle \left[1 + \frac{k_{7c}}{k_7} + \frac{k_{7c}}{k_7} \left(\frac{e^{-k_{-7c}t} - 1}{k_{-7c}t} \right)^{-1/2} \right]$$

where t is the reaction time, to compensate for the drift in the radical concentration. Since the rate constant, k_{-7c} is not known, such corrections are not possible to carry out; however, we suspect that they are not of large numerical magnitude. A

rough check of this position would be afforded if the measured activation energy obtained from equation (9) were to agree with the other two when these expressions are plotted in the Arrhenius form. The experimental points for equations (8) and (9) have been plotted in Figure 14. Least mean squares analysis of these results gives the Arrhenius rate constants:

$$k_8/k_{7d'}^{\frac{1}{2}} = 10^{(21.0 \pm 1.5)} \exp -(30.4 \pm 2.9)/RT \qquad \frac{molec.^{\frac{1}{2}}}{cc.^{\frac{1}{2}} sec.^{\frac{1}{2}}}$$

$$k_8/k_7^{\frac{1}{2}} = 10^{(21.0 \pm 2.4)} \exp -(31.2 \pm 4.7)/RT$$

Results for equation (10) are inaccurate in three cases because the benzene yield approaches the cyclohexene yield. However similar treatment gives

$$k_8/(k_{7d'} + k_{7d''}) = 10^{(22.9 \pm 2.4)} \exp -(34.8 \pm 4.9)/RT$$

The reasonable agreement between these three determinations supports the mechanistic interpretation.

Analysis of representative runs indicates that hydrogen gas production is less than one percent of methane production. Using this as an estimate for the maximum perturbation caused by un-analyzed hydrogen, we derive

$$\frac{k_8(max)}{k_{7d'}^{\frac{1}{2}}} = \frac{1}{\sqrt{2}} \frac{R_{C_6H_{10}} + 0.01 R_{CH_4}}{R_{C_6H_8-1,3}^{\frac{1}{2}}} = 10^{(20.2 \pm 1.3)} \exp -\left(\frac{(28.9 \pm 2.6)}{RT}\right)$$

$$\frac{k_8(max)}{k_7^{\frac{1}{2}}} = \frac{R_{C_6H_{10}} + 0.01 R_{CH_4}}{R_6^{\frac{1}{2}}} = 10^{(20.1 \pm 2.2)} \exp -\left(\frac{(29.5 \pm 4.2)}{RT}\right)$$

Thus the error in neglecting hydrogen is not significant at the 5 % level.

<u>Discussion</u> Within the limitations discussed above, the rate constant for the decomposition of the cyclohexadienyl radical has been measured with respect to the disproportionation of the cyclo-

Figure 14. Unimolecular Decomposition of the Cyclohexadienyl Radical
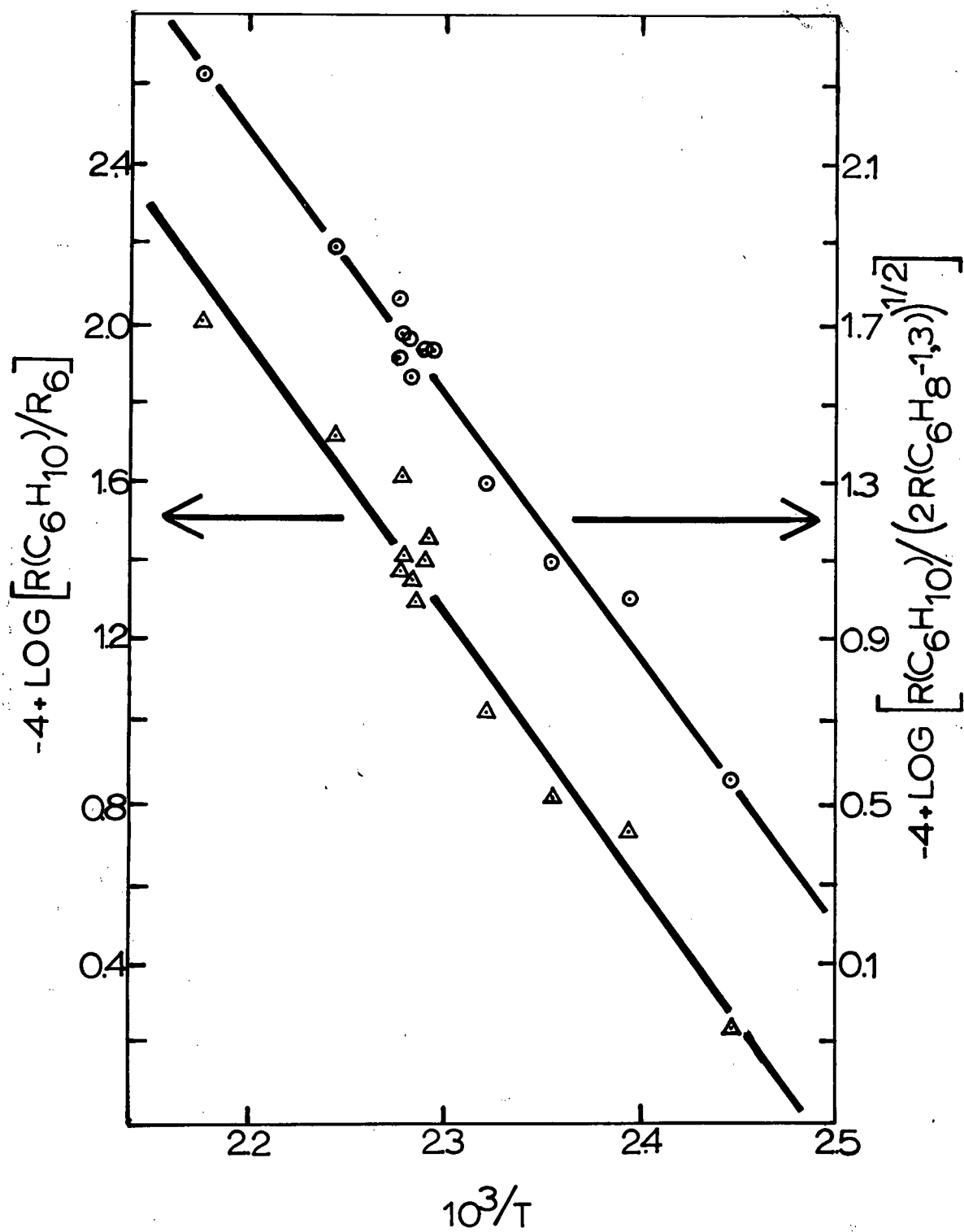
hexadienyl radical. We shall accept the result,

$$k_8/k_7^{\frac{1}{2}} = 10^{(21.0 \pm 2.4)} \exp -(31.2 \pm 4.7)/RT \quad (cm^3/molecule\ sec.)^{\frac{1}{2}}$$

as representative. Yang's result[84] for the back reaction

$$k_{-8} = 10^{-12.2}\ T^{\frac{1}{2}} \exp -3.5/RT \quad (cm^3/molecule\ sec.)$$

will be of use in interpretation of the measurement. This rate

constant can be written in the Arrhenius form

$$k_{-8} = e^{\frac{1}{2}}\ 10^{-12.2} \langle T \rangle^{\frac{1}{2}} \exp(-3.5 - \frac{1}{2}R\langle T \rangle)/RT \quad (cm^3/molecule\ sec.)$$

$$= 2.3 \times 10^{-11} \exp(-3.9/RT) \quad (cm^3/molecule\ sec.)$$

if $\langle T \rangle = 434^{\circ}K$.

From the activation energy, $E_8 = 31.2 \pm 4.7$ kcal./mole for

cyclohexadienyl radical decomposition, and $E_{-8} = 3.9$ kcal./mole

for the addition of hydrogen atoms to benzene,[84] we calculate

the heat of the overall reaction,
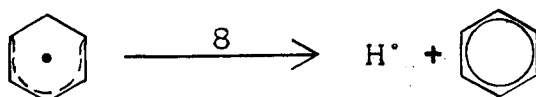
to be $\triangle H_8 = 27.3 \pm 4.7$ kcal./mole. The resonance energy, Q, of

the cyclohexadienyl radical can be calculated from the following,

thermochemical cycle.
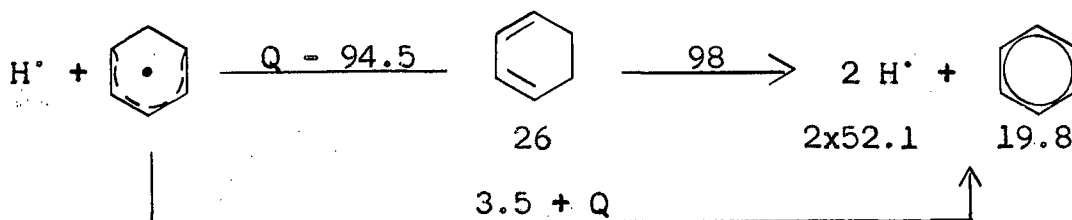
(all heats expressed in kilocalories/mole.)

Here we have adopted D°(secondary C-H) = 94.5 kcal./mole[14]

$\triangle H_f^{\circ}(C_6H_8-1,3) = 26$ kcal./mole[91] and other standard values.[92]

The relation $3.5 + Q = D^{\circ}(C_6H_6-H) = 31.2 \pm 4.7 - 3.9$, gives

$Q = 23.8 \pm 4.7$ kcal./mole. This value is in complete agreement

with Benson's recent suggestion[13] that the resonance energy

should lie between 23 and 25 kcal./mole. Furthermore, 23.8

kcal./mole weakening of the methylenic C-H bond of cyclohexadiene-1,4 would suggest a bond energy of 94.5 - 23.8 = 70.7 kcal./mole. This quantity has been reported[11] to be 74 kcal./mole. We can reconcile the present results for the decomposition reaction with the Arrhenius parameters of the back reaction. To make the calculations for this comparison, we must have information about k_7 and about the overall entropy change of the reaction. Recent experiments of Rabinovitch[32] indicate lower steric factors for recombination of delocalized radicals than are common for simple alkyl radicals. Thus the steric factor for methyl plus allyl recombination is 5×10^{-3} compared with ca. 10^{-1} for alkyl radicals. Trotman-Dickenson[38] has calculated a steric factor of $3 \times 10^{-3}$ for methyl plus benzyl recombination and recent experiments substantiate a low value.[93] The phenomenon may be more pronounced for recombination of two delocalized species.[34] Certainly the value of $k_8/k_7^{\frac{1}{2}} = 10^{21}$ (cm^3/molec.sec.)$^{\frac{1}{2}}$ is very high and if $p_{7c} = 0.1$ and therefore $k_7 = p_{7c}Z(k_7/k_{7c}) = 10^{-10.33}$ cm^3/molec.sec. at 434°K., then the pre-exponential factor A_8 has the improbably high value of $10^{15.84}$ sec.$^{-1}$. Such a high pre-exponential factor is unlikely for a decomposition where an atom is liberated which cannot attain extra, rotational freedom in the transition state. Indeed, as we shall see below, calculation of A_8 from A_{-8} measured in the study of hydrogen atom addition to benzene indicates a value of $A_8 \leqslant 10^{13.9}$ sec.$^{-1}$

The situation is improved if the decomposition of $C_{12}H_{14}$ isomers has a "normal" pre-exponential factor, around 10^{13} sec.$^{-1}$. If this is the case, then p_7 will be around 10^{-3} and A_8 will become $10^{14.84}$ sec.$^{-1}$; still about two powers of ten above the "normal" 10^{13} sec.$^{-1}$, but well within the error of $10^{\pm 2.4}$ sec.$^{-1}$

It is possible to calculate the value of A_8 from the measurement[84] of $A_{-8} = 10^{-10.64}$ cm^3/molecules sec. $= 10^{8.59}$ (atm sec.)$^{-1}$ at 434°K. Reaction of an atom with a molecule results in conversion of two rotational motions into vibrations and a steric factor of about 10^{-2} is expected.[94] Assuming a mean collision diameter of 3.5 Å., the collision yield of hydrogen atoms with benzene at 434°K. is 1.2×10^{-9} cm^3/molec. sec.; Yang's temperature dependent pre-exponential factor, $10^{11.6}T^{\frac{1}{2}} = 1.4 \times 10^{-11}$ cm^3/molec. sec., is therefore in agreement with a steric factor of 10^{-2}. We may use this result in conjunction with an estimate of the overall entropy change of the equilibrium,

$$C_6H_7^{\cdot} \; \underset{-8}{\overset{8}{\rightleftharpoons}} \; H^{\cdot} + C_6H_6$$
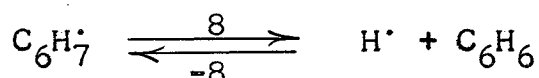
at 434°K., to calculate a value of A_8 that is compatible with $A_{-8} = 10^{-10.64}$ cm^3/molec. sec.

Since the $C_6H_7^{\cdot}$ radical is planar,[58,95] it structurally resembles benzene. Correcting the standard entropy of benzene (64.3 eu./mole) from the symmetry number twelve to two, and adding a spin degeneracy contribution R ln2 gives an estimate of the cyclohexadienyl radical's entropy. We obtain $S^o(C_6H_7^{\cdot}) = 69.2$ eu./mole at 298°K. The entropy gain in the forward direction is then $64.3 + 27.4 - 69.2 + 1.9 = 24.4$ eu./mole after correcting to 434°K., and assuming equal specific heat capacities for benzene and for the cyclohexadienyl radical. Using this value and the equation,

$$A_8/A_{-8} = 10^{\triangle S/4.575} \; \text{(atmospheres)}^{-1},$$

we obtain the result $A_8 = 10^{13.9}$ sec.$^{-1}$. This is probably an upper limit since most likely we underestimate the entropy of the cyclohexadienyl radical by relating it to the entropy of the structurally very rigid benzene molecule. Examination of the

addition reaction, therefore, does not indicate a high pre-exponential factor. This calculated pre-exponential factor is in reasonable agreement with the measured value.

The value of 24 kcal./mole for the resonance energy of the cyclohexadienyl radical is much lower than that predicted by Fisher[12] using molecular orbital and valence bond calculations, which give 29.3 and 30.0 kcal./mole respectively. Electron spin resonance investigations indicate that the unpaired electron of the phenoxy[96] and of the benzyl radical[97] resides within the ring to a substantial degree, thus resonance forms with the cyclohexadienyl structure cannot be of extremely high energy with respect to the benzene structure.

From a practical viewpoint, the 24 kcal. of resonance energy may be compared with the allyl resonance energy of 13 kcal./mole.[98] Reactive C-H bonds are thus weakened about twice as effectively with two adjacent olefinic linkages than one, the 2 kcal. discrepancy being explained by strain energy in the $C_6H_7^{\cdot}$ system.

CH_2—H   bond weakened by 13 kcal./mole

CH H   bond weakened by 24 kcal./mole
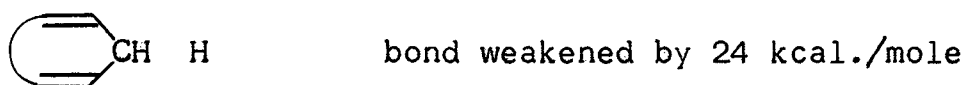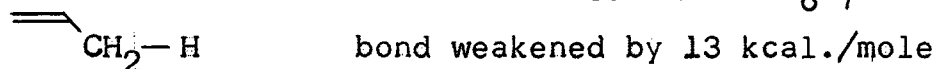
This is at least an intuitively appealing result and may be compared with the observation[11] that the benzene resonance (37 kcal./mole) is approximately three times the allyl radicals resonance energy.

The resonance energy of 24 kcal./mole for the cyclohexadienyl radical, however, is substantially greater than the 15.5 kcal./mole resonance energy that has been measured for the open chain, pentadienyl radical.[13] The difference may result from the extra inter-

action involving the methylenic carbon atom that is not possible
for the open chain system. The electron spin resonance spectrum
shows that the coupling constant to the methylenic hydrogen atoms
is 50 Oe., whereas only 30 Oe. would normally be observed for
such protons if they were not specifically involved in the
system.[12] Hanazaki et al.[99] have assumed a hyperconjugative
interaction between the π system and the methylenic hydrogen
atoms during quantum mechanical treatment of the cyclohexadienyl
cation. Fisher[12] has treated the bonding of the cyclohexadienyl
radical as a superposition of the valence bond structures:

I   II   III   IV   V   and

VI   ,   VII
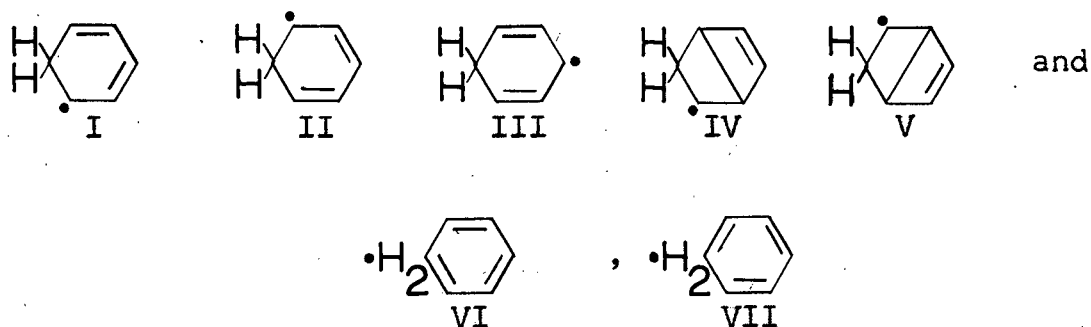
and finds that the structures VI and VII have significant repre-
sentation, and that the unpaired electron is to be found upon the
methylenic hydrogen system accounting for the large observed
coupling constants.

If the above interpretation is correct, the resonance energy
of the cyclohexadienyl radical is not typical of a simple 5
electron system and the observation that the 24 kcal. resonance
energy is approximately twice the allyl resonance energy and
two-thirds the benzene resonance energy will bear no theoretical
significance.

As we shall see, interaction of the cyclohexadienyl radical
with an alkyl radical, eg. the isopropyl radical, does not produce
either of the cyclohexadienes as a product; the disproportionation

always involves the transfer of a methylenic hydrogen atom from
the cyclohexadienyl radical to produce benzene. If the cyclo-
hexadienyl free valence is strongly delocalized onto the methyenic
hydrogen atoms, then these may well be abnormally activated and
the product distribution will contain no cyclohexadienes.

Troughton[100] has recently measured several decompositions
of free radicals under similar conditions to those of this work.
The systems studied can be generally represented as

$$CH_3CH_2CH_2\overset{\cdot}{C}HCH_2\text{-}X \quad \xrightarrow{k} \quad CH_3CH_2CH_2CH=CH_2 + X\cdot$$
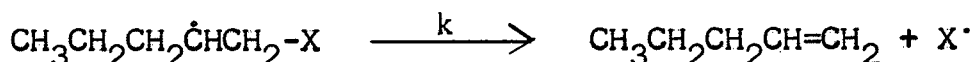
where X = -OH, $-\overset{O}{\overset{\|}{O}}CCH_3$, $-O\overset{O}{\overset{\|}{C}}C_2H_5$, $-OC_2H_5$, -OAllyl, -Allyl, and
$-\overset{O}{\overset{\|}{O}}CH$. Arrhenius parameters measured showed that, in general,
reaction heats were close to the measured activation energies.
In contrast to the results for the cyclohexadienyl radical de-
composition, the pre-exponential factors were uniformly low,
about 10^{11} sec.$^{-1}$, for each substituent, except for X =-OH or
$-OC_2H_5$. In these cases alone, the pre-exponential factor was
$10^{13.7}$ sec.$^{-1}$ and $10^{13.1}$ sec.$^{-1}$ respectively, values which are
similar to the preferred pre-exponential factor for cyclohexa-
dienyl decomposition. It is probable that resonance stabilizes
the decomposition transition state for those examples with the
low pre-exponential factor. Effective resonance implies a part-
icular molecular configuration with attendant low entropy or low
pre-exponential factor for decomposition. As resonance or
specific orientation is not possible for the hydrogen atom, the
higher pre-exponential factor, $10^{14.8}$ sec.$^{-1}$ fits into this
pattern.

The decomposition of the cyclohexadienyl radical has been
observed in the mechanism of interaction of hot tritium atoms

with benzene.[8] In the gas phase experiments, $C_6H_6T\cdot$ radicals generated by addition of recoil tritium atoms to benzene decompose to benzene-t and hydrogen atoms. This decomposition was substantially reduced in the liquid phase, indicating the reaction of excited cyclohexadienyl-t radicals.

The disproportionation of cyclohexadiene-1,4 to cyclohexene and benzene has been observed in other work. When the diene is exposed to sunlight in the presence of dissolved, molecular iodine,[101] hydrogen iodide is generated which initiates the following chain disproportionation process,

$$HI + \text{[cyclohexadiene]} \longrightarrow \text{[iodocyclohexene]} \xrightarrow{\ I\cdot\ } \text{[cyclohexenyl radical]} + I_2 \xrightarrow{\ \text{[cyclohexadiene]}\ }$$

$$\text{[cyclohexene]} + \text{[cyclohexadienyl radical]} + I_2$$

$$\text{[cyclohexadienyl radical]} + I_2 \longrightarrow \text{[benzene]} + HI \; I\cdot$$
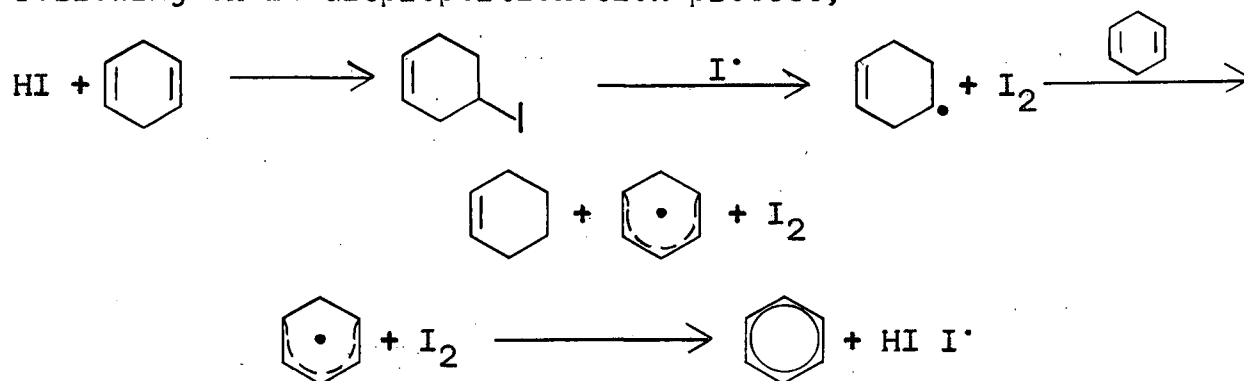
The cyclohexen-4-yl radical assumes the same role as has been postulated here for the gas phase, thermal reaction.

Similarly, in radiolysis of liquid cyclohexadiene-1,4,[10] cyclohexene is believed to arise through the processes

$$\text{[cyclohexadiene]} + H\cdot \longrightarrow \text{[cyclohexenyl radical]}$$

$$\text{[cyclohexenyl radical]} + \text{[cyclohexadiene]} \longrightarrow \text{[cyclohexene]} \quad \text{[cyclohexadienyl radical]}$$
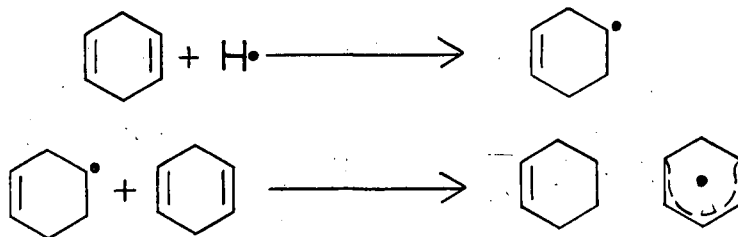
E.s.r. experiments did not detect the $C_6H_9\cdot$ radical indicating its rapid removal by hydrogen abstraction from C_6H_8-1,4. The $C_6H_7\cdot$ radical was readily detectable, however. An analogous process is believed to cause disproportionation in the action of tert-butoxy anions on cyclohexadienes.[102] Thus the neutralization

reaction

$$\text{(cyclohexadiene)} \quad \text{or} \quad \text{(cyclohexadiene)} \; + \; \underline{t}\text{-BuO}^{\ominus} \longrightarrow \underline{\text{tert-BuOH}} \; + \; \text{(cyclohexadienyl anion)}^{\ominus}$$
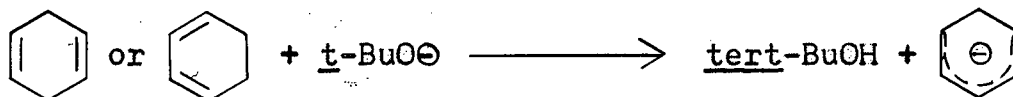
produces the cyclohexadienyl anion which can reduce the diene by hydride transfer, giving benzene and the strong, conjugate base of cyclohexene.

$$\text{(cyclohexadienyl anion)}^{\ominus} + \text{(cyclohexadiene)} \quad \text{or} \quad \text{(cyclohexadiene)} \longrightarrow \text{(benzene)} + \text{(cyclohexenyl)}^{\ominus} \xrightarrow{\underline{\text{tert-Bu-OH}}}$$

$$\underline{\text{tert-BuO}}^{\ominus} + \text{(benzene)} + \text{(cyclohexene)}$$
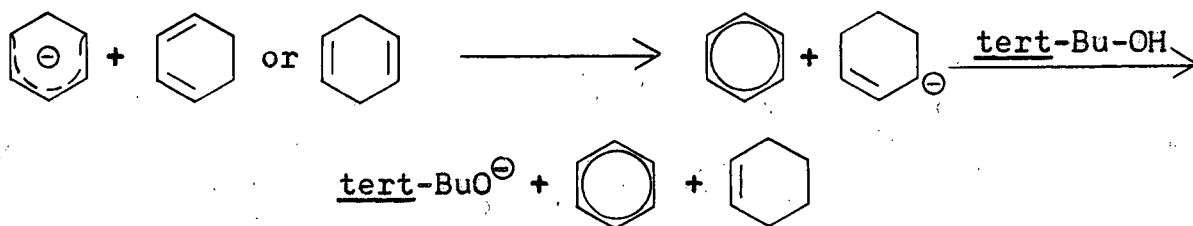
The disproportionation is therefore a generally favourable reaction and is initiated in widely different systems.

B. Di-isopropyl Ketone as Initiator

1. Pure di-isopropyl ketone photolysis

In recent years, di-isopropyl ketone has occasionally been used as source of isopropyl radicals for kinetic studies. It was extensively studied by Heller and Gordon[103,104] who photolyzed the ketone[103] and the ketone deuterated in the α-H position.[104] This work was done at temperatures mainly above those of interest for use of the ketone as a source of isopropyl radicals, but indicated that below 200° and above 70° the ketone would provide a convenient source of isopropyl radicals, at least at high intensities of illumination. Previous work by Whiteway and Masson[105] had shown that it was decomposed by 3130 Å. radiation with a quantum yield of unity from 50 to at least 150°. Accordingly, experiments were done on pure di-isopropyl ketone to assess its usefulness and confirm the results of Heller and Gordon in the temperature range of interest from 70 to 200°.

Experimental Di-isopropyl ketone was photolyzed with 3130 $\overset{o}{A}$. radiation using pressures from 10 to 14 mm. of the ketone. Most experiments were done using the full intensity of illumination available at 3130 $\overset{o}{A}$. from the B.T.H. Hg. arc lamp affording about 10^{13} molec./cm.^{3} sec. CO gas production at the ketone pressures used. Some experiments were done with a reduced intensity of light for greater precision in measurement of the abstraction reaction. In these experiments, the full intensity of the lamp was attenuated with a neutral density filter of optical density 1.3, affording a 20:1 reduction in intensity. Measurements were attempted in 18 experiments between 71° and 193°, although at the lower limit of the temperature range, the metathetical reaction proceeds too slowly to permit meaningful rates to be determined at convenient photolysis rates.

In individual experiments, di-isopropyl ketone was measured out into the photolysis cell in the usual way. Generally, the full vapour pressure at room temperature was used as higher con-centrations of ketone would have been desirable. This would have required heating of the connecting tubing that services the cell and preparative line which was not convenient with the use of mercury cut-offs, therefore pressures approaching the 14 mm. vapour pressure of di-isopropyl ketone had to be accepted as the maximum. After photolysis, the reaction mixture was allowed to distil into the analytical line where the traps were set at the following temperatures:

1st Variable temperature trap	- 78°
Spiral trap	-215°
2nd Variable temperature trap	-140°

Under these conditions, the CO was collected into the gas burette

and measured. Analysis of this fraction using a silica gel column
at room temperature and flame ionization detection showed it to be
pure and free from traces of methane.

Following CO analysis, the spiral trap was allowed to warm to
room temperature allowing the C_3 fraction to be collected into the
gas burette, measured, and then analyzed in each experiment on a
2 meter silica gel column at 110°. This fraction was found to
consist entirely of propane and propylene. Analysis for the rela-
tive pressures of these components could be made if the chromato-
graphic area of the propane peak were multiplied by 0.913. Coupled
with the total C_3 yield measured manometrically, this information
permitted calculation of the rates of formation of C_3H_6 and C_3H_8
individually.

After removal of the C_3 fraction, the 2nd variable temper-
ature trap was warmed to -94° where pure di-isopropyl was collect-
ed into the gas burette. When appropriate, a correction for non-
ideal behavior was made from Van der Waals constants tabulated in
the "Handbook of Chemistry and Physics".

Values of the experimental conditions, rates of formation
of products and certain other derived quantities to be discussed
below have been compiled in Table VI.

Although not routinely required for determination of rate
data, analyses were occasionally run on the liquid residues using
the capillary polyethylene glycol column. Particular attention
was paid to the possible presence of isobutyraldehyde suspected
to form in the low temperature experiments. Although it was
demonstrated that traces of this material could pass through this
column, none was ever detected in the photolysis products. No
peak attributable to dimethyl ketene was observed either, which

TABLE VI

Photolysis of Pure Di-isopropyl Ketone

T (^{o}K)	t (sec.)	$[D]^a$	CO	C_3H_8	C_3H_6	C_6H_{14}	M	k_3/k_2	$10^{13} k_4/k_2^{1/2}$ ($\frac{cc^{1/2}}{mol^{1/2} sec^{1/2}}$)
345	3600	3.36	10.61	3.86	3.81	6.59	0.985	0.58	0
346	3600	3.20	10.35	3.75	3.79	6.53	0.994	0.58	0
353	3600	3.08	11.25	4.06	4.09	7.06	0.998	0.58	0
356[b]	18000	2.63	1.16	0.488	0.406	0.675	(0.973)	(0.60)	1.94
369[b]	18000	2.88	1.16	0.459	0.417	0.647	(0.958)	(0.66)	1.81
373	3600	2.98	11.17	4.13	3.93	6.74	1.03	0.58	2.58
396[b]	14400	3.28	0.448	0.185	0.124	0.285	(1.05)	(0.44)	3.5
398	3600	2.91	10.48	4.13	3.50	6.31	0.996	0.56	8.6
410	3600	2.47	8.89	3.43	3.05	5.26	0.978	0.58	6.7
418	1800	2.81	18.43	7.16	6.43	12.3	1.05	0.52	7.4
425	3600	2.47	7.99	3.22	2.66	4.43	0.958	0.60	10.8
425[b]	14400	2.82	0.560	0.350	0.196	0.356	(1.27)	(0.56)	9.1
433[b]	10800	1.86	0.646	0.318	0.168	0.258	(0.891)	(0.65)	15.9
435[b]	14400	2.22	0.609	0.378	0.177	0.246	(1.02)	(0.72)	18.2
437	3600	2.61	9.92	4.30	3.12	5.45	0.983	0.57	19.4
452	3600	2.38	8.92	4.20	2.69	4.75	1.00	0.57	29.1
452	3600	2.71	9.37	4.37	2.88	4.90	0.989	0.59	24.8
466	3600	2.70	10.44	5.20	3.07	5.21	0.995	0.59	34.6

$10^{-12}R_X$ (molec./cm^3 sec.)

Mean value, excluding values in parentheses — 0.99 — 0.58

Limit of error at 5% probability level — ±0.05 — ±0.04

a $10^{17}[D]$ = Concentration of di-isopropyl ketone (molecules/cm^3)

b Measured at reduced light intensity. (See page 108)

is reasonable as Heller and Gordon[104] report that formation of this compound dies out below the lowest temperature of this work.

Treatment of the data In view of the previous work reported[103,104] on di-isopropyl ketone photolysis, and of the range of temperatures studied here, the present results were examined for consistency with the simple Scheme F.

$$h\nu + C_3H_7COC_3H_7 \xrightarrow{1} 2\ C_3H_7^{\cdot} + CO$$

$$2\ C_3H_7^{\cdot} \xrightarrow{2} C_6H_{14}$$

$$\xrightarrow{3} C_3H_8 + C_3H_6 \qquad\qquad F$$

$$C_3H_7^{\cdot} + C_3H_7COC_3H_7 \xrightarrow{4} C_3H_8 + {}^{\cdot}C_3H_6COC_3H_7$$

$$C_3H_7^{\cdot} + {}^{\cdot}C_3H_6COC_3H_7 \xrightarrow{5} C_6H_{13}COC_3H_7$$
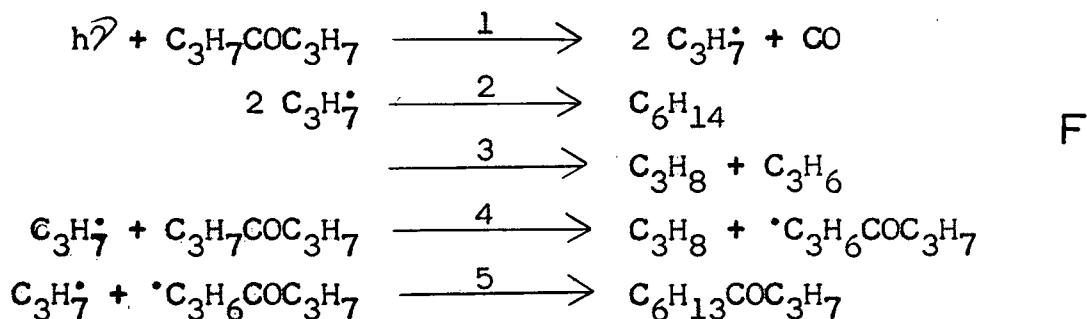
The adequacy of this mechanism to explain the measurements made, at least at the higher light intensities, is discussed below.

From the steady-state equations,

$$k_3/k_2 = R_{C_3H_6}/R_{C_6H_{14}} \tag{11}$$

$$k_4/k_2^{\frac{1}{2}} = \left(R_{C_3H_8} - R_{C_3H_6}\right)/[D]R_{C_6H_{14}}^{\frac{1}{2}} \tag{12}$$

where $[D]$ is the concentration of di-isopropyl ketone. Furthermore, from the above mechanism, we may define a "material balance" M where

$$M = \left(R_{C_3H_8} + R_{C_6H_{14}}\right)/R_{CO} \tag{13}$$

This follows since one molecule of CO is equivalent to two iso-propyl radicals, or to one molecule of either C_3H_8 or C_6H_{14}, providing the above mechanism holds. Values of these three quantities are listed in Table VI for each kinetic run. Experiments using the lower intensities of light are indicated and have not been included in the statistical analysis of k_3/k_2 values, or of M values because deviation from the simple mechanism apparently is

evident at the lower intensities, as may be expected when radical termination is not efficient at elevated temperatures. The low intensity experiments give satisfactory measurements of $k_4/k_2^{\frac{1}{2}}$ however, and this is expected even in the presence of the complications indicated by Heller and Gordon[103] for this temperature range. Values of $13 + \log_{10} k_4/k_2^{\frac{1}{2}}$ have been plotted in Figure 15 as a function of $10^3/T$, along with the values calculated from the paper of Heller and Gordon.[103] Reasonable agreement is evident.

<u>Discussion</u> For the high intensity experiments, statistical analysis shows $M = 0.99 \pm 0.05$ and $k_3/k_2 = 0.58 \pm 0.04$ at the 5 % probability level. The very small deviation of M from unity confirms the simple mechanism under the high intensity conditions. The analytical technique is also confirmed. The presence of isobutyryl radicals, $C_3H_7\overset{\bullet}{C}O$, in kinetically important quantities is inconsistent with such values of M. As reactions of such radicals would be expected to remove CO from the system in a way not leading to the production of the free gas, we would expect M to rise above unity, whereas the measured values are very slightly below, over the entire temperature range. Furthermore, the absence of isobutyraldehyde indicates efficient disruption of the isobutyryl radical,

$$(CH_3)_2\overset{\bullet}{C}HC=O \longrightarrow C_3H_7^{\bullet} + CO$$
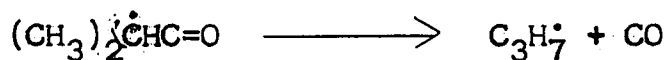
above 71°, the lowest temperature studied.

The measured value of $k_3/k_2 = 0.58$ lies between values previously measured using di-isopropyl ketone as a source of the isopropyl radical (Heller and Gordon,[103] 0.6; Dominguez et al.,[57] 0.65) and using azoisopropane as a source (Reim and Kutschke,[106] 0.53). The high intensity experiments are expected to provide

Figure 15. Metathesis between the Isopropyl Radical and Di-
isopropyl Ketone
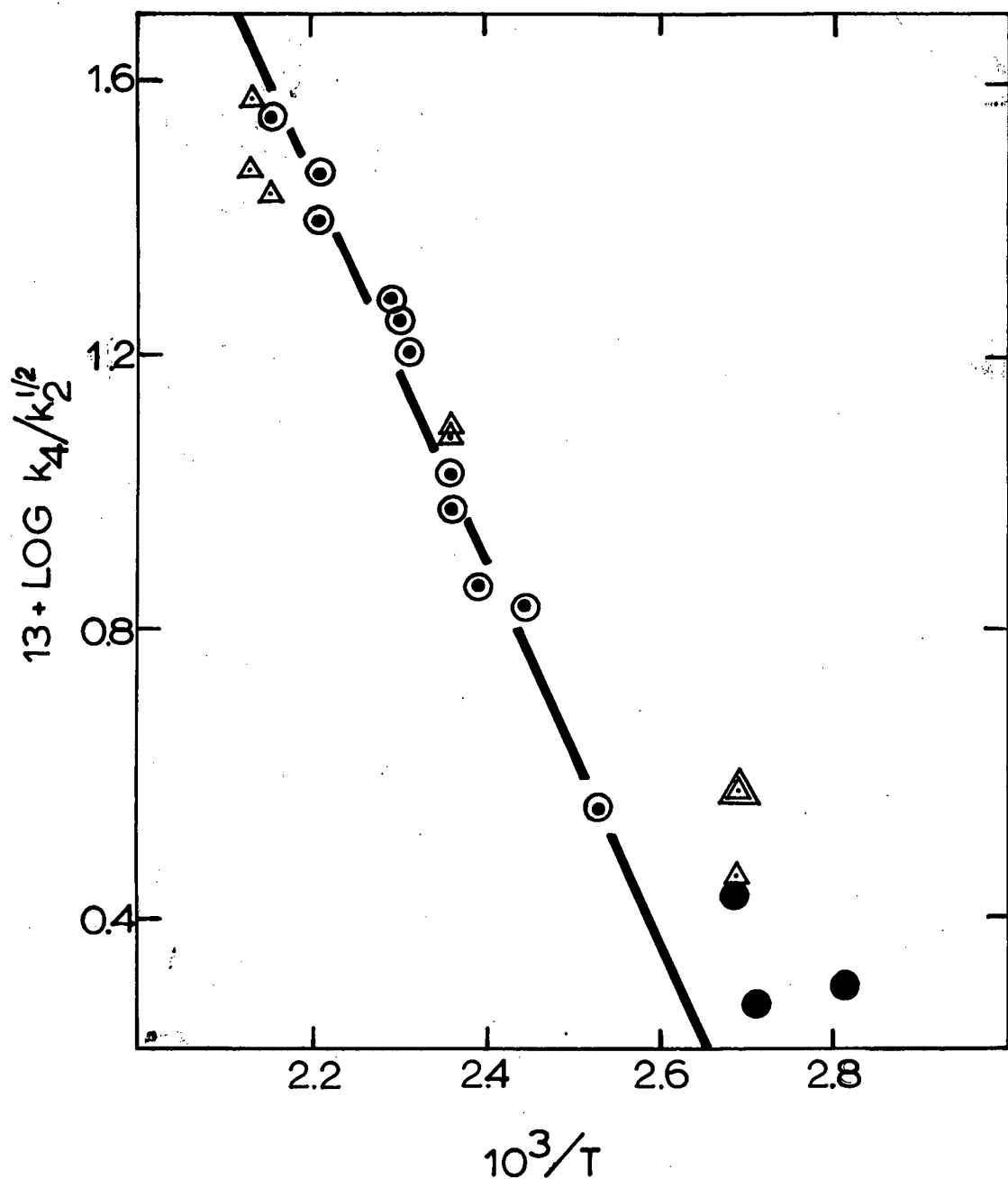
● Not included in the statistical analysis --
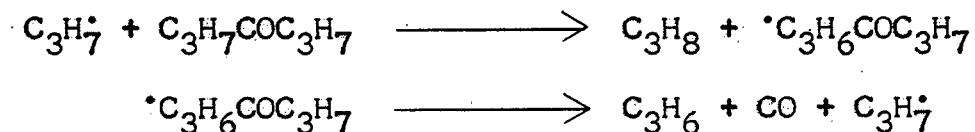   extent of metathesis is too low to permit
   accurate analysis.

△ Points measured by Heller and Gordon.

the most reliable determination of this quantity.

In the low intensity experiments, general agreement with the high intensity measurements of M were obtained, but greater scatter was evident. Values of k_3/k_2 were also scattered and may drift upwards at higher temperatures (433, 435°K.) due to the chain reaction:

$$C_3H_7^{\cdot} + C_3H_7COC_3H_7 \longrightarrow C_3H_8 + {\cdot}C_3H_6COC_3H_7$$

$${\cdot}C_3H_6COC_3H_7 \longrightarrow C_3H_6 + CO + C_3H_7^{\cdot}$$

which was reported by Heller and Gordon.[103] This complication is apparently quenched at higher intensities by efficient termination of the ketonyl radicals.

The abstraction of hydrogen atoms (reaction 4) has been calculated by equation(12) for each run and the results are shown in Figure 15. As can be seen, these values are in excellent numerical agreement with those calculated from Heller and Gordon's results[103] (entered as triangles on the figure). The high and low intensity measurements are in agreement indicating that the only complexity at the lower intensities is the chain decomposition of ketonyl radicals, which would not interfere with $k_4/k_2^{1/2}$ measurements. The actual values of the abstraction constants are very small in this temperature range, and quite unmeasureable below 110°, under the conditions of these experiments. As this rate of abstraction is much lower than the rate of attack of isopropyl radicals on cyclohexadiene-1,4 and cyclohexadiene-1,3, it would appear that di-isopropyl ketone is a good source of isopropyl radicals at high intensity of illumination in the temperature range from 70-200°.

No significance can be attached to Arrhenius parameters

calculated from the $k_4/k_2^{1/2}$ data, as examination of the results shows that the precise slope of the line is strongly dependent on the calibration of the analytical gas chromatograph. This is so since $k_4/k_2^{1/2}$ depends critically upon the value of $R_{C_3H_8} - R_{C_3H_6}$ where, except at the highest temperatures, $R_{C_3H_8}$ is only slightly larger than $R_{C_3H_6}$. Heller and Gordon's measurements over a wide range of temperatures to 400° are much superior for this purpose than the present data, and no reason exists to doubt their results. However, for purposes of making a correction (always very small) to the propane yield in ketone-cyclohexadiene mixture experiments to be considered below, a value of the abstraction rate constant ratio is needed. Without attaching any significance to the coefficients as Arrhenius parameters, least mean squares analysis of the points of Figure 15 with temperatures at or above 125°, gives the following result:

$$13 + \log_{10} \frac{k_4}{k_2^{1/2}} = 7.506 - 2.753 \frac{10^3}{T}$$

This has been used to estimate the extent of isopropyl radical attack upon di-isopropyl ketone in subsequent experiments.

2. **The high intensity photolysis of di-isopropyl ketone-cyclohexadiene-1,4 mixtures**

To extend the data on $\triangle(R, C_6H_7^{\cdot})$ and abstraction rate data to the isopropyl radical, the high intensity photolysis of di-isopropyl ketone-cyclohexadiene-1,4 mixtures was investigated. The method is conceptually identical to that already discussed for azomethane as the initiator system and only the technical variations will be emphasized here.

Experimental. The system was examined in 14 experiments carried out between the temperatures 74 and 136°. Very nearly the

full vapour pressure of the ketone at room temperature was employed in each run in order to obtain maximum radical concentrations when irradiated. The unattenuated light from the B.T.H. Hg arc lamp at 3130 $\overset{o}{A}$. was employed for photolysis. Smaller pressures, from 1-5 mm., of cyclohexadiene-1,4 were employed depending on the reaction temperature. These reagents were measured out, mixed and photolyzed in the usual way. After photolysis, the reaction mixture was allowed to distil into the analytical line where the various traps were set at the following temperatures:

1st Variable temperature trap	$- 78^{o}$
Spiral trap	-215°
2nd Variable temperature trap	-140°

Under these conditions, the carbon monoxide and C_3 products were collected and measured in exactly the same way as was done in the experiments with pure di-isopropyl ketone.

Unfortunately, it was not possible to measure C_6H_{14} manometrically in the presence of cyclohexadiene-1,4. Therefore, after completion of the CO and C_3 analyses, the remaining reaction mixture was mixed with the n-heptane internal standard, removed from the vacuum line and subjected to the usual gas chromatographic analysis using packed and capillary polyethylene glycol columns. The packed column analysis yielded peaks for di-isopropyl, n-heptane, benzene, and cyclohexadiene-1,4, the latter being used to correct the benzene peak for benzene present in the starting material. The molar ratio of di-isopropyl:n-heptane was obtained from the peak areas if the di-isopropyl peak was multiplied by a calibration factor, 1.165. The molar ratio of benzene to n-

heptane could be found if the benzene peak area was multiplied by
1.095. The capillary column analysis was run for 10 minutes at
room temperature, which allowed passage of the pentene-1 solvent,
n-heptane, benzene, and cyclohexadiene-1,4 peaks after which the
column was rapidly heated to 120° and held there while the ketone
peak followed by the final pair of peaks due to compounds I and II
were eluted. No cyclohexadiene-1,3 was ever observed, although
it could have been sensitively detected in the capillary column
analysis.

The conditions of the experiments, concentrations of reac-
tants and rates of formation of the detected products have been
compiled in Table VII along with other derived data to be dis-
cussed below.

<u>Treatment of the data</u> Along with the reactions of the iso-
propyl radical with di-isopropyl ketone discussed under "The
Photolysis of Pure Di-isopropyl Ketone" we must consider the pos-
sible reactions in the photolysis of mixtures of the ketone with
cyclohexadiene-1,4, which are labelled 6 in Scheme G. We shall see
that the last reactions (6e) do not contribute to a measureable
degree to the fates of the cyclohexadienyl radicals in the sys-
tem, therefore we are able to write the rate equations analogous
to those of the methyl case. From the steady-state treatment
(and using $k_{6e} = 0$), we obtain:

$$\frac{k_6}{k_2^{\frac{1}{2}}} = \frac{R_{C_3H_8} - R_{C_3H_6} - R_{C_6H_6}}{[B] R_{C_6H_{14}}^{\frac{1}{2}}} - \frac{k_4}{k_2^{\frac{1}{2}}} \frac{[D]}{[B]} \qquad (14)$$

$[D]$ and $[B]$ are the concentrations of di-isopropyl ketone and
cyclohexadiene-1,4 respectively. Also $k_4/k_2^{\frac{1}{2}}$ refers to the ab-

$$C_3H_7\overset{O}{\overset{\|}{C}}C_3H_7 + h\gamma \xrightarrow{\quad 1 \quad} 2\ C_3H_7\cdot + CO$$

$$2\ C_3H_7\cdot \xrightarrow{\quad 2 \quad} C_6H_{14}$$

$$\xrightarrow{\quad 3 \quad} C_3H_8 + C_3H_6$$

$$C_3H_7\cdot + C_3H_7\overset{O}{\overset{\|}{C}}C_3H_7 \xrightarrow{\quad 4 \quad} C_3H_8 + \cdot C_3H_6\overset{O}{\overset{\|}{C}}C_3H_7$$

$$C_3H_7\cdot + \cdot C_3H_6\overset{O}{\overset{\|}{C}}C_3H_7 \xrightarrow{\quad 5 \quad} C_6H_{13}\overset{O}{\overset{\|}{C}}C_3H_7$$

G

I   II
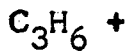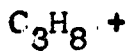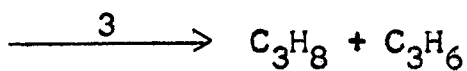
TABLE VII

Metathesis between the Isopropyl Radical and Cyclohexadiene-1,4

T (°K)	t (sec.)	$[D]^a$	$[B]^a$	CO	C_3H_8	C_3H_6	C_6H_6	C_6H_{14}	M^*	k_3/k_2	$10^{13} k_6/k_2^{1/2}$ $\left(\frac{cc^{1/2}}{mol^{1/2}sec^{1/2}}\right)$	$\Delta(1)^b$	$\Delta(2)^c$	k_{6c}^{I}/k_{6c}^{II}
				$10^{-12} R_X$ (molecules/cm^{3}sec.)										
348	3600	2.57	1.99	11.80	8.63	2.76	1.40	4.88	1.03	0.57	102	0.46	0.47	0.86
348	3600	2.54	1.65	10.12	6.14	2.34	0.81	2.66	(0.79)	(0.88)	112	0.35	(0.36)	0.88
353	3600	2.80	1.53	14.91	8.81	3.77	1.46	6.03	(0.90)	0.63	95	0.69	(0.90)	(0.60)
355	3600	2.88	2.04	17.13	12.80	3.84	2.21	6.25	0.98	0.61	132	0.49	0.58	0.88
359	3600	2.42	1.49	8.96	6.68	1.91	1.29	3.91	1.04	(0.49)	118	0.59	0.47	0.81
361	1800	2.69	1.63	5.91	5.51	1.22	0.78	1.50	1.05	(0.81)	175	0.29	(0.36)	(1.00)
368	3600	2.28	1.23	7.50	5.98	1.62	1.26	2.55	0.97	0.64	158	0.69	0.56	0.80
370	1800	2.94	1.08	10.57	8.21	2.32	2.00	4.00	0.97	0.58	177	(1.09)	(0.74)	0.82
376	3600	2.61	1.21	9.69	7.85	2.08	1.70	3.71	1.02	0.56	171	0.75	0.54	0.79
381	3600	2.57	1.65	10.70	9.87	1.80	1.92	3.11	1.01	0.62	189	0.46	0.47	0.90
394	3600	2.71	1.94	9.27	9.96	1.03	2.04	1.69	1.04	0.61	268	0.43	0.52	0.84

TABLE VII (continued)

T (°K)	t (sec.)	$[D]^a$	$[B]^a$	$10^{-12}R_X$ (molecules/cm³·sec.) CO	C_3H_8	C_3H_6	C_6H_6	C_6H_{14}	M^*	k_3/k_2	$10^{13}\,k_6/k_2^{1/2}$ $\left(\dfrac{cc.^{1/2}}{mol.^{1/2}sec.^{1/2}}\right)$	$\triangle(1)^b$	$\triangle(2)^c$	k_{6c}^{I}/k_{6c}^{II}
396	1800	1.97	0.95	7.14	7.14	1.36	1.17	2.00	(1.12)	(0.68)	337	0.35	0.51	(1.00)
403	1800	2.60	0.69	14.64	11.59	3.03	2.09	5.15	1.00	0.59	398	0.51	0.50	0.81
409	1800	2.57	0.57	17.73	13.14	4.10	2.31	6.64	0.99	0.62	437	0.58	0.58	0.93
Mean value, excluding entries in parentheses									1.01	0.60		0.51	0.52	0.85
Limits of error at 5% probability level									±0.05	±0.05		±0.30	±0.09	±0.09

a $10^{17}\,[D]$ = Concentration of di-isopropyl ketone (molecules/cm³)
   $10^{17}\,[B]$ = Concentration of cyclohexadiene-1,4 (molecules/cm³)

b $(1) = R_{C_6H_6}/(R_{C_3H_8} - R_{C_3H_6} - 2 R_{C_6H_6} - \dfrac{k_4}{k_2^{1/2}} R_{C_6H_{14}}^{1/2} D)$

c (2) calculated as described in the text, page 121.

straction of hydrogen atoms from di-isopropyl ketone by isopropyl radicals. The extent of this reaction was measured and reported under "Pure di-isopropyl ketone photolysis". The correction for the abstraction from the ketone was always extremely small, and completely negligible below 90° due to the inertness of the ketone towards isopropyl radical attack. Values of $k_6/k_2^{1/2}$ calculated from equation (6) have been calculated for each kinetic run and entered into Table VII. These have been plotted as a function of $10^3/T$ in Figure 16. Statistical least mean squares analysis shows that the data fit the following Arrhenius expression:

$$10^{13}\frac{k_6}{k_2^{1/2}} = 10^{(6.0 \pm 0.7)}\exp\left(\frac{-6.4 \pm 1.1}{RT}\right) \quad \left(\frac{cm^3}{molec. \; sec.}\right)^{1/2}$$

where the errors are expressed at the 5 % probability level.

The value of M^*, where

$$M^* = \frac{R_{C_3H_8} + R_{C_6H_{14}} - R_{C_6H_6}}{R_{CO}}$$

should be unity if no addition of isopropyl radicals takes place to the double bonds of cyclohexadiene-1,4, and providing the analytical method is sufficient. M^* has been calculated and presented in Table VII for each run. It is indeed very close to unity for all the experiments and we conclude that addition is unimportant for isopropyl radical attack on cyclohexadiene-1,4. This point will be further considered below.

Values of k_3/k_2, where $k_3/k_2 = R_{C_3H_8}/R_{C_6H_{14}}$ have been calculated for each run and entered into Table VII. The close agreement of the mean value, $k_3/k_2 = 0.60 \pm 0.05$, to that measured in experiments with the pure ketone, $k_3/k_2 = 0.58 \pm 0.04$, indicates, though not as sensitively as in another test, the absence of

Figure 16. Metathesis between the Isopropyl Radical and Cyclohexadiene-1,4
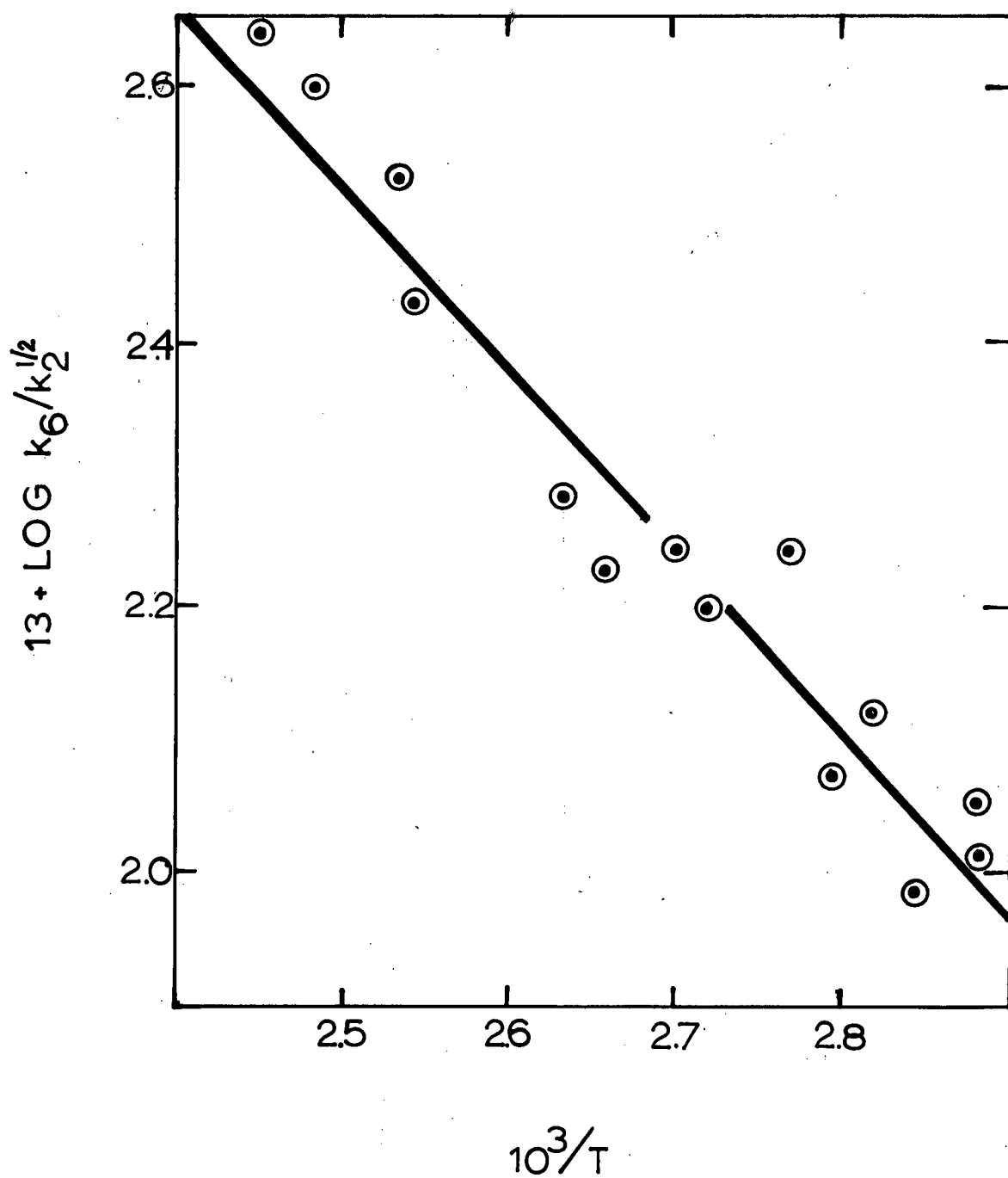
reactions (6e).

Reactions (6e) can also be eliminated by the following test. First, no cyclohexadiene-1,3 is found amongst the products of this series of experiments, showing that, if 6e occurs, it must generate cyclohexadiene-1,4 which cannot be seen. We shall discuss in the next section the photolysis of di-isopropyl ketone-cyclohexadiene-1,3 mixtures where the cyclohexadienyl radical is generated by the similar reaction

$$C_3H_7^{\cdot} + \text{⬡} \longrightarrow \text{⬡} \cdot + C_3H_8$$
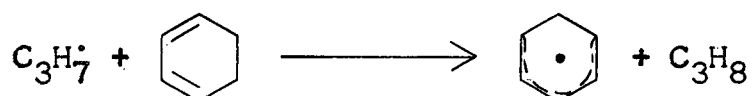
In this system, no cyclohexadiene-1,4 was generated, although it could have been easily detected. As a practical matter, the formation of the cyclohexadienes may be said to be less than one percent of the formation of benzene. Therefore we see that isopropyl may recombine with cyclohexadienyl radicals, or disproportionate with them to form benzene and propane, but not to form cyclohexadiene and propylene. Apparently the formation of benzene is able to activate the disproportionation step which otherwise does not occur significantly. Brown[1] also found the formation of benzene but not of either of the cyclohexadienes in a study of the ethyl radical with both the 1,3- and 1,4-cyclohexadienes.

The values of k_{6c}^{I}/k_{6c}^{II}, listed in Table VII were calculated directly from the peak areas of compounds I and II in the capillary column analysis, assuming equal sensitivity of the gas chromatograph's detector towards each of the isomeric substances. Thus k_{6c}^{I}/k_{6c}^{II} = Area (I)/Area (II) = 0.85 $\pm$ 0.09, independent of temperature.

The columns headed $\triangle$1) and $\triangle$2) in Table VII refer to the results of the two different methods of calculation of

$k_{6d}/(k_{6c}^I + k_{6c}^{II}) = \triangle(C_3H_7^{\cdot}, C_6H_7^{\cdot})$. These two calculations have been set up in the same manner as was done in the treatment of the methyl experiments.

Thus $\triangle(1)$ refers to values of the expression:

$$\triangle(1) = \frac{R_{C_6H_6}}{R_{C_3H_8} - R_{C_3H_6} - 2\,R_{C_6H_6} - \dfrac{k_4}{k_2^{1/2}}[D]R_{C_6H_{14}}^{1/2}} \tag{15}$$

$$= 0.51 \pm 0.30 \quad (\text{median value} = 0.50)$$

from $\quad R_6 = R_{6c}^I + R_{6c}^{II} + R_{6d}$ $\quad$ and

$$R_6 = R_{C_3H_8} - R_{C_3H_6} - R_{C_6H_6} - (k_4/k_2^{1/2})[D]R_{C_6H_{14}}^{1/2}$$

The values of $\triangle(2)$ listed in Table VII were found from the capillary column peak areas of benzene, I, and II using the $\triangle(1)$ values to calibrate the detector just as was done for methyl plus cyclohexadienyl experiments. In this case, a considerable increase in precision was realized since scatter is readily induced into values calculated from equation (15) because of the differences taken in the denominator of quantities of comparable magnitude. No systematic error is anticipated, however. This is substantiated by the agreement of the median value with the mean. To obtain the values of $\triangle(2)$, the quotient

$$Q = \frac{\text{Area (I)} + \text{Area (II)}}{\text{Area }(C_6H_6)}$$

was found for each experiment, having the value $Q = 2.3 \pm 0.4$ independent of temperature. Each Q value was multiplied by the corresponding value of $\triangle(1)$ calculated from equation (15) giving $P = 1.18 \pm 0.20$ independent of temperature with a median value of 1.17. The mean value was used as a calibration factor and individual values of $\triangle(2)$ were calculated from individual Q
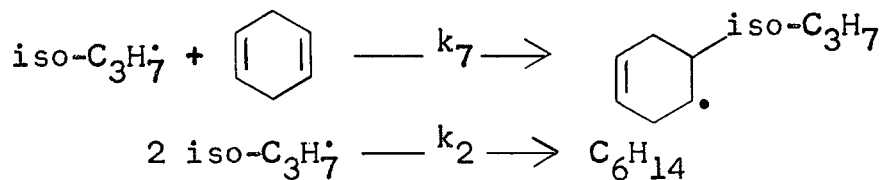
values by the relation:

$$\triangle(2) = \frac{k_{6d}}{k_{6c}^{I} + k_{6c}^{II}} = \triangle(C_3H_7^{\cdot}, C_6H_7^{\cdot}) = \frac{1.18}{Q}$$

which yields $\triangle(2) = 0.52 \pm 0.09$. Individual values of the logarithm of this quantity, and also of k_{6c}^{I}/k_{6c}^{II} have been plotted in Figure 17 as a function of $10^3/T$. No indication of temperature dependence is evident in view of the experimental errors.

Discussion The significance of the metathetical rate constants, $k_6/k_2^{\frac{1}{2}}$ and of the disproportionation to combination ratios for isopropyl and cyclohexadienyl radicals will be discussed in the "General Discussion" section of this thesis along with similar results determined with other initiator systems.

The lack of addition of isopropyl radicals to cyclohexadiene-1,4 is evidenced by the fact that M determined for each experiment is never significantly below unity.

It is of interest to determine the maximum possible value that the addition rate constant ratio $k_7/k_2^{\frac{1}{2}}$, referring to the reactions

$$\text{iso-}C_3H_7^{\cdot} + \text{[benzene ring]} \xrightarrow{\quad k_7 \quad} \text{[ring]} \overset{\text{iso-}C_3H_7}{\underset{\cdot}{}}$$

$$2 \text{ iso-}C_3H_7^{\cdot} \xrightarrow{\quad k_2 \quad} C_6H_{14}$$

could have, and still remain undetectable. An estimate of this maximum rate constant ratio can be obtained for each experiment if we suppose that addition is undetectable until it proceeds at a rate fast enough to cause the value of M to fall below 0.98. Such a value of M would correspond to a rate constant ratio of

$$\frac{k_7(\text{max})}{k_2^{\frac{1}{2}}} = \frac{0.02 \ R_{CO}}{[B]R_{C_6H_{14}}^{\frac{1}{2}}}$$

Figure 17. Combination and Disproportionation of the Isopropyl
Radical with the Cyclohexadienyl Radical.
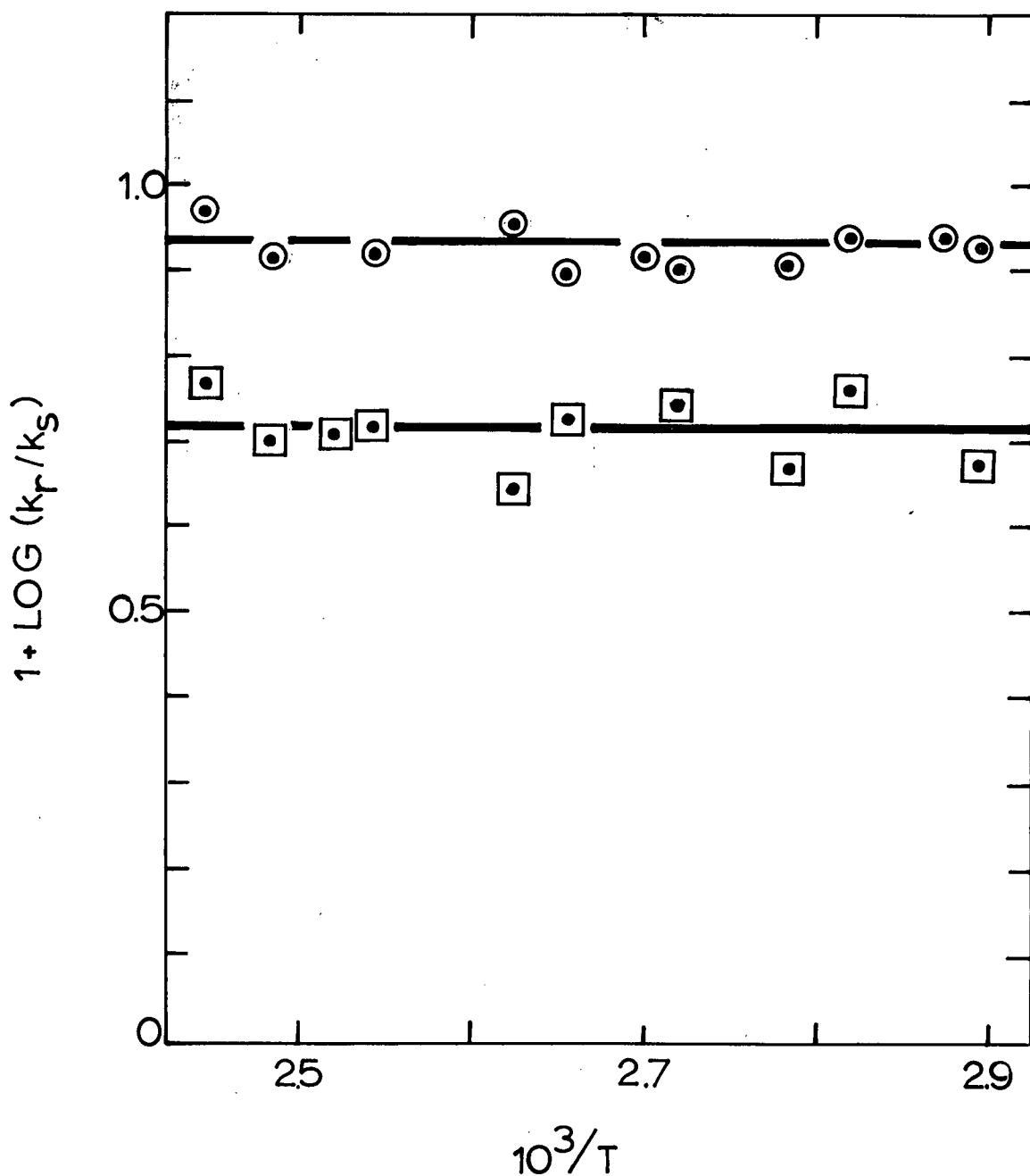
$$\square \quad k_r/k_s = k_{6c}^{I}/k_{6c}^{II}$$

$$\odot \quad k_r/k_s = k_{6d}/(k_{6c}^{I} + k_{6c}^{II})$$

Accordingly, values of this quantity, and of $k_7(max)/k_6$ have been presented in Table VIII for each kinetic run. Clearly the rate of addition is less than 5 % of the rate of metathesis; it may well be very much less, indeed.

Brown[1] found that addition of ethyl radicals to cyclohexadiene-1,4 was unmeasurable in his systems and had accessible upper limits comparable in magnitude to those found here for isopropyl radicals.

3. Di-isopropyl ketone-Cyclohexadiene-1,3 mixtures - high intensity photolysis

The examination of the reactions of the isopropyl radical with cyclohexadiene-1,3 may clarify questions concerning the interactions of cyclohexadienyl radicals with isopropyl radicals. For example the product cyclohexadiene-1,4 cannot be detected in the di-isopropyl ketone-cyclohexadiene-1,4 system. In the cyclohexadiene-1,3 system, however, it may be possible to discount the process

$$\text{iso-}C_3H_7^{\cdot} + \bigotimes \xrightarrow{6e} C_3H_6 + \bigbox$$
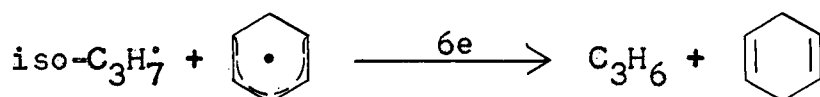
more certainly than merely by observing that $R_{C_3H_6}/R_{C_6H_{14}}$ does not increase. This has indeed been the case.

Furthermore, the rate constant of metathesis from the 1,3-diene by isopropyl is of intrinsic interest in comparison to that already measured for metathesis from cyclohexadiene-1,4. Recent experiments[107] performed on equilibrium mixtures of the 1,3- and 1,4-cyclohexadienes show that the standard free energy of the conjugated isomer lies only 0.58 kcal./mole below that of the unconjugated one. Furthermore, early hydrogenation experiments by Kistiakowsky and coworkers[108,109] show that the heat of hydrogenation of the double bonds of cyclohexadiene-1,3 is only 1.8 kcal.

TABLE VIII

Upper Accessible Limits for the Addition of the Isopropyl Radical
to Cyclohexadiene-1,4

$(°K)$	$(cm^3/molec.\ sec.)^{1/2}$	
T	$10^{13}\ \dfrac{0.02\ R_{CO}}{[B]R_{C_6H_{14}}^{1/2}}$ [a]	$\dfrac{k_7(max)}{k_6}$
348	5.36	0.053
348	7.51	0.067
353	7.94	0.084
355	6.72	0.051
359	10.6	0.098
361	5.94	0.034
368	7.64	0.048
370	9.76	0.055
376	8.30	0.049
381	7.35	0.039
394	7.36	0.027
396	10.6	0.031
403	18.7	0.047
409	24.2	0.055

[a] $[B]$ = Concentration of cyclohexadiene-1,4 (molec./cm^3)

less than twice the heat of hydrogenation of cyclohexene. Both molecules, therefore, stand to gain very nearly the same amount of resonance energy in forming the cyclohexadienyl structure. The metathetical rate constant for ethyl attack[1] on cyclohexadiene-1,3 has been found to be distinctly lower than that for attack on cyclohexadiene-1,4, so further study is indicated.

The conjugated double bond structure of the 1,3-diene activates this molecule towards addition of free radicals. A comparison of the reactivity of the isopropyl radical's reactivity towards addition with that of the ethyl radical promised to be instructive. Insofar as the 1,4-diene does not display any reactivity towards the addition of isopropyl radicals, and its kinetics had been previously studied with the isopropyl radical, the analysis of this more complex system was rendered more tractable. Addition of radicals to cyclohexadiene-1,3 has been studied previously for the methyl,[110] ethyl[111] and polyacrylonitrile[112] radicals. Homopolymerization[113-115] and copolymerization[112,116] of cyclohexadiene-1,3 have also been described. In each of these systems, the addition of the radical to the 1,3-diene was shown to occur much more rapidly than the corresponding addition to cyclohexadiene-1,4. Cyclohexadiene-1,3 is also the more reactive isomer towards the formation of a 1:1 adduct with ethyl azodicarboxylate,[117] although this process is unaffected by hydroquinone, a free radical scavenger, and hence is not likely a free radical process.

In the discussion of the addition reaction, we shall assume that the addition occurs at a terminal unsaturated carbon atom; in this way the allylic resonance energy is released and will

cause the terminal addition process to be the more exothermic one. Terminal addition has been observed both for 2,3-dimethylbutadiene-1,3[118,119] and for hexadiene-2,4,[119,120] although steric conditions vary greatly at the terminal atoms of these two systems. This pattern has accordingly been adopted in reaction (7) below.

Experimental The photolysis of di-isopropyl ketone-cyclohexadiene-1,3 mixtures was examined in eleven experiments, from 42 to 133°. A sufficiently high rate of photolysis of ketone was maintained to ensure that all secondary radicals were terminated by isopropyl radicals.

The reactants were measured into the cell in the usual way, mixed, and then photolyzed with 3130 Å. radiation from the medium pressure Hg lamp. The reactant pressures used have been tabulated in Table IX along with temperatures, the rates of formation of the products determined as described below and certain derived quantities. The reaction time was 300 seconds in each instance.

After photolysis, the reaction mixture was allowed to distil into the analytical line where the various traps were set at the following temperatures:

1st Variable temperature trap	- 78°
Spiral trap	-215°
2nd Variable temperature trap	-140°

The same distribution of temperatures was used for the di-isopropyl ketone-cyclohexadiene-1,4 experiments. Under these conditions, the CO was removed pure, into the gas burette and measured. Warming of the spiral trap permitted collection of the propane and propylene into the gas burette, and these gases were analyzed just as previously described. No attempt was made to analyze

TABLE IX

Addition and Metathesis between the Isopropyl Radical and Cyclohexadiene-1,3 [b]

($^\circ$K)			$10^{-12}R_X$ (mol./cm^{3}sec.)				(cm^3/molecule sec.)$^{1/2}$					
T	$[D]^a$	$[B]^a$	CO	C_3H_8	C_3H_6	M'^c	10^{13} U_o	10^{13} U	10^{13} $k_6/k_2^{1/2}$	10^{13} V_o	10^{13} $V_o+0.342U$	10^{13} $k_7/k_2^{1/2}$
315	3.14	1.53	33.9	11.2	10.00	0.841	17	13	$(7)^d$	85	89	95
323	2.97	0.867	30.5	10.9	9.22	0.879	49	37	$(29)^d$	107	120	127
330	3.08	1.47	33.0	11.4	8.62	0.795	51	38	30	119	132	141
340	2.71	1.01	34.6	11.9	9.37	0.811	62	46	35	162	178	190
349	2.46	1.07	28.8	9.9	7.13	0.771	74	55	43	176	195	207
363	3.59	1.08	38.1	12.7	8.68	0.725	128	95	77	251	283	302
374	2.84	0.628	39.4	13.9	9.25	0.757	180	134	107	382	428	456
384	2.84	0.427	34.6	12.6	8.60	0.794	226	168	136	434	491	522
395	2.54	0.277	38.7	14.3	10.70	0.846	271	202	166	502	571	608

TABLE IX (continued)

(°K)			$10^{-12}R_X$ (mol./cm³ sec)				(cm³/molecule sec.)$^{1/2}$					
T	$[D]^a$	$[B]^a$	CO	C_3H_8	C_3H_6	M'^c	10^{13} U_o	10^{13} U	10^{13} $k_6/k_2^{1/2}$	10^{13} V_o	10^{13} $V_o+0.342U$	10^{13} $k_7/k_2^{1/2}$
400	2.49	0.260	35.4	12.9	9.45	0.825	290	216	173	590	664	708
406	2.48	0.292	35.6	13.2	8.93	0.804	330	246	202	609	693	738

a $[D]$ = Concentration of di-isopropyl ketone (molecules/cm³)
  $[B]$ = Concentration of cyclohexadiene-1,3 (molecules/cm³)

b Reaction time = 300 sec.

c $M' = R_{C_3H_8} - R_{C_6H_6} + R_{C_3H_6}/0.58\ R_{CO}$, where $R_7 - R_{7d} = (1 - M')R_{CO}$

d The values in parentheses were excluded on statistical grounds.

the di-isopropyl yield manometrically. The remaining material was mixed with a small amount of n-heptane as an internal chromatographic standard and removed from the vacuum system into a cold finger. Pentene-1 solvent was added as the sample was opened, the whole was mixed and about 5 μl. was immediately injected into the Perkin Elmer 154 Vapour fractometer using a 2 meter polyethylene glycol packed column which resolved peaks for pentene-1 (solvent), di-isopropyl, n-heptane(internal standard), cyclohexadiene-1,3 starting material, benzene, and cyclohexadiene-1,4. A second 5 μl. sample was analyzed on the Perkin Elmer model 226 gas chromatograph using the capillary polyethylene glycol column to analyze for the heavy products of the reaction. At room temperature pentene-1 (solvent), n-heptane (internal standard), cyclohexadiene-1,3, and benzene eluted. After heating the column to 120°, di-isopropyl ketone eluted followed by three peaks close together, the first quite small, the second and third corresponding to the products I and II observed in the di-isopropyl ketone-cyclohexadiene-1,4 experiments. In these experiments, however, the peak I was consistently larger than the peak II. After 20 minutes of heating at 120°, a group of three peaks of about equal area were eluted. These were not present in the cyclohexadiene-1,4 experiments and probably correspond to isomeric addition products of formula $C_{12}H_{22}$, ie. products VI and VII (Scheme H).

Treatment of the data   The products of this photolytic system have been considered as arising from the reactions (1) to (7e). (Scheme H)

The previous study of the behavior of cyclohexadienyl radicals had shown that no cyclohexadiene-1,3 was formed, although small amounts of it could have been detected. This furnished
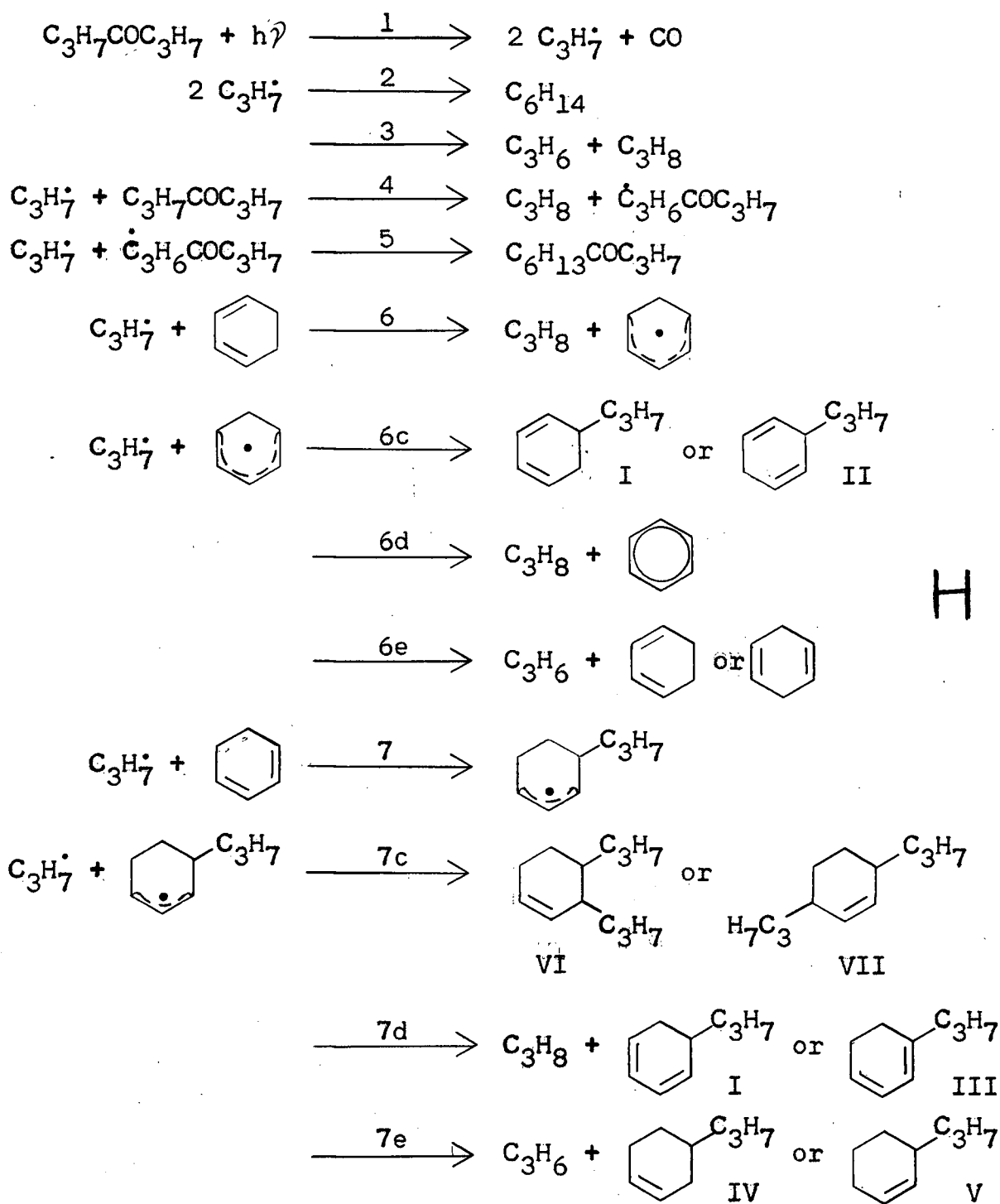
conclusive evidence that no mutual termination of cyclohexadienyl radicals occured under the experimental conditions, and also that reactions (6e) leading to cyclohexadiene-1,3 did not proceed. In the present system, no cyclohexadiene-1,4 was formed thereby confirming that the cyclohexadienyl radical did not react significantly with any radical other than isopropyl, and that reactions (6e) were negligible.

The combination and disproportionation reactions (6c) and (6d) therefore remain as the only significant reactions of the cyclohexadienyl radical. The products I and II from combination, and the benzene from disproportionation were separated and measured by gas chromatography in the study of isopropyl and cyclohexadiene-1,4, giving the ratios $k_{6d}/k_{6c} = 0.52 \pm 0.09$ and $k_{6c}^{I}/k_{6c}^{II} = 0.85 \pm 0.09$. In the present system the products I and II could be identified and estimated by gas chromatography, but the amount of benzene formed in reaction (6d) was less than the residual benzene in the reactant cyclohexadiene-1,3 which could not conveniently be further purified. For greater predision, therefore, the results of the previous study were used to estimate the benzene yield from the identity

$$R_{C_6H_6} = R_6 k_{6d}/(k_{6c} + k_{6d}) = 0.342 \, R_6 \qquad (16)$$

where R_6 is the rate of metathesis from cyclohexadiene-1,3, and can be calculated from accessible data using equation (19).

Addition of the isopropyl radical to cyclohexadiene-1,3 yields the radical C_9H_{15}; we have made the reasonable assumption that the radical will resemble the cyclohexadienyl radical by reacting exclusively with isopropyl radicals. The relevant reactions are then (7c-e).

$$C_3H_7COC_3H_7 + h\gamma \xrightarrow{\ 1\ } 2\ C_3H_7^\cdot + CO$$

$$2\ C_3H_7^\cdot \xrightarrow{\ 2\ } C_6H_{14}$$

$$\xrightarrow{\ 3\ } C_3H_6 + C_3H_8$$

$$C_3H_7^\cdot + C_3H_7COC_3H_7 \xrightarrow{\ 4\ } C_3H_8 + \overset{\cdot}{C}_3H_6COC_3H_7$$

$$C_3H_7^\cdot + \overset{\cdot}{C}_3H_6COC_3H_7 \xrightarrow{\ 5\ } C_6H_{13}COC_3H_7$$

The disproportionation reaction (7d) yields the product I, which is also formed by the combination reaction (6c). Appropriately, the corresponding ratio of peak areas A(1)/A(II) exceeds the value of 0.85 ± 0.09 found in the isopropyl-cyclohexadiene-1,4 system. Comparison of the observed value of A(I)/A(II) with 0.85 allows the estimation of the rate of formation of product I by

reaction (7d). This rate has been equated to the rate of propane formation by reaction (7d); this is completely accurate only if product III gives a chromatographic peak which augments the area of the peak due to product I, or if product III is formed in a negligible amount. A very small peak appears just before the peaks of compounds I and II; it cannot be definitely assigned and may be due to one or more of the products III-V. The formation of product III may be discriminated against since it involves the transfer of a hydrogen atom shielded by the isopropyl group. Despite uncertainties, the rate of (7d) has been estimated from the areas of the peaks due to I and II by means of the expression:

$$\frac{R_{7d}}{R_6} = \frac{k_{6c}}{k_{6c} + k_{6d}} \cdot \frac{A(I) - (k_{6c}^{I}/k_{6c}^{II})A(II)}{\left[1 + (k_{6c}^{I}/k_{6c}^{II})\right]A(II)}$$

$$= \frac{A(I) - 0.85\ A(II)}{2.81\ A(II)} = H \tag{17}$$

When the propane formed due to the reaction (7d) is estimated by this procedure, corrections can be applied to values of $k_7/k_2^{1/2}$ and $k_6/k_2^{1/2}$ determined in the usual way. The corrections due to this source of error are not significant at the 5 % probability limits of error; hence insufficiencies in the analytical technique described above are not overly important.

Reaction (6e) has been shown to be negligible for the cyclo-hexadienyl radical, and very probably (7e) is negligible for the $C_9H_{15}^{\cdot}$ radical. The only chromatographic peak which could be reasonably assigned to products IV or V is the particularly small one mentioned above. This leaves reaction (3) as the only significant source of propylene. The rate of formation of di-isopropyl can bee can be estimated by the equation: $R_{C_6H_{14}} = (k_2/k_3)R_{C_3H_8} =$

$0.58 R_{C_3H_8}$. This method gave results which were consistent with, but more precise than, those obtained from the direct estimation of the di-isopropyl in the chromatographic analysis of the C_6 fraction, which is considerably less precise than the manometric analysis of propylene. Since the estimation of the addition rate constant requires evaluation of a material balance involving di-isopropyl rate, the alternative method of analysis indicated above is preferable.

The recombination reaction(7c) should yield four products, as VI and VII each represent a pair of geometrical isomers. Three peaks of about equal area were found on the chromatogram at appropriate retention times; perhaps one of the stereoisomers was not formed, or the column failed to resolve one of the pairs.

The repective fractions, F and G of the $C_6H_7^{\cdot}$ and $C_9H_{15}^{\cdot}$ radicals suffering disproportionation are:

$$F = \frac{k_{6d}}{k_{6c} + k_{6d}} = 0.342 \qquad\qquad G = \frac{k_{7d}}{k_{7d} + k_{7c}}$$

The kinetic analysis requires a procedure for estimation of R_6, R_7 and G from accessible data.

Propylene is formed only in reaction (3), propane only in reactions (3), (4), (6), (6d) and (7d). Moreover $R_{6d} = FR_6$, $R_{7d} = GR_7 = HR_6$, and $R_6 = k_6 [B](R_{C_6H_{14}}/k_2)^{\frac{1}{2}}$ where $[B]$ is the concentration of cyclohexadiene-1,3. We estimate $R_{C_6H_{14}} = R_{C_3H_6}/0.58$. Probably H is temperature dependent whereas F and G are not.

The evaluation of $k_6/k_2^{\frac{1}{2}}$ and $k_7/k_2^{\frac{1}{2}}$ is based upon the equations:

$$R_{C_3H_8} = R_3 + R_4 + R_6 + R_{6d} + R_{7d} \qquad\qquad (18)$$

Applying equation (23) yields the value G = 0.08 ± 0.03 independent of temperature, as expected. Let U and V_o be defined by the equations

$$U = \frac{1}{1 + F}\left[\frac{R_{C_3H_8} - R_{C_3H_6}}{[B](R_{C_3H_6}/0.58)^{1/2}} - \frac{[D]k_4}{[B]k_2^{1/2}}\right]$$

$$V_o = \frac{R_{CO} - R_{C_3H_8} - R_{C_3H_6}/0.58}{[B](R_{C_3H_6}/0.58)^{1/2}}$$

It is easily shown that:

$$\frac{k_6}{k_2^{1/2}} = \frac{(1 + F)(1 - G)U - GV_o}{1 + F - G} = 0.979\,U - 0.064\,V_o \qquad (24)$$

$$\frac{k_7}{k_2^{1/2}} = \frac{(1 + F)(V_o - FU)}{1 + F - G} = 1.064\,V_o + 0.346\,U \qquad (25)$$

Discussion   The kinetic results obtained for addition and metathesis between the isopropyl radical and cyclohexadiene-1,3 are given in Figure 18 and Tables IX and X. The importance of reactions (6d) and (7d) in the reaction scheme can be judged by comparison of the last six columns of the tables. The effect of neglecting propane from reaction(7d) can be found by placing G = 0 in equations (24) and (25) when $k_6/k_2^{1/2} \longrightarrow U$ and $k_7/k_2^{1/2} \longrightarrow V_o + 0.342\,U$; the corresponding values are given in Table IX. Statistical analysis reveals that neglect of reaction(7d) leads to no significant change in the values of the rate constants at 100° or in the Arrhenius parameters; the pairs of values are compared in Table X. The effect of neglecting both reactions (6d) and (7d) can be found by placing F = G = 0 in equations (24) and (25) when $k_6/k_2^{1/2} \longrightarrow U_o$ and $k_7/k_2^{1/2} \longrightarrow V_o$, where $U_o = (1 + F)U = 1.342\,U$. Table IX shows that this leads to much larger errors in the rate

Figure 18. Addition and Metathesis between the Isopropyl Radical and Cyclohexadiene-1,3.

⊙ $13 + \log_{10}(k_7/k_2^{1/2})$

▣ $13 + \log_{10}(k_6/k_2^{1/2})$
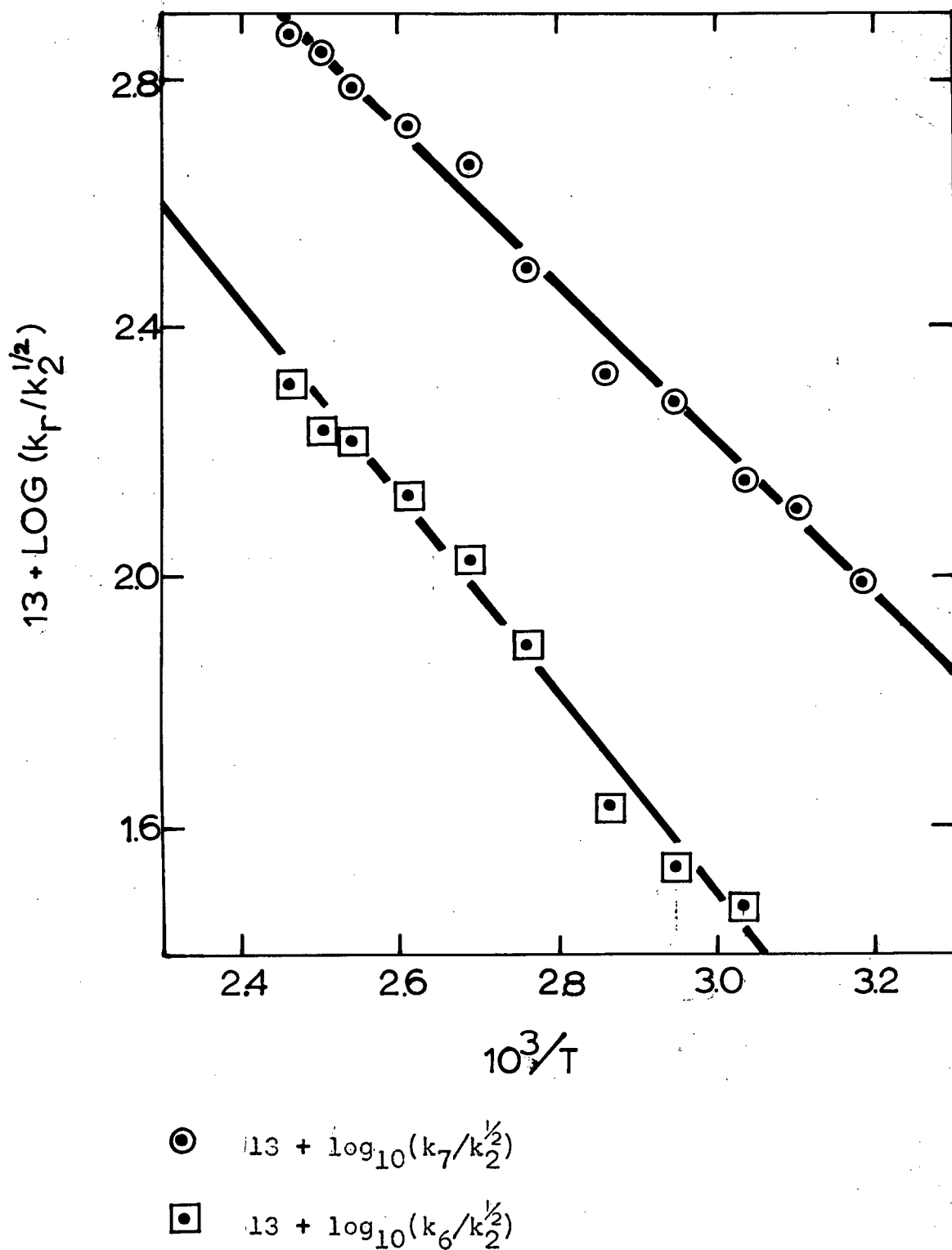
TABLE X

Rate Constants for Reaction of the Isopropyl Radical with Cyclohexadiene-1,4 and

Cyclohexadiene-1,3.

substrate	reaction	no. of expt's.	C	B	$13 + \log A_r/A_2^{1/2}$	(kcal./mole) $E_r - \frac{1}{2}E_2$	$13 + \log k_r/k_2^{1/2}$ [b]
cyclohexadiene-1,3	Addition	11	6.024	1.276	6.0 ± 0.2	5.8 ± 0.4	2.61 ± 0.06
cyclohexadiene-1,3	Addition	11	6.016	1.283	6.0 ± 0.2	5.9 ± 0.3	2.58 ± 0.06
cyclohexadiene-1,3	Metathesis	9	6.156	1.557	6.2 ± 0.4	7.1 ± 0.7	1.98 ± 0.09
cyclohexadiene-1,3	Metathesis	9	6.136	1.514	6.1 ± 0.4	6.9 ± 0.6	2.08 ± 0.08
cyclohexadiene-1,4	Metathesis	14	6.047	1.408	6.0 ± 0.6	6.4 ± 1.0	2.27 ± 0.13

[a] The underlined values were calculated without correcting for the propane formed in reaction 7d; B and C are coefficients of the straight line $13 + \log_{10} k_r/k_2^{1/2} = C - 10^3 B/T$, fitted to the experimental results; k_r represents k_6 and k_7, respectively, for metathesis and addition; all limits of error are expressed at the 5 % probability level.

[b] At 100°.

constants, and the corresponding Arrhenius parameters deviate significantly from the more accurate values of Table X. It has been concluded that equations (24) and (25) are adequate to yield accurate values of rate constants and Arrhenius parameters from the experimental data of this investigation.

Cyclohexadiene-1,3 is much more reactive towards the isopropyl radical in addition than in metathesis; the ratio of the rate constants is 4.3 ± 1.5 at 100°. This difference in activity is due to a difference in the activation energies of 1.3 ± 1.1 kcal./mole.

High intrinsic reactivity for cyclohexadiene-1,3 in radical polymerization is implicit in the value of 1.76 for the Alfrey-Price parameter Q.[112] It is not surprising therefore, that high polymer is formed both by radical homopolymerization of cyclohexadiene-1,3 in the solid state as a canal complex with thiourea at room temperature[121] and by the radical copolymerization of cyclohexadiene-1,3 with acrylonitrile in the liquid state at 60°.[112] In contrast, attempts to homopolymerize cyclohexadiene-1,3 under homogeneous, free-radical conditions have not succeeded in forming polymer with a higher degree of polymerization than 12.[116] Clearly, some process of structural chain termination is able to compete with the process of propagation far more efficiently in the third system than in the other two. During publication of this work,[122] a referee had suggested that this competing process is mutual combination, and its unusual efficiency in the third system is due to an exceptional slowness of homopropagation associated with the delocalized cyclohexenyl structure of the propagating radical species. This explanation must be reconciled with formation of high copolymer with a very nearly 1:1 molar compo-

sition from mixtures of cyclohexadiene-1,3 and acrylonitrile covering a wide range of composition. In such systems, the corresponding copropagation process between a radical chain terminated by a cyclohexenyl unit and a molecule of acrylonitrile cannot be exceptionally slow, or inhibition would result. No doubt a favourable polar effect promotes addition in this instance, but clearly delocalization of the free valence alone is not enough to confer upon a radical the property of sluggish addition to an olefinic linkage.

Degradative, chain transfer to monomer may be considered as an alternative or complementary process for efficient structural termination in the homogeneous homopolymerization of cyclohexadiene-1,3. The cyclohexadienyl radical formed is very much stabilized and unlikely to reinitiate by addition to cyclohexadiene-1,3. Degradative chain transfer competes with propagation for the same reactant species, and these processes are therefore analogues of reactions (6) and (7) in which a substituted cyclohexenyl radical has replaced the isopropyl radical. As the difference $E_6 - E_7$ is small, we may reasonably predict that the corresponding difference $E_f - E_p$ is also small, and that the ratio k_7/k_6 will provide a measure of the order of magnitude of k_p/k_f, the ratio of the rate constants of propagation and degradative chain transfer. The low degree of polymerization is then consistent with the low value of k_p/k_f given above.

Mutual termination of polymer radicals is eliminated from the mechanism of the emulsion homopolymerization of cyclohexadiene-1,3, and therefore the competition between the propagation and degradative chain transfer processes for polymer radicals can be assessed directly in an emulsion system.

In emulsion polymerization, the chain growth occurs in a micelle into which the diene feed diffuses, and which, at any time, contains only one active radical centre until it becomes terminated by acquiring another radical centre from the aqueous phase. Thus, termination is controlled, not by bimolecular kinetics as in bulk phase polymerization, but by the rate of supply of initiator radicals from the aqueous phase, which may be very low. In this way, very long chain polymers are synthesized.

An emulsion polymerization experiment was carried out on a mixture of cyclohexadiene-1,3 (4.3 g.) in water (7.7 g.) containing sodium stearate (0.21 g.) and potassium persulfate (0.0064 g.) for 200 minutes at 50°, under constant, vigorous stirring. The reactants had been previously thoroughly degassed and the reaction was run in an atmosphere of nitrogen. After the reaction time had elapsed, the emulsion was broken by adding a concentrated solution of calcium chloride in water. The oily layer was extracted into chloroform and the calcium stearate filtered off. The volatile organic materials were removed under vacuum and the residue was dissolved in benzene which was again pumped off at ice temperature (freeze drying). A very low yield of polymeric material (0.007 g.) was isolated by this procedure.

The n.m.r. spectrum of this material in deuterochloroform showed very broad, poorly resolved peaks centred around 4.1 Υ and from 8-9 Υ. Similar spectra[123] have been observed for styrene-cyclohexadiene-1,3 copolymers in samples where the mole fraction of styrene becomes very low.

A degree of polymerization of 6 was estimated for the homopolymer using a Mechrolab Model 301A osmometer with benzene as solvent. This value is of the same order of magnitude as those

obtained for homogeneous, homopolymerizations under comparable conditions,[116] and therefore, degradative chain transfer is the principal cause of low degree of polymerization of cyclohexadiene-1,3 under these homogeneous conditions. The very low yield of polymer in the emulsion system is consistent with low reactivity of the cyclohexadienyl radical produced in the degradative chain transfer.

The rate constant of metathesis with the isopropyl radical at 100° is significantly higher for cyclohexadiene-1,4 than for cyclohexadiene-1,3, but limits of error do not allow the identification of any significant variation among the Arrhenius parameters. Energetic and steric factors may be expected to combine to make cyclohexadiene-1,3 the less reactive isomer. First, it has the lower standard free energy of formation;[107,124] secondly, its methylene groups are adjacent, so that an unfavourable steric factor may be imposed by mutual crowding of the methylene groups.

A comparison of rate constants for corresponding reactions measured for the ethyl radical[1] to those measured here with the isopropyl radical is given in Table XI. An interesting feature of these results is the difference in steric factors for ethyl and isopropyl radicals. There seems to be about a factor of ten between them in all cases. Of course, this result depends upon the accuracy of determinations of the radical recombination rate constants for ethyl[19] and isopropyl[26] radicals, but would seem to be significant in view of the magnitude of the effect. No apparent reason for the high efficiency of isopropyl attack exists.

The abstraction from cyclohexadiene-1,3 has significantly higher activation energy for isopropyl attack than for ethyl

TABLE XI

Comparison of the Ethyl and the Isopropyl Radical in reactivity towards the Cyclohexadiene

Molecules

$$\left(\text{kcal./mole}\right)$$

reaction	reagent	$E_r - \frac{1}{2}E_2$	$13 + \log_{10}A_r/A_2^{\frac{1}{2}}$ [b]	$\log_{10}A_r$	$10^3 p$ [c]
addition to C_6H_8-1,3	$C_2H_5^{\cdot}$ [a]	5.2 ± 0.3	5.5 ± 0.2	-12.7	0.40
	$C_3H_7^{\cdot}$	5.8 ± 0.4	6.0 ± 0.2	-12.0	2.2
abstraction from C_6H_8-1,3	$C_2H_5^{\cdot}$	5.4 ± 0.5	5.0 ± 0.3	-13.3	0.11
	$C_3H_7^{\cdot}$	7.1 ± 0.7	6.2 ± 0.4	-11.8	3.5
abstraction from C_6H_8-1,4	$C_2H_5^{\cdot}$	5.8 ± 0.1	5.7 ± 0.1	-12.5	0.58
	$C_3H_7^{\cdot}$	6.5 ± 1.0	6.0 ± 0.6	-12.0	2.4

[a] Values for ethyl radicals are from the Ph.D. thesis of A. C. R. Brown, University of British Columbia, (1962). Values for isopropyl are from this work.

[b] A factors are in (cm^3/molecule sec.).

[c] Assumes collision diameters of 4.0, 4.75 and 6.5 $\overset{o}{A}$. for ethyl, isopropyl and cyclohexadiene respectively. Also, A_2 has been taken as $10^{-10.48}$ and $10^{-9.9}$ cm^3/molec.sec. for ethyl and isopropyl respectively.

attack at the 5 % probability level. This higher activation en-
ergy is just what is anticipated on the basis of the C-H bond
dissociation energy of the attacking radical,[125,126] which is
about 3.5 kcal. less for isopropyl than for ethyl, according to
recent determinations.[14,127] The difference is not significant
for the abstraction reactions from cyclohexadiene-1,4 and, in
fact, consideration of the results from all of the attacking
radicals studied here indicates that the difference is very small
indeed, because tert-butyl attack has a low activation energy. It
is strange that a difference in activation energies is observed
for the 1,3-diene, and not for the 1,4-diene.

C. 2,2'-Azoisobutane as Initiator

1. Preliminary kinetic examination of 2,2'azoisobutane
photolysis

As the photolysis of 2,2'-azoisobutane was anticipated to be
a clean source of tert-butyl radicals, in common with other azo-
alkanes, but has not previously been examined kinetically, ex-
periments were undertaken to determine its suitability as an
initiator system.

The pyrolysis of 2,2'-azoisobutane has been examined in two
previous studies by Levy and Copeland[128] and by Blackham and
Eatough.[129]

Levy and Copeland[128] have pyrolyzed 2,2'-azoisobutane in a
static system between 180 and 220°. They found the reaction to
proceed homogeneously forming nitrogen gas and isobutane. Con-
siderable polymeric material was also formed on the glass walls
of the vessel. Interestingly enough, no isobutylene was found
that would arise from tert-butyl disproportionation; indeed,
they found that isobutylene was consumed when it was added to the

pyrolysis system. They suggested that the tert-butyl radicals presumably released on pyrolysis efficiently attack the primary product, isobutylene, and ultimately this process leads to polymeric residues. The added isobutylene did not suppress the rate of decomposition so they concluded that chain decomposition of the azo compound was unimportant in this system. This follows from the fact that isobutylene would be expected to be a more effective chain breaking agent than propylene, which is known to be an active inhibitor of radical chains at high temperatures because of its labile hydrogen atoms available for metathesis.

From pressure measurements, Levy and Copeland find that the decomposition,

$$(CH_3)_3C-N=N-C(CH_3)_3 \xrightarrow{\quad k \quad} N_2 + 2 (CH_3)_3C\cdot$$
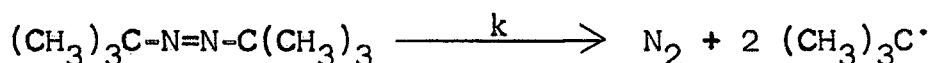
has the rate constant $k = 10^{16.34}\exp(-42.8/RT)$ sec.$^{-1}$.

Blackham and Eatough[129] have examined the pyrolysis from 250 to 290° in a flow system using hydrogen and helium as carrier gases. They used the nitrogen evolved as index of the amount of decomposition and found Arrhenius parameters in essential agreement with those of Levy and Copeland. They measured $k = 10^{17.11}\exp(-43/RT)$ sec.$^{-1}$ corresponding to a positive entropy of activation of 16 eu/mole. Using a flow system which protects products from secondary reaction, they were able to recover isobutylene as well as isobutane in equimolar amounts.

The results of these two authors are consistent with the initial decomposition of azoisobutane into nitrogen and tert-butyl radicals which do not attack the starting material to an appreciable extent.

The photo-oxidation of 2,2'-azoisobutane in oxygen rich atmospheres at 25° has been examined by Thomas and Calvert.[130]

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Their observations are consistent with an excited molecule decomposition in the primary process, since they have measured a pressure dependence on the quantum yield of nitrogen produced at 25°. This is in contrast to the azomethane photolysis[65] which exhibits a nitrogen quantum yield of unity, independent of pressure. A pressure dependence has also been observed for the photo-decomposition of 1,1'-azo-n-butane[37] where a more complete study has shown the decomposition of the photo-excited molecule to require 3,800 cal. of activation energy for decomposition. Also azoethane[76] and azoisopropane[106] have been found to have pressure and temperature sensitive nitrogen quantum yields. The same situation is likely to prevail for the 2,2'-azoisobutane case, and may be general for the larger, more complex azoalkane systems.

Thomas and Calvert[130] suggest the sequence of processes I to explain the photo-decomposition of 2,2'-azoisobutane.

$$AIB + h\nu \xrightarrow{\;Ia\;} AIB^*$$
$$AIB^* + M \xrightarrow{\;Ib\;} AIB + M^* \qquad\qquad \text{I}$$
$$AIB^* \xrightarrow{\;Ic\;} 2\,(CH_3)_3C^{\cdot} + N_2$$

where AIB = 2,2'-azoisobutane
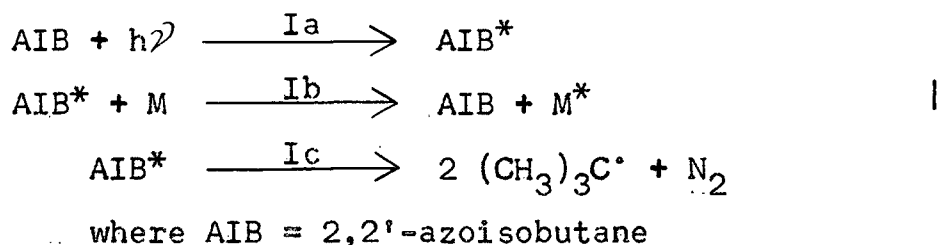
In their system, the tert-butyl radicals thus produced react exclusively with oxygen molecules and initiate a photo-oxidation sequence.

The measurement of $\triangle$(tert-Bu, tert-Bu) has been reported several times and, in this case, no particular agreement has been reached. Thus Kraus and Calvert[36] reported $\triangle$(tert-Bu, tert-Bu) = 4.59 from photolysis of di-tert-butyl ketone; Dominguez et al.[57] reported 3.19 from the same source; Birell and Trotman-Dickenson[131] reported 4.38 from the photolysis of pivaldehyde; Boddy and Robb[132] reported 2.2 from study of the mercury photo-sensitized addition

of hydrogen atoms to isobutylene. Furthermore, Blackham and
Eatough[129] found their data consistent with a value of 1.4, al-
though this must be viewed with reserve because of the high tem-
peratures and attendant mechanistic complexities not fully con-
sidered. In no case were the analytical results consistent with
a material balance between the radicals generated and the products
removed from the system.

In any event, the $\triangle$ ratio for tert-butyl radicals is in
need of clarification; since azoalkane photolysis is frequently
found to be a clean source of alkyl radicals, free of troublesome
side effects, the 2,2'-azoisobutane system promised to be conven-
ient.

Experimental   Due chiefly to difficulties in analysis, dif-
ferent techniques have been employed in this system than have been
used in the case of other initiators.

The photolysis of 2,2'-azoisobutane has been examined for the
pure compound and for the photolysis in the presence of a large
excess of cyclohexadiene-1,4 which functions as an efficient
scavenger. These photolyses comprise eight experiments, between
23 and 153°. The results and conditions of these experiments
have been collected in Table XII.

The reactants were measured out as usual from storage cells
and photolyzed with 3660 Å. actinic light. After photolysis was
complete, the reaction mixture was allowed to distil into the
analytical line where the various traps were maintained at the
following temperatures.

        1st Variable temperature trap   - 90°

        Spiral trap   -198°

        2nd Variable temperature trap   -112°

TABLE XII

Photolysis of pure 2,2'-Azoisobutane

($^{\circ}$K)	(sec.)			$10^{-12}R_X$ (molec./cm^{3}sec.)				$\dfrac{cc.^{1/2}}{mol.^{1/2}sec.^{1/2}}$
T	t	$[A]^a$	$[B]^a$	N_2	C_4H_8	C_4H_{10}	$k_3/k_2{}^b$	$10^{13}\,k_4/k_3{}^{1/2}$
297	900	2.58	–	69.1	49.7	49.7	2.56	–
360	72000	0.478	11.8	0.219	0.0	0.431	–	–
362	7200	4.07	–	4.64	3.27	3.27	2.39	–
362	7200	4.21	–	1.80	1.19	1.24	2.22	1.09
362	75600	0.580	11.8	0.0703	0.0	0.142	–	–
366	300	4.46	–	127.	97.6	97.6	(3.28)	–
400	7200	1.90	–	1.15	0.685	0.845	2.24	10.1
426	7200	1.36	–	1.44	0.448	1.65	c	132.

Mean value, excluding entries in parentheses 2.35

Limits of error at 5 % probability level $\pm$0.68

^{a} $10^{17}[A]$ = Concentration of 2,2'-azoisobutane (molecules/cm^3)
$10^{17}[B]$ = Concentration of cyclohexadiene-1,4 (molecules/cm^3)

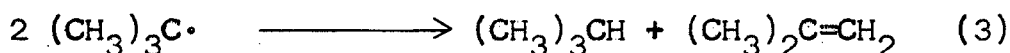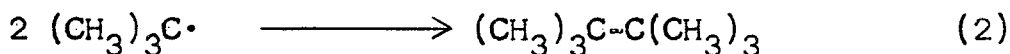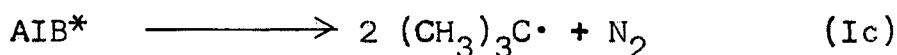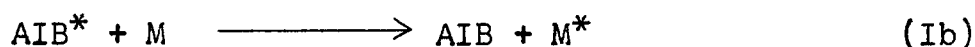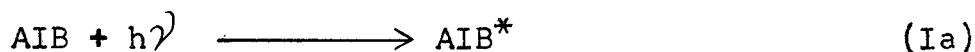^{b} $k_3/k_2 = R_{C_4H_8}/(R_{N_2} - R_{C_4H_{10}})$

^{c} $R_{C_4H_{10}} > R_{N_2}$

Nitrogen gas was collected pure into the gas burette, under these conditions and measured. After pumping out the gas burette, the spiral trap was warmed to room temperature and a mixture of iso-butane and isobutylene was collected into the gas burette and measured. This fraction was found to be free of any appreciable impurities by examination by gas chromatography. In routine runs, this C_4 fraction was analyzed on a silica gel packed column at 180°. A greaseless sampling valve was used to avoid absorption of the butane or butene into the tap lubricant. The ratio of pressures of isobutane to isobutylene could be found by multiplication of the peak area ratio by 0.97. This calibration factor was found in the usual way by running chromatograms of synthetic mixtures of isobutane and isobutylene. This, together with the total amount of both gases from the gas burette measurement gave the separate amounts of each component.

No convenient analysis for the di-tert-butyl product was established. On all packed columns available, this compound was not separated from the azoisobutane peak in a sufficient amount to yield reasonable analysis. It appears that this compound is amazingly similar to its azoisobutane precursor, perhaps due to the fact that the bulky tert-butyl groups effectively shield the nitrogeneous portion of the azoisobutane molecule. Analysis of the residues from photolysis on the capillary polyethylene glycol column did succeed in splitting the azoisobutane peak, showing the presence of the di-tert-butyl product, but still was not convenient for quantitative purposes. No other compounds were evident in the capillary column analysis, even after the column was baked at 120° (the maximum operating temperature) for extended periods.

Treatment of the data   There is no evidence in the analytical data for any products other than isobutane, isobutylene and di-tert-butyl. Furthermore, as Table XII reveals, in those runs where no cyclohexadiene-1,4 has been added, and below 127°, the isobutane yield is seen to be equal to the isobutylene yield. Under these conditions, it is proposed that Scheme J below completely accounts for the products.

$$AIB + h\nu \longrightarrow AIB^* \tag{Ia}$$

$$AIB^* + M \longrightarrow AIB + M^* \tag{Ib}$$

$$AIB^* \longrightarrow 2\,(CH_3)_3C\cdot + N_2 \tag{Ic}$$

J

$$2\,(CH_3)_3C\cdot \longrightarrow (CH_3)_3C\text{-}C(CH_3)_3 \tag{2}$$

$$2\,(CH_3)_3C\cdot \longrightarrow (CH_3)_3CH + (CH_3)_2C\text{=}CH_2 \tag{3}$$

$$\text{where AIB} = 2,2'\text{-azoisobutane}$$

In this regime,

$$\frac{k_3}{k_2} = \frac{R_{C_4H_8}}{R_{C_8H_{18}}} = \frac{R_{C_4H_8}}{R_{N_2} - R_{C_4H_{10}}} \tag{26}$$

and calculated values have been presented in Table XII. This relation depends upon the assumption that tert-butyl radicals do not add to the double bond of the azo compound in the way methyl radicals add to azomethane. In view of the steric conditions prevailing around the N=N double bond, this assumption seems justified. Even in the azomethane case, the addition is suffuciently slow that it would not be observed at the high rate of photolysis used during experiments with azoisobutane-cyclohexadiene-1,4 mixtures, which are listed in Table XIII, and which provide substantially the same result as found here for $\triangle$(tert-Bu, tert-Bu). The value for $\triangle$(tert-Bu, tert-Bu) measured in this way is 2.35 $\pm$ 0.68. This is verified, and considerably improved in accuracy in

runs with added cyclohexadiene-1,4, to be described in the next section of this thesis.

The excellent agreement in the rates of isobutane and of iso-butylene below 127° indicates that the metathetical reaction,

$$(CH_3)_3\overset{\cdot}{C} + (CH_3)_3CN=NC(CH_3)_3 \overset{4}{\longrightarrow} (CH_3)_3CH + (CH_3)_2(\overset{\cdot}{C}H_2)CNNC(CH_3)_3$$

does not proceed under these conditions. An experiment at 89° does show a slight excess of isobutane over isobutene and indicates a value of $k_4/k_2^{1/2} = 1.09 \times 10^{-13}$ $(cm^3/molec.sec.)^{1/2}$. If this is ac-cepted as accurate, then the metathetical reaction with this com-pound is 3.2 times slower than the comparable process measured for azomethane. Kraus and Calvert[36] found di-tert-butyl ketone inert towards the tert-butyl radical up to 322° under similar conditions of rapid photolysis. The experiments at 127 and 153° show less isobutylene than isobutane; this may indicate the onset of reaction (4), or, alternatively, may be caused by the consum-sumption of isobutylene by tert-butyl radicals as observed by Levy and Copeland for their pyrolysis system.[128] If it is the abstraction reaction (4) that is responsible, then equation (26) should still apply assuming termination of secondary radicals by tert-butyl radicals. However, the result at 153° has $R_{C_4H_{10}} > R_{N_2}$, hence application of equation (26) fails. On the other hand, consumption of the isobutylene seems unlikely at these low con-versions. The effect may, after all, be a separate thermal re-action yielding isobutane. At any rate, below 100°, the system seems safe from interference from this cause, and use of the 2,2'-azoisobutane system as an initiator has been limited to this low temperature range.

Two experiments have been done with a twentyfold excess of

cyclohexadiene-1,4 at 87 and 89°. Low light intensities have been employed to ensure scavenging by the reaction:

$$\cdot C(CH_3)_3 + \text{[cyclohexadiene]} \xrightarrow{6} \text{[radical]} + (CH_3)_3CH$$
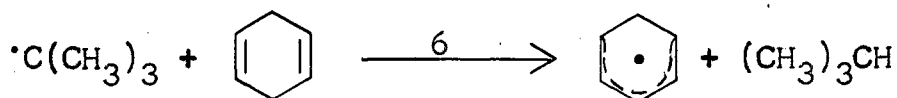
The ratio $R_{C_4H_{10}}/R_{N_2}$ then takes the values of 1.97 and 2.02 respectively at 87 and 89°, in close agreement with the predicted value of 2.00. The molecular elimination reaction:

$$(CH_3)_3C-N=N-C(CH_3)_3 + h\nu \xrightarrow{\phi_m^{Ia}} N_2 + (CH_3)_3C-C(CH_3)_3$$
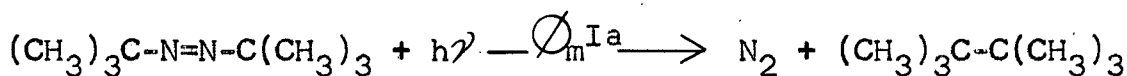
is therefore unlikely to account for more than 1 % of the nitrogen formed; it is therefore not more important than it is for azomethane. Klein et al.[42] have suggested that large values of ϕ_m may exist for azoisopropane photolysis in order to explain certain of their results. In view of this tert-butyl result, a large ϕ_m for the isopropyl system seems unlikely.

Discussion These experiments on azoisobutane photolysis have yielded a value of $\triangle$(tert-Bu, tert-Bu) = 2.35 ± 0.68 based upon the assumption that the tert-butyl radical does not add to the double bond of the azo compound. Results from the experiments on cyclohexadiene-1,4-2,2'-azoisobutane mixtures agree with this measurement and provide greater precision. These results are listed in Table XIII and will be described in detail. All of the experiments taken together yield the value $\triangle$(tert-Bu, tert-Bu) = 2.33 ± 0.28, independent of temperature from 23 to 127°; the error expressed at the 5 % probability level. An Arrhenius plot of these total results has been included on Figure 20. This value is considerably lower than that of previous measurements save for that of Boddy and Robb[132] ($\triangle$ = 2.2) and the rather uncertain measurement of Blackham and Eatough,[129] ($\triangle$ = 1.4).

A re-evaluation of the results of Kraus and Calvert[36] is instructive. They have measured the ratio, k_3/k_2 where $k_3/k_2 = (R_{C_4H_8} + R_{C_4H_{10}})/2 R_{C_8H_{18}} = 4.4 \pm 0.7$ (102 to 178°). However, an alternative interpretation of their results yields the value:

$$k_3/k_2 = R_{C_4H_8} / \left[R_{CO} - \tfrac{1}{2}(R_{C_4H_8} + R_{C_4H_{10}}) \right] = 2.3 \pm 1.1$$

over the same temperature range in close agreement with the present results. The ambiguity in the interpretation of their results arises from a failure to achieve a material balance, expressed by the ratio:

$$R_{C_8H_{18}} / R_{CO} - \tfrac{1}{2}(R_{C_4H_8} + R_{C_4H_{10}}) = 0.50 \pm 0.16$$

whereas their mechanism predicts the value 1.00.

A consideration of the previous measurements of $\triangle$ values for the various n-alkyl radicals suggests that the azo compounds may provide the most reliable results. Determinations of $\triangle$(Et, Et) = 0.14,[77] $\triangle$(n-Pr, n-Pr) = 0.16,[133] $\triangle$(Me, n-Bu) = 0.15[134] lead one to expect values of ca. 0.15 for disproportionation ratios of n-alkyl radicals. However, $\triangle$(n-Bu, n-Bu) has been found to have the value 0.94,[134] much higher than for similar n-alkyl systems, during chemically sensitized decomposition of n-butyl formate. Trotman-Dickenson[39] found the ratio to be temperature dependent during photolysis of n-valeraldehyde. However, the recent redetermination of $\triangle$(n-Bu, n-Bu)[37] using the photolysis of 1,1'-azo-n-butane yielded the value 0.14; this was observed in both the flash photodecomposition of the azobutane and in the stationary state photolytic system. This result is in accord with expectations based on the behavior of the lower homologues. Furthermore, results from azoalkane photolysis for the lower

homologues are also lower than those for ketone photolysis, but the effect is much smaller. Thus $\triangle$(Et, Et) = 0.12 from azo-ethane[76] and $\triangle$(iso-Pr, iso-Pr) = 0.54 from azoisopropane[106] vs. 0.14 and 0.58 respectively from ketone systems.

From the above considerations, it is concluded that the "low" value of the disproportionation-combination ratio of tert-butyl radicals observed during 2,2'-azoisobutane photolysis may be the most representative one. Furthermore, redetermination of $\triangle$ values for all the higher molecular weight alkyl radicals using azo-alkane photolysis as the radical source seems advisable. In the meantime, Kraus and Calvert's suggestion[36] that $\triangle$ values for the butyl radical isomers are in the same ratio as the number of hy-drogen atoms available for disproportionation is uncertain.

2. The photolysis of 2,2'-azoisobutane-cyclohexadiene-1,4 mixtures

In order to extend the information on alkyl radical reactiv-ity with cyclohexadiene-1,4 and cyclohexadienyl radicals, the photolysis of the mixed vapours of 2,2'-azoisobutane and cyclo-hexadiene-1,4 has been examined. The nature of the experiments was the same as that already discussed for azomethane and di-isopropyl ketone photolysis in the presence of cyclohexadiene-1,4.

Experimental The system has been examined in eight experi-ments from 26 to 100°. The mixed vapours have been photolyzed with 3660 Å. radiation using the full light intensity available at that wavelength from the B.T.H. medium pressure mercury lamp.

After photolysis, the reaction mixture was allowed to distil into the analytical line where the various traps were maintained at the following temperatures:

1st Variable temperature trap $- 90^\circ$

    Spiral trap -198°

2nd Variable temperature trap -112°

Nitrogen was removed pure into the gas burette, and measured.
Following this, the spiral trap was warmed and butane and butyl-
ene were collected and measured in the same way as for the analy-
sis of the pure azoisobutane photolyses.

Following the analysis of the gases, the residues in the
analytical line were allowed to vapourize, were mixed with a
manometrically measured amount of 3-methylpentane as an internal
gas chromatographic standard, and removed from the vacuum system.
Since the usual internal standard, n-heptane, was not separated
sufficiently from the azoisobutane peak on the preferred analyti-
cal column, the isomeric hexane, 3-methylpentane, was used in-
stead.

This sample was mixed with a small amount of pentene-1 sol-
vent and injected onto a specially prepared 1 meter, packed 20 %
hexadecane on firebrick column run at 54°. This column was effect-
ive in separating the reaction mixture into the following com-
ponents in order of elution: pentene-1 (solvent), 3-methylpentane
(internal standard), benzene, cyclohexadiene-1,4 and finally azo-
isobutane and di-<u>tert</u>-butyl together.

The benzene yield could be found from the known amount of
3-methylpentane by comparison of their peak areas if the benzene
peak area were multiplied by 0.971. It was not possible to drive
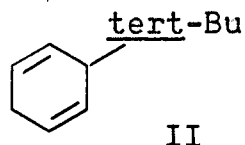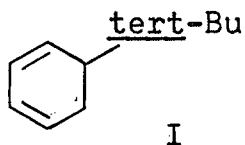off the expected compounds I and II

          tert-Bu   tert-Bu

               I   II

TABLE XIII

Metathesis between the tert-Butyl Radical and Cyclohexadiene-1,4

($^{\circ}$K)	(sec.)			$10^{-12}R_X$ (molec./cm^3·sec.)					(sec.$^{-1}$)			$\left(\dfrac{cc.^{1/2}}{mol.^{1/2}sec.^{1/2}}\right)$
T	t	$[A]^a$	$[B]^a$	N_2	C_4H_8	C_4H_{10}	C_6H_6	$([A]+[B])^a$	$R_{N_2}/[A]$	k_3/k_2	$\triangle^b$	$10^{13} \dfrac{k_6/k_3^{1/2}}{}$
300	1800	7.00	3.22	108.2	66.6	88.5	8.50	10.22	15.5	2.33	(1.74)	51.0
303	1800	6.14	3.14	104.8	61.6	88.4	9.78	9.28	17.1	2.36	1.36	69.0
320	1800	5.05	1.36	98.7	62.4	78.4	5.65	6.41	19.3	2.31	1.20	96.6
326	1800	6.51	1.37	115.3	73.8	92.2	6.64	7.88	17.7	2.49	1.30	100.
337	1800	5.65	1.18	97.9	61.0	79.0	6.50	6.83	17.3	2.40	1.30	125.
357	1800	5.16	1.03	93.9	54.9	78.3	8.00	6.19	18.2	2.33	(1.08)	202.
370	900	3.35	0.816	115.6	64.0	96.2	11.70	6.16	21.6	2.13	1.33	324.
373	300	5.51	0.668	126.7	73.6	103.8	11.25	6.18	23.0	2.16	1.46	330.
				Mean value, excluding entries in parentheses						2.32	1.33	
				Limits of error at 5 % probability level						$\pm$0.29	$\pm$0.24	

a $10^{17}[A]$ = Concentration of 2,2'-azoisobutane (molecules/cm^3)
   $10^{17}[B]$ = Concentration of cyclohexadiene-1,4 (molecules/cm^3)

b $\triangle = R_{C_6H_6}/\left(R_{C_4H_{10}} - R_{C_4H_8} - 2 R_{C_6H_6}\right)$

at the maximum temperature (85-90°) that the column will safely withstand.

Supplementary analysis of a portion of the reaction mixture on the capillary polyethylene glycol column at room temperature separated the reaction mixture into the following components in order of elution: pentene-1 (solvent), 3-methylpentane (internal standard), azoisobutane and benzene together, preceded by an almost resolved di-_tert_-butyl shoulder, and cyclohexadiene-1,4. Heating the column gradually to 120° caused the elution of another, single peak judged to be the two, unresolved compounds, I and II, in analogy with the other systems studied. In this case, these two compounds are so similar in vapour pressure and chemical properties that the capillary column is no longer effective in resolving them. No analysis for the ratio k_{6c}^{I}/k_{6c}^{II} was possible, therefore, in the case of the reactions of _tert_-butyl radicals with the cyclohexadienyl radical.

The capillary column analysis would have shown the presence of any cyclohexadiene-1,3 present in the reaction products. None was observed during any run.

The experimental conditions, and rates of formation of the various products have been collected in Table XIII along with results to be explained below.

Treatment of the data   In view of the previous study of the photolysis of 2,2'-azoisobutane, and by analogy with the other high intensity studies of initiator systems with cyclohexadiene-1,4, the results have been considered to arise from the mechanism of Scheme K.

Although no direct experimental evidence has been found to disprove the reactions (6e):

$$(CH_3)_3C\cdot + C_6H_7^\cdot \xrightarrow{\quad 6e \quad} (CH_3)_2C=CH_2 + (C_6H_8\text{-}1,3 \text{ or } C_6H_8\text{-}1,4)$$
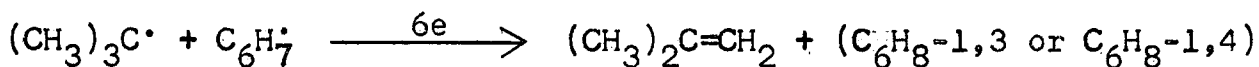
this has not been considered in the mechanism because (a) it does not occur for either ethyl or isopropyl radicals and (b) by the material balance method of analysis for reaction (6c) used in the kinetic analysis, whence $k_{6d}/k_{6c} = R_{6d}/(R_6 - R_{6d})$, neglect of (6e) would lower k_{6d}/k_{6c} values, where in fact we shall see that it is surprisingly high. Similarly, k_3/k_2 values would be abnormally high, especially at the higher temperatures if reaction (6e) were important, whereas the measured value, 2.33, is lower than previous determinations.

$$AIB + h\nu \xrightarrow{\quad Ia \quad} AIB^*$$

$$AIB^* + M \xrightarrow{\quad Ib \quad} AIB + M^*$$

$$AIB^* \xrightarrow{\quad Ic \quad} 2\,(CH_3)_3C\cdot + N_2$$

$$2\,(CH_3)_3C\cdot \xrightarrow{\quad 2 \quad} (CH_3)_3C\text{-}C(CH_3)_3 \qquad\qquad \mathbf{K}$$

$$\xrightarrow{\quad 3 \quad} (CH_3)_3CH + (CH_3)_2C=CH_2$$

$$C_6H_8\text{-}1,4 + (CH_3)_3C\cdot \xrightarrow{\quad 6 \quad} (CH_3)_3CH + C_6H_7^\cdot$$

$$(CH_3)_3C\cdot + C_6H_7^\cdot \xrightarrow{\quad 6c \quad} \text{[C}_4\text{H}_9 \text{ cyclohexadiene] or [C}_4\text{H}_9 \text{ cyclohexadiene]}$$

$$\xrightarrow{\quad 6d \quad} (CH_3)_3CH + C_6H_6$$
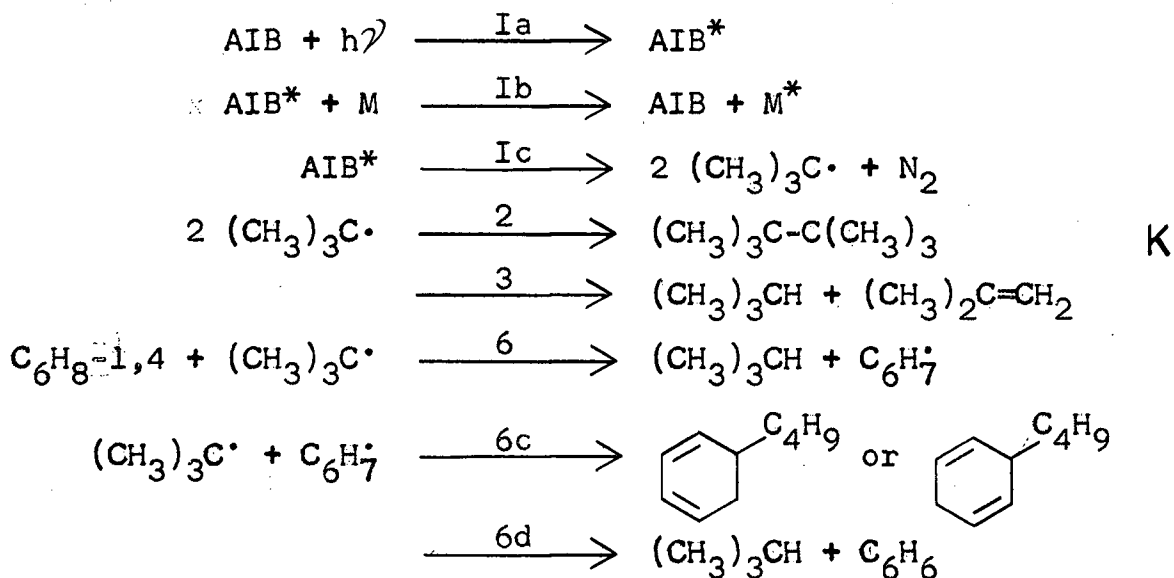
No metathetical reaction from the azo compound has been considered as the preliminary investigation of 2,2'-azoisobutane photolysis did not reveal such reactivity below 127°. In this study, all experiments were done below 100°. Similarly, no addition reaction has been considered; such a reaction would not alter conclusions about metathesis from the diene or subsequent reactivity of the cyclohexadienyl radical, even if it were to occur.

Assuming the simple mechanism above, Scheme K, the following

steady-state equations are readily derived.

$$\frac{k_6}{k_3^{1/2}} = \frac{R_{C_4H_{10}} - R_{C_4H_8} - R_{C_6H_6}}{R_{C_4H_8}^{1/2} [\text{CHD-1,4}]} \tag{27}$$

$$\frac{k_3}{k_2} = \frac{R_{C_4H_8}}{R_{N_2} - R_{C_4H_{10}} + R_{C_6H_6}} \tag{28}$$

$$= \frac{k_{6d}}{k_{6c}} = \frac{R_{C_6H_6}}{R_6 - R_{C_6H_6}} \tag{29}$$

$$= \frac{R_{C_6H_6}}{R_{C_4H_{10}} - R_{C_4H_8} - 2\,R_{C_6H_6}}$$

Here, the ratio $k_6/k_3^{1/2}$ has been calculated in preference to the more usual $k_6/k_2^{1/2}$ since the rate of formation of the dimeric product, di-tert-butyl, was impossible in this series of experiments. As both reactions are probably without activation energy, this is of no serious consequence. Because of the lack of analysis for di-tert-butyl, the rate of its formation has been assumed to be $R_{C_8H_{18}} = R_{N_2} - R_3 - R_6 + R_{6d}$; this leads to the form of equation (28).

Values for $k_6/k_3^{1/2}$, k_3/k_2 and $\triangle = k_{6d}/k_{6c}$, have been listed in Table XIII. The results for abstraction of hydrogen from cyclohexadiene-1,4 by tert-butyl radicals are plotted on Figure 19.

Statistical analysis of the results shows that

$$10^{13} \frac{k_6}{k_2^{1/2}} = 10^{(5.6 \pm 0.5)} \exp\frac{(-5.3 \pm 0.8)}{RT} \left(\frac{cm^3}{\text{molec. sec.}}\right)^{1/2}$$

Also, for the disproportionation ratios, statistical analysis

Figure 19. Metathesis between the tert-Butyl Radical and Cyclohexadiene-1,4
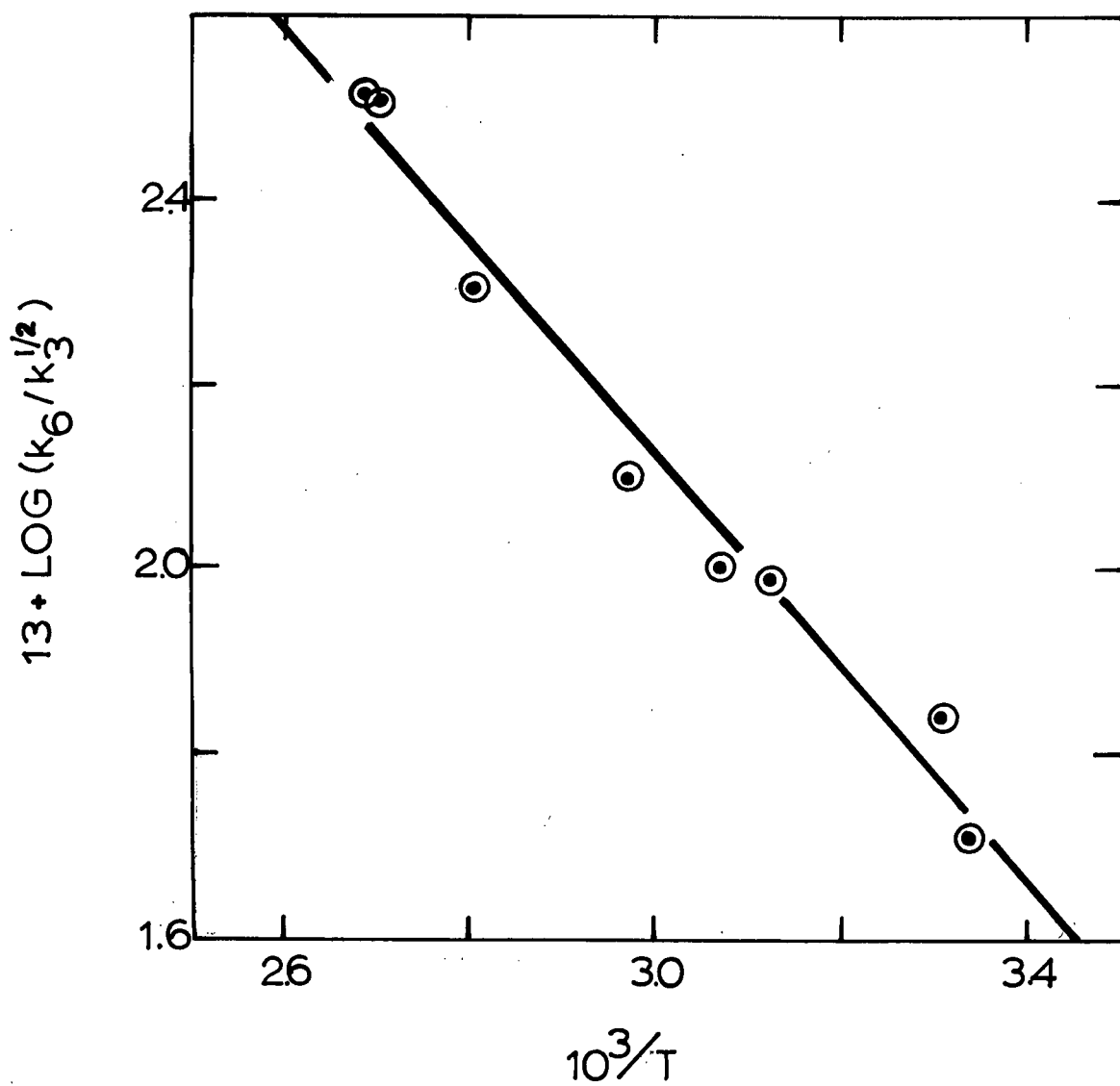
shows k_3'/k_2 = 2.3 + 0.3 and k_{6d}/k_{6c} = 1.3 + 0.2 independent of temperature in both cases within experimental error.

Also in Table XIII are values of $R_{N_2}/[AIB]$ and of $[AIB]$ + $[CHD-1,4]$. To the approximation that the intensity of the light source remains constant from run to run, one expects $R_{N_2}/[AIB]$ to be nearly constant if the quantum yield of nitrogen is invariant with temperature and total pressure. As this ratio increases steadily from the lowest to the highest temperature, it is a qualitative indication that either pressure or temperature or both influence the primary photochemical process. Since both temperature and pressure vary, it is not possible to specify the details, but the scheme given in the proposed mechanism seems to be reasonably well established for similar azoalkane systems.[76,106]

Discussion   As has already been mentioned, the value of $\triangle$(tert-Bu, tert-Bu) = 2.3 ± 0.3 measured here agrees with the measurement made on the pure 2,2'-azoisobutane system and appears to be representative.

In this system, the value of k_{6d}/k_{6c} = $\triangle$(tert-Bu, C_6H_7) has not been calculated from the capillary column peak areas for compounds I, II and C_6H_6 as was done for azomethane and di-isopropyl ketone experiments because the benzene peak was not resolved from azoisobutane. However, sufficient precision was obtained from the material balance technique (ie., by equation (29)) to obtain a reliable value. The two methods are adjusted to give the same value, anyway, and the capillary column technique is used only to improve the errors, which are not severe in these experiments in measurement of k_{6d}/k_{6c}.

The numerical value of the disproportionation to combination ratio is surprisingly high, in the case of tert-butyl radical. It

is consistent with 57 % of tert-butyl-cyclohexadienyl interactions leading to disproportionation and 43 %, the smaller fraction, recombining. The surprising tendency for the higher molecular weight, branched radicals to disproportionate when the number of hydrogen atoms available for disproportionation remains constant is contrary to the usual expectations. Thus intuitively one may expect tert-butyl to be a sluggish hydrogen atom remover as it has the weaker C-H bond. These factors are considered more fully in relation to the whole series of radicals in the "General Discussion" section of this thesis.

No temperature dependence has been found for the $\triangle(\text{tert-Bu}, C_6H_7^.)$ values, as is evident from Figure 20.

D. Diethyl Ketone as Initiator

Diethyl ketone has been examined and used extensively in this laboratory as an ethyl radical source in photochemical systems. No complications have arisen to impair its usefullness.

The diethyl ketone-cyclohexadiene-1,4 system has been studied earlier by Brown[1] and this work has been described in the "Introduction" section as background for the present research. His experiments yielded the results:

$$10^{13} \frac{k_6}{k_2^{1/2}} = 10^{(5.7 \pm 0.1)} \exp \frac{-(5.8 \pm 0.1)}{RT} \left(\frac{cm^3}{molec.sec.} \right)^{1/2}$$

and $\triangle(\text{Et}, C_6H_7^.) = k_{6d}/k_{6c} = 0.38 \pm 0.03$ independent of temperature for the reactions

$$C_2H_5^. + C_6H_8\text{-}1,4 \xrightarrow{\ 6\ } C_2H_6 + C_6H_7^.$$
$$C_2H_5^. + C_6H_7^. \xrightarrow{\ 6d\ } C_2H_6 + C_6H_6$$

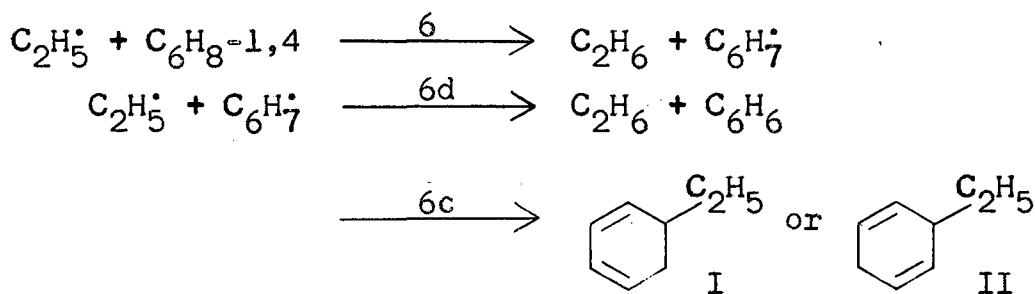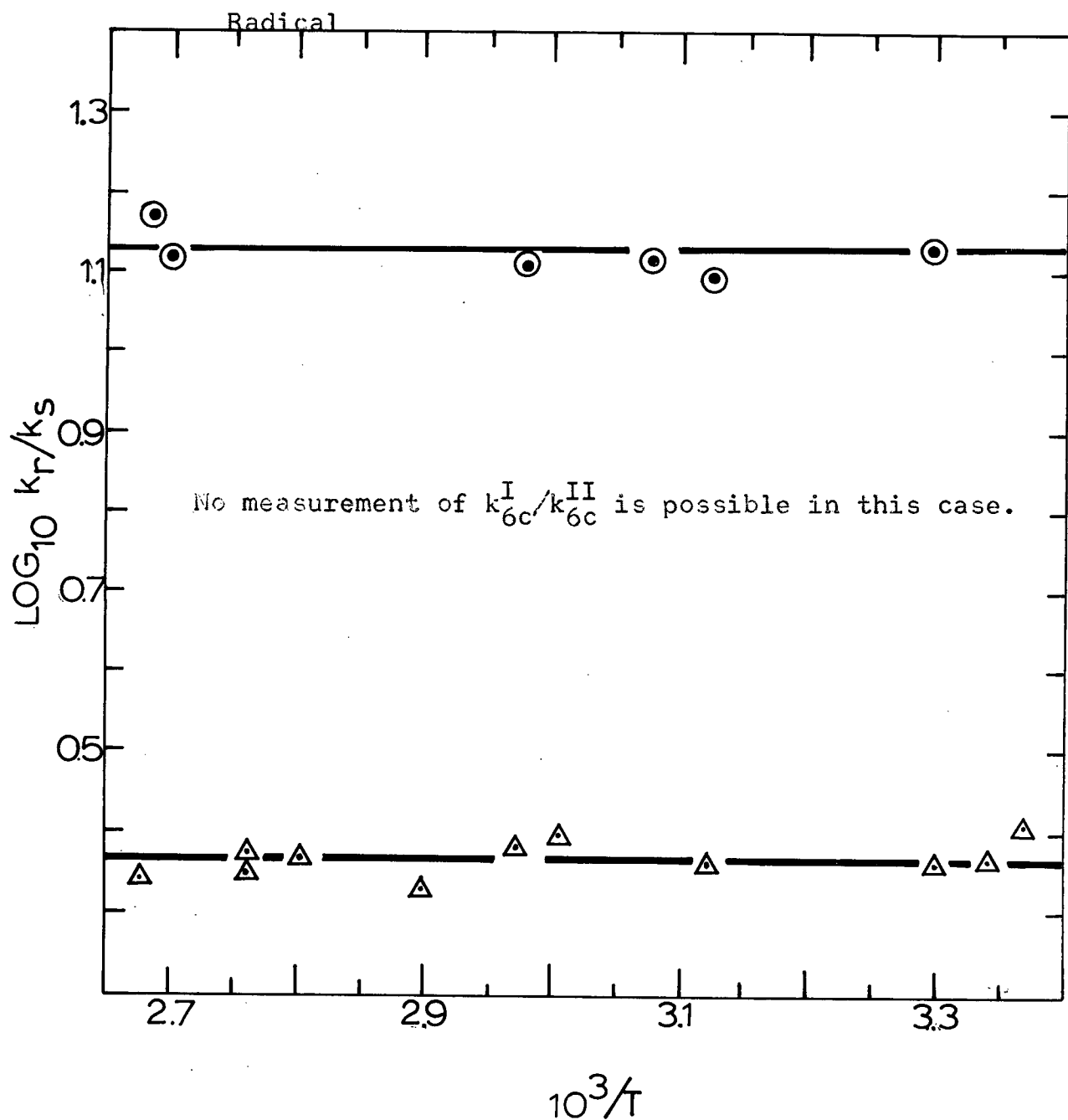$$\xrightarrow{\ 6c\ }$$

I or II

Figure 20. Disproportionation and Combination of the tert-Butyl Radical with Itself and with the Cyclohexadienyl Radical

$$k_r/k_s = 10\ k_{6d}/(k_{6c}^{I} + k_{6c}^{II})$$

See Scheme J

$$k_r/k_s = k_2/k_3$$

Since he did not have the use of temperature-programmed capillary columns when his investigation was carried out, no analysis of the relative yields of I and II was obtained.

In order to complete the investigation of the ethyl-cyclohexadienyl radical interactions, some experiments have been carried out using the more complete analytical procedure for the heavy reaction products.

Experimental Six experiments between 34 and 84° have been performed on gaseous mixtures of diethyl ketone and cyclohexadiene-1,4.

No detailed product analysis was attempted, as the aim of this study was only to obtain data on the dimeric products from reaction (6c). After photolysis of the mixture with 3130 Å. radiation under the conditions listed in Table XIV, the gaseous products were pumped off through a dry ice - acetone trap and the liquid residues were removed from the vacuum line and mixed with pentene-1 solvent. This mixture was then immediately analyzed on the polyethylene glycol capillary gas chromatography column.

The column was held at room temperature for 10 minutes while pentene-1, benzene, cyclohexadiene-1,4 and diethyl ketone were eluted. After heating the column to 120°, the expected pair of peaks due to compounds I and II were observed. The area ratio of these peaks was measured and this was assumed to be equal to the mole ratio of I:II in the mixture; thus Area(I)/Area(II) = k_{6c}^{I}/k_{6c}^{II}. This ratio has been entered for each run in Table XIV and the function 1 + $\log_{10}(k_{6c}^{I}/k_{6c}^{II})$ has been plotted as a function of $10^3/T$ in Figure 21. These data are consistent with k_{6c}^{I}/k_{6c}^{II} = 0.811 $\pm$ 0.088, independent of temperature.

TABLE XIV

Reactions of the Ethyl Radical with the Cyclohexadienyl Radical

($^{\circ}$K) T	(sec.) t	$[D]^a$	$[B]^a$	k_{6c}^{I}/k_{6c}^{II}
307	3600	10.0	1.55	0.812
307	1200	8.76	1.05	0.834
322	1200	7.80	1.58	0.780
334	1200	6.89	1.32	0.870
336	1200	7.64	1.67	0.792
358	1200	7.23	1.37	0.776
	Mean value			0.811
	Limits of error at 5 % probability level			$\pm$0.088

^{a} 10^{17} [D] = Concentration of diethyl ketone (molecules/cm^3)
10^{17} [B] = Concentration of cyclohexadiene-1,4 (molecules/cm^3)

Figure 21. Disproportionation and Combination of the Ethyl
Radical with the Cyclohexadienyl Radical
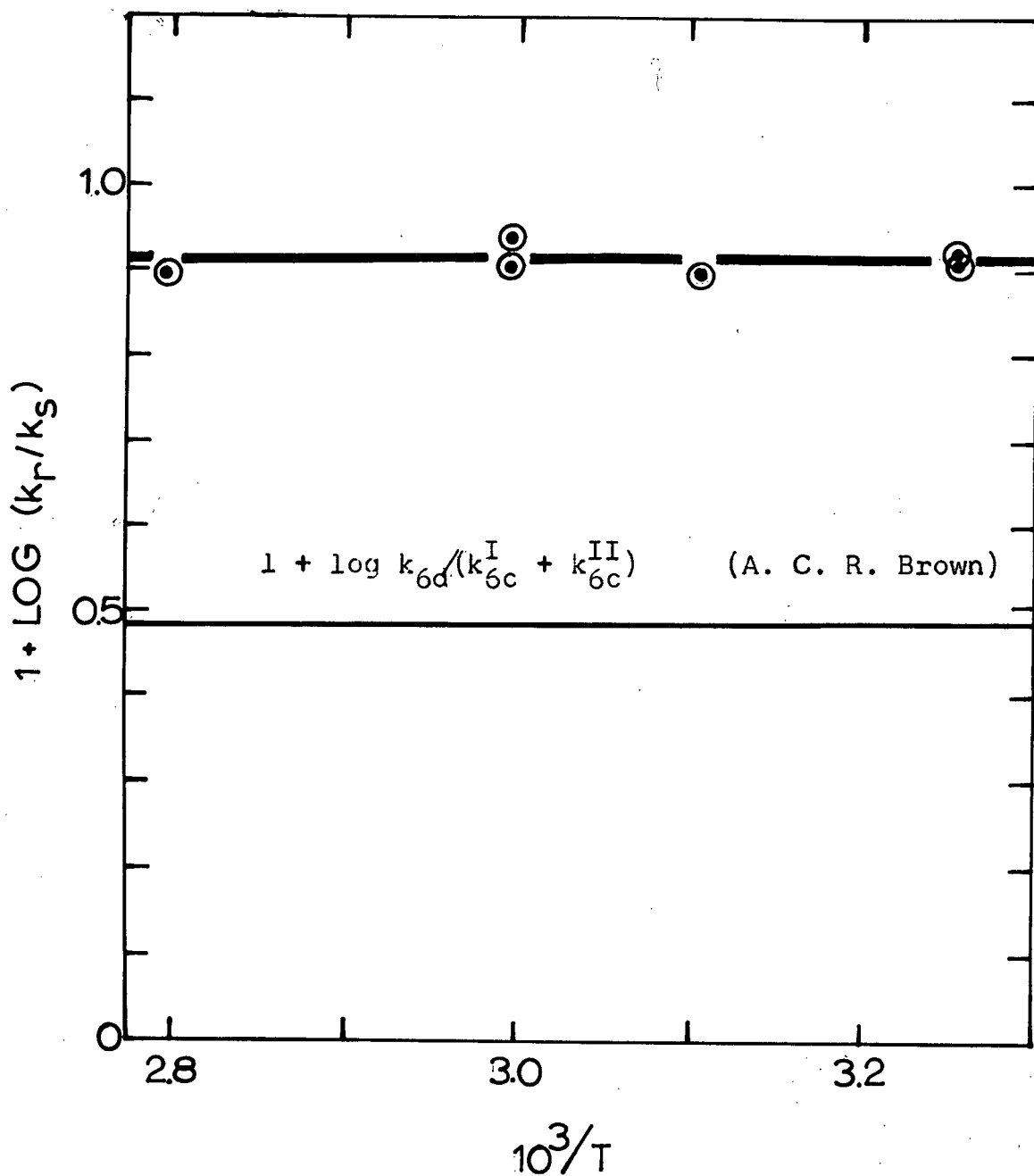
$$k_r/k_s = k_{6c}^I/k_{6c}^{II}$$

$1 + \log k_{6d}/(k_{6c}^I + k_{6c}^{II})$ measured by A. C. R. Brown.

E. Rate Constants, Arrhenius Parameters and Statistical Data

A summary of all the rate constants measured in this work has been compiled in Table XV. Also listed are the constants B and C obtained by fitting the experimental data to the straight line:

$$13 + \log_{10}\frac{k_r}{k_2^{\frac{1}{2}}} = (C \pm \sigma_C) - \frac{10^3}{T}(B \pm \sigma_B)$$

In the table, σ_B, σ_C and σ_k are standard deviations of C, B and of the individual measurements of $13 + \log_{10}k_r/k_2^{\frac{1}{2}}$. The constants and standard deviations were calculated using the least mean squares technique. Calculations were carried out using an IBM 7040 computer and a library program available through the University Computer Centre. Errors calculated from the standard deviations have been expressed at the 5 % probability level.

In Table XVI, the steric factor, p, has been calculated for each reaction studied assuming values for the collision diameter as listed in the table. The collision yield has been determined at the mean temperature (T_m) over which the rate measurements were made. The values used for the rates of the pertinent radical recombination reactions are tabulated. In view of the uncertainties in these rates and in the selection of collision diameters, these steric factors are only crude approximations at best.

TABLE XV

Reaction Arrhenius Parameters and Statistical Data

reaction	No. of runs	C^b	B	$\widetilde{\sigma_k}$	$\widetilde{\sigma_C}$	$\widetilde{\sigma_B}$	$13 + \log\dfrac{A_r}{A_2^{\frac{1}{2}}}$	$E_r - \frac{1}{2}E_2$ (kcal./mole)
$CH_3^{\cdot} + CH_3NNCH_3$ (M)[a]	14	6.009	1.883	0.0565	0.137	0.0506	6.0 ± 0.3	8.6 ± 0.5
$CH_3^{\cdot} + CH_3NNCH_3$ (A)	13	4.717	1.295	0.0387	0.094	0.035	4.7 ± 0.2	5.92 ± 0.35
$C_3H_7^{\cdot} + C_3H_7COC_3H_7$ (M)	11	7.506	2.753	0.155	0.526	0.222	7.5 ± 1.2	12.6 ± 2.3
$C_3H_7^{\cdot} + C_6H_8\text{-}1,3$ (M)	9	6.156	1.557	0.0388	0.182	0.067	6.2 ± 0.4	7.1 ± 0.7
$C_3H_7^{\cdot} + C_6H_8\text{-}1,3$ (A)	11	6.024	1.276	0.0285	0.100	0.036	6.0 ± 0.2	5.8 ± 0.4
$CH_3^{\cdot} + C_6H_8\text{-}1,4$ (M)	16	5.882	1.207	0.0341	0.1072	0.0361	5.9 ± 0.2	5.52 ± 0.35
$C_2H_5^{\cdot} + C_6H_8\text{-}1,4$ [d] (M)	7	5.724	1.270	0.0074	0.038	0.0137	5.7 ± 0.1	5.8 ± 0.1
$C_3H_7^{\cdot} + C_6H_8\text{-}1,4$ (M)	14	6.047	1.408	0.0596	0.302	0.112	6.05 ± 0.66	6.4 ± 1.1
$C_4H_9^{\cdot} + C_6H_8\text{-}1,4$ (M)	8	5.618	1.166	0.0492	0.220	0.073	5.6 ± 0.5^c	5.3 ± 0.8

[a] The letters in parentheses refer to the metathetical (M) and addition (A) reactions.

[b] B and C are the coefficients of the straight lines $13 + \log_{10}(k_r/k_2^{\frac{1}{2}}) = +C - 10^3B/T$ fitted to the experimental data. σ_k, σ_C and σ_B are the standard deviations in $13 + \log_{10}k_r/k_2^{\frac{1}{2}}$, C and B respectively. The limits of error are calculated at the 5 % probability level.

[c] For this case, this result represents $13 + \log_{10}A_6/A_3^{\frac{1}{2}}$, rather than $13 + \log_{10}A_6/A_2^{\frac{1}{2}}$.

[d] A. C. R. Brown.[1]

TABLE XVI

Absolute Rate Constants of the Addition and Metathetical Reactions [a]

| reaction	$13 + \log_{10}A_r/A_2^{\frac{1}{2}}$	$\log_{10}A_2$	$\log_{10}A_r$	T_m [e] ($^\circ$K)	$\tilde{\sigma}_{12}$ ($\overset{\circ}{A}$)	$\log_{10}Z$	$10^3 p$	$\log_{10}k_r(60^\circ)$ (cm^3/molec.sec.)
$CH_3^\cdot + CH_3NNCH_3$ (M)[b]	6.0	-10.3	-12.14	373	4.5	-9.29	1.41	-17.8
$CH_3^\cdot + CH_3NNCH_3$ (A)	4.7	-10.3	-13.44	373	4.5	-9.29	0.0707	-17.3
$C_3H_7^\cdot + C_6H_8$-1,3 (M)	6.2	- 9.9	-11.74	368	5.6	-9.28	3.47	-16.4
$C_3H_7^\cdot + C_6H_8$-1,3 (A)	6.0	- 9.9	-11.94	361	5.6	-9.28	2.19	-15.7
$CH_3^\cdot + C_6H_8$-1,4 (M)	5.9	-10.3	-12.24	343	5.0	-9.20	0.912	-15.8
$C_2H_5^\cdot + C_6H_8$-1,4 (M)[f]	5.7	-10.5	-12.52	358	5.3	-9.28	0.575	-16.3
$C_3H_7^\cdot + C_6H_8$-1,4 (M)	6.05	- 9.9	-11.89	379	5.6	-9.27	2.40	-16.1
$C_4H_9^\cdot + C_6H_8$-1,4 (M)	5.6 [c]	- 9.8 [d]	-12.29	337	6.0	-9.28	0.967	-15.8

[a] All pre-exponential factors and collision frequencies expressed in (cm^3/molec.sec.)

[b] The letters in parentheses refer to the metathetical (M) and addition (A) reactions.

[c] For this case, this result represents $13 + \log_{10}A_6/A_3^{\frac{1}{2}}$, rather than $13 + \log_{10}A_6/A_2^{\frac{1}{2}}$.

[d] This entry is $\log_{10}A_3$ where A_3 has been assumed to be 10^{11}(1./mole sec.) $= 10^{-9.8}$(cm^3/mol.sec.) in the absence of a measured value.

[e] T_m = mean temperature over which A_r was measured.

[f] A. C. R. Brown.[1]

GENERAL DISCUSSION

A. Disproportionation and Combination Reactions of the Cyclohexadienyl Radical

1. Summary of the experimental observations.

The numerical results for the disproportionation reactions observed in the experiments reported above have been collected in Table XVII. Also, in this table, the results of a similar investigation of the combination reactions of the methyl radical with the phenoxy and ortho-methylphenoxy radicals[135] have been compiled. The reaction scheme used by Mulcahy and Williams[135] to explain the product distribution is
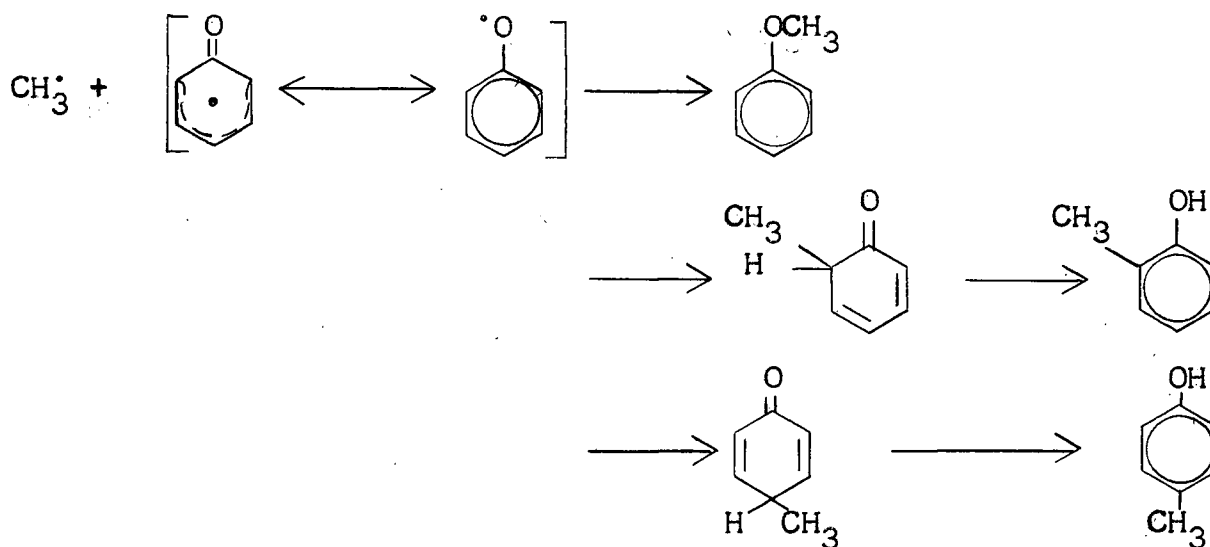
A similar scheme describes the results of the o-methylphenoxy case. As the reacting species is a cyclohexadienyl type radical in at least some of its resonance forms, the obvious similarity of this study to the work reported here will provide a useful comparison in subsequent discussion.

The isomerization of the unsaturated ketone intermediates is assumed to occur without any disturbance of the initially formed ortho-para distribution.

TABLE XVII

Termination Reactions of Cyclohexadienyl and Phenoxy Radicals

reactants	para comb.	ortho comb.	other [a]	$\triangle(R, C_6H_7^{\bullet})$	k_{6c}^{I}/k_{6c}^{II}
$CH_3^{\bullet}$ + phenoxy [b]	45 %	49 %	6 %	-	-
$CH_3^{\bullet}$ + o-methylphenoxy [b]	66	26	8	-	-
$CH_3^{\bullet}$ + cyclohexadienyl [c]	45	34	21	0.27 ± 0.07	0.76 ± 0.16
$C_2H_5^{\bullet}$ + cyclohexadienyl	40 [c]	33 [c]	27 [d]	0.38 ± 0.03 [d]	0.81 ± 0.10 [c]
iso-$C_3H_7^{\bullet}$ + cyclohexadienyl [c]	36	30	34	0.52 ± 0.09	0.85 ± 0.09
tert-$C_4H_9^{\bullet}$ + cyclohexadienyl [c]	43		57	1.33 ± 0.24	-
cyclohexadienyl + cyclohexadienyl [c]	69		31	0.45 ± 0.12	-

[a] For phenoxy radicals, this column refers to oxygen attack; for cyclohexadienyl, this column refers to disproportionation, where $C_6H_7^{\bullet}$ donates a hydrogen atom.

[b] M. F. R. Mulcahy and D. J. Williams, Nature, 199, 761 (1963).

[c] This work.

[d] A. C. R. Brown.[1]

As we can see from Table XVII, the ratio of ortho to para combination generally favours the para position to an extent that exceeds the expected statistical distribution that requires twice as much ortho combination as para combination, except for the o-methylphenoxy and methyl system.
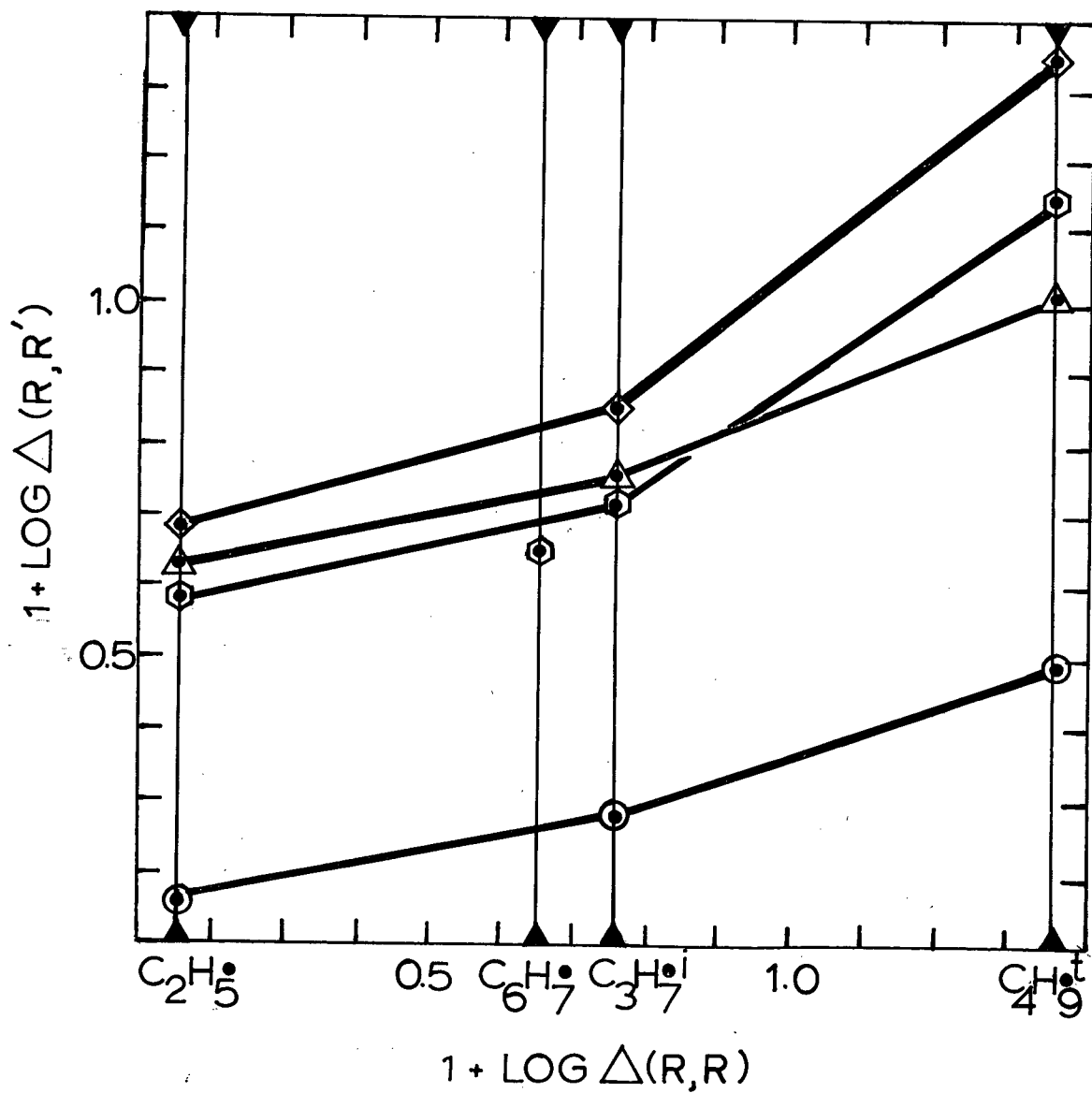
Also, the combination ratio k_{6c}^{I}/k_{6c}^{II} for the compounds studied presently does not vary significantly from compound to compound, in view of the experimental error. In view of the constancy of the k_{6c}^{I}/k_{6c}^{II} ratios, it is quite probable that the corresponding ratio for tert-butyl radical is in the region of 0.77 ± 0.17 as for the other radicals.

On the contrary, the $\triangle(R, C_6H_7^{\cdot})$ values vary smoothly from the lowest, $\triangle(Me, C_6H_7^{\cdot})$, through the ethyl and isopropyl values to the highest, $\triangle(tert-Bu, C_6H_7^{\cdot})$. This trend is quite real at the 5 % probability level of experimental error, and spans a factor of five from methyl to tert-butyl radicals.

In Figure 22 the $\triangle(R, C_6H_7^{\cdot})$ results measured here are presented in a "log-log plot" in the form $1 + \log\triangle(R, C_6H_7^{\cdot})$ plotted against $1 + \log\triangle(R, R)$ for the ethyl radical and its higher homologues. Also plotted are similar results measured in other laboratories for hydrogen donor radicals other than $C_6H_7^{\cdot}$. The values adopted have been listed in Table II where the preferred result has been underlined.

In this figure, it can be seen that the tendency to disproportionate increases with considerable regularity for a given constant hydrogen donor as the conjugate reactant changes from ethyl to tert-butyl. This behavior is in contrast to the predictions of Kraus and Calvert[36] who suggested that the $\triangle$ values of the radicals would be in proportion to the number of available

Figure 22. Comparison of $\triangle(R, C_6H_7^{\cdot})$ values to similar results for Alkyl Radicals

$1 + LOG \triangle(R,R')$ (y-axis)

$1 + LOG \triangle(R,R)$ (x-axis)

x-axis labels: $C_2H_5^{\cdot}$, 0.5, $C_6H_7^{\cdot}$, $C_3H_7^{\cdot i}$, 1.0, $C_4H_9^{\cdot t}$

◈ $R' =$ tert-Butyl

▲ $=$ Isopropyl

⬡ $=$ Cyclohexadienyl

◉ $=$ Ethyl

hydrogen atoms for disproportionation. In Figure 22, all connected points would then lie on a horizontal straight line. The number of available hydrogen atoms is clearly not sufficient to explain $\triangle$ values, even in related systems.

The value for $\triangle(C_6H_7^{\cdot}, C_6H_7^{\cdot})$ has been measured in the low intensity photolysis of azomethane-cyclohexadiene-1,4 mixtures. Its position on Figure 22 is reasonably close to the line defined by the other radicals; however, as will be discussed in a later paragraph, the cyclohexadienyl radical does not behave typically as a hydrogen atom acceptor in its reactions with the alkyl radicals. It is likely that the point for $\triangle(C_6H_7^{\cdot}, C_6H_7^{\cdot})$ is not to be expected to correlate with the $\triangle(R^{\cdot}, C_6H_7^{\cdot})$ results.

The results of the measurements on the alkyl plus cyclohexadienyl systems studied here lead to the following observations,

1. $\triangle(R, C_6H_7^{\cdot})$ values increase by a factor of 5 from $R = CH_3^{\cdot}$ to $R = \underline{tert}$-butyl.

2. The ratio k_{6c}^{I}/k_{6c}^{II} is reasonably constant; the value 0.77 ± 0.17 is characteristic of all the alkyl radicals studied. It seems likely that the $\underline{tert}$-butyl radical would reveal a similar result, were it measureable.

3. The recombination consistently favours the unconjugated diene structure, not only for the results of this study, but also for an independent but related study of the recombination of methyl radicals with phenoxy radicals.

4. Neither k_{6c}^{I}/k_{6c}^{II} nor $\triangle$ ratios show any significant temperature dependence. (Figures 9, 17, 20 and 21)

5. Although formally there exists the possibility that the radicals methyl, isopropyl and $\underline{tert}$-butyl may disproportionate with the cyclohexadienyl radical to form one of the cyclohexa-

dienes and the corresponding olefins (reactions (6e)), this mode
of reactivity is never observed. All disproportionation yields
the benzene product.

Thermochemistry   Crude estimates of the energy liberated
in various termination reactions involving the cyclohexadienyl
radical have been made and the results tabulated in Table XVIII.

Table XVIII: Thermochemistry of the interactions of radicals,
R, with the cyclohexadienyl radical.

Reactants	Heat liberated in forming the products (kcal./mole)		
$R + C_6H_7^{\cdot}$	$RH + C_6H_6$	$R-C_6H_7$	$R(-H) + C_6H_8$
$CH_3^{\cdot} + C_6H_7^{\cdot}$	77	$60 = 84 - Q$	--
$C_2H_5^{\cdot} + C_6H_7^{\cdot}$	71	$57 = 84 - Q - 3$	32.5
$C_3H_7^{\cdot i} + C_6H_7^{\cdot}$	67.5	$56 = 84 - Q - 4$	32
$C_4H_9^{\cdot t} + C_6H_7^{\cdot}$	64	$52 = 84 - Q - 8$	25
$C_6H_7^{\cdot} + C_6H_7^{\cdot}$	44	$32 = 80 - 2Q$	44

In preparing this compilation the following values have been
adopted: Q = resonance energy of $C_6H_7^{\cdot}$ = 24 kcal./mole;
$D(CH_3-C_6H_7^{\cdot})$ = 84 - Q where 84 = $D(CH_3-CH(CH_3)_2)$;[11] the decrements
in bond dissociation energies of the alkyl-C_6H_7 compounds are the
same as in the series CH_3-CH_3, $CH_3-C_2H_5$, $CH_3-CH(CH_3)_2$ and
$CH_3-C(CH_3)_3$, ie. 3, 4, and 8 kcal.;[11] $\triangle H_f^o(C_6H_7^{\cdot})$ = 45 kcal./mole
and $\triangle H_f^o(C_6H_8-1,4)$ = $\triangle H_f^o(C_6H_8-1,3)$ = 26 kcal./mole[91] (the slight
difference between the enthalpies of these two isomers will be of
no consequence here and has been neglected). From the table it
is evident that the formation of the disproportionation products,
RH and C_6H_6, is energetically more favourable than the recombin-
ation products. The disproportionation to $R(-H) + C_6H_8$ liberates

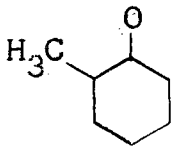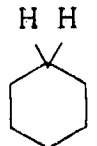only about one-half as much energy as benzene formation.

Some question exists as to whether the observed distribution of the products I and II is characteristic of the initial attack on the ring position by the alkyl radical, or whether the final distribution results from unimolecular isomerization of the hot recombination products before they can be collisionally stabilized. Under the experimental conditions, an excited CH_3-$C_6H_7^*$ molecule can be expected to undergo from 10^8 to 10^9 collisions per second with surrounding molecules. Let us tentatively assume that the hydrogen transfer rate constant can be expressed as

$$k(\text{isomerization}) = A\left(\frac{E - E_o}{E}\right)^{s-1} \qquad \text{sec.}^{-1}$$

where for C_6H_7-CH_3^*, $s = 3 \times 7 - 6 = 15$, using only skeletal vibrations, and $E = 60$ kcal./mole from the calculation outlined above (Table XVIII). For E_o we assume a minimum value of 30 kcal. based on the observation of ter Borg et al.[137] that 31.5 kcal./mole are required to move the hydrogen atom around the ring of the cycloheptatriene molecule in solution. Also Frey finds a barrier of 32.8 kcal./mole opposing hydrogen migration in 2-methylpentadiene-1,3[138] and 31.2 kcal./mole in cis-1-methyl-2-vinyl cyclopropane.[139] These examples have activated complexes with five or six membered rings and may be markedly more favourable both energetically and sterically than the isomerization, I ⇌ II, which must pass through a four centre complex. Using $E_o = 30$ kcal./mole, the isomerization rate constant is $6.1 \times 10^{-5} A$ sec.$^{-1}$, so if A has the usual value of 10^{13} sec.$^{-1}$, then the collision rate is about equal to the estimated isomerization rate. However, the high pressure pre-exponential factor should be equal to A, according to the

Kassel theory that is the basis for the expression used for the calculation of k(isomerization). The pre-exponential factor measured by ter Borg in the cycloheptatriene case is only $10^{10.2}$ sec.$^{-1}$, therefore probably we overestimate the isomerization rate using the simple Kassel expression. The consistency of the results, and the fact that the unconjugated structure,II, seems to be favoured over the very slightly more stable structure, I, in all cases, suggests that isomerization is unimportant under the experimental conditions. The higher homologues should be less sensitive to hot molecule reactions than the methyl case.

Since the ratio k_{6c}^{I}/k_{6c}^{II} is insensitive to the alkyl radical involved, the ortho-para combination ratio is determined by properties of the cyclohexadienyl system. One possible explanation is that the density of the unpaired electron in the ring effectively controls the distribution of attack of the reacting radical. Electron spin resonance experiments have been performed on the cyclohexadienyl radical[58] and on the phenoxy and o-methyl-phenoxy[96] radicals. In these studies the electron spin densities have been determined assuming that they are proportional to measured coupling constants to the appropriate ring proton. These electron spin densities have been put on the following diagrams relative to the para spin density taken as unity.

O >0.26	O 0.23	H H	
0.63	H₃C 0.52	0.70 −0.2	For methyl attack:
1.0	1.0	1.0	
1.1 ± 0.1	0.4 ± 0.1	0.76 ± 0.16	$\dfrac{R(\text{ortho recomb.})}{R(\text{para recomb.})}$
2	1	2	Ratio expected statistically

In all cases, the para spin density substantially exceeds that measured at the ortho position. Similarly para recombination is much favoured over recombination at the ortho site. The availability of the valence electron therefore offers a convenient explanation for the distribution of the recombination products.

Unfortunately, this simple picture cannot be generally sufficient to explain observed $\triangle$ values. In a recent publication,[93] Mulcahy has reported no recombination of $CH_3^\cdot$ radicals to the ring positions of the benzyl radical, even though a significant electron density exists there;[97] all termination in this system apparently occurs by recombination at the $-\overset{\cdot}{C}H_2$ position.

2. Transition state of the disproportionation reaction

Bradley has pointed out[136] that the conventional linear transition state typical of the metathesis reactions would lead to far too great a loss of entropy and hence to pre-exponential factors that are too low to be applicable to the disproportionation reaction.
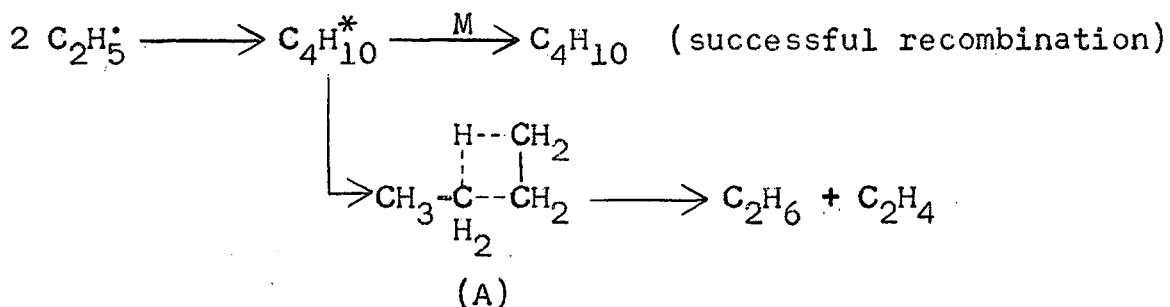
Furthermore, we make the experimental observation that the power of an alkyl radical to remove a hydrogen atom from another radical (eg. $C_6H_7^\cdot$) in a disproportionation reaction lies in the order tert-Bu $>$ iso-Pr $>$ Et $>$ Me. This order is the reverse of that experienced in normal hydrogen abstraction reactions where strong C-H bond formers are expected to be the best hydrogen atom abstractors.

Ideas about the transition states of the termination reactions have been advanced by Bradley and Rabinovitch,[136,53] Kerr and Trotman-Dickenson,[38] and by Benson.[30]

The disproportionation model of Kerr and Trotman-Dickenson

Kerr and Trotman-Dickenson's[38] proposal is the most detailed and

specific. These authors envisioned the disproportionation reaction as arising from a tight, highly energized molecule formed by the recombination of two radicals. The energy released in this recombination process is available, in their view, to cause the subsequent rearrangement and fission of the hot molecule into the products of disproportionation. High entropy in the transition state would be assured because the recombination step leading to the energized molecule is rate controlling, and is governed by a freely rotating transition state.

The formulation of the Kerr-Trotman-Dickenson proposal considers hydrogen transfer to occur between reacting radicals by way of a "four centre complex". For example, the ethyl radical disproportionation would pass through the configuration A.

$$2\ C_2H_5^{\cdot} \longrightarrow C_4H_{10}^{*} \xrightarrow{\ M\ } C_4H_{10} \quad (\text{successful recombination})$$

$$\begin{array}{c} H\text{--}CH_2 \\ \vert \quad \vert \\ CH_3\text{--}\underset{H_2}{C}\text{--}CH_2 \end{array} \longrightarrow C_2H_6 + C_2H_4$$

(A)

The application of this idea to the present system leads us to configurations such as B

(B)

(C)
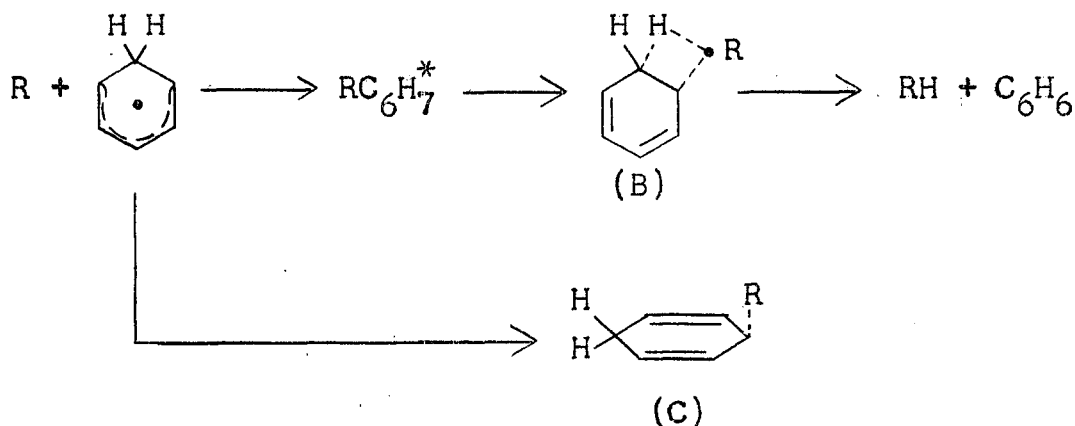
resulting in the disproportionation products RH and benzene. The configuration C resulting from para attack on the cyclohexa-

dienyl radical cannot conveniently form a "four cetre" structure which embodies a reactive hydrogen atom.

If we insist on four centre configurations leading to disproportionation, we may suppose that the preference observed for para recombination arises from this cause. Thus ortho attack leads to both disproportionation and combination, while para attack must entirely end up as a combination product. Taken together, this would cause a net favouring of para recombination, if the overall probability of interaction with an ortho site is closely comparable to that of interaction with a para site. Table XIX shows that this explanation of observed k_{6c}^{I}/k_{6c}^{II} values is entirely compatible with the $\triangle(R, C_6H_7^{\cdot})$ measurements. In this table, the probability of ortho attack ω, and the probability that ortho attack will lead to a disproportionation, x, have been calculated to be consistent with the measured values of $\triangle(R, C_6H_7^{\cdot})$ and of k_{6c}^{I}/k_{6c}^{II} for a particular alkyl radical, R. The probability of para attack, π, is $1 - 2\omega$

A slight change in the probability of ortho (ω) or para (π) attack is sufficient to cause the observed product ratios, according to the four centre complex proposal.

It is not likely that this can be the correct explanation of the unusually large extent of para recombination. The results of Mulcahy and Williams,[135] listed in Table XVII, show that the attack of the methyl radical on the phenoxy and o-methylphenoxy radicals also favours the para attack to a greater extent than that anticipated statistically. In this example, there is no mechanism where the ortho recombination can be lowered by four centre complexes. Some attack on the oxygen atom does occur, but probably this is fundamentally no different in mechanism

than recombination to one of the ring positions. Furthermore, the variation of the probability, x, is probably the reverse to that expected on the basis of the rather tight, well defined transition state of Kerr and Trotman-Dickenson. Steric conditions around the reactive carbon atom in the more complex alkyl radicals, particularly the tert-butyl radical should cause a decrease in the probability, x, rather than the increase seen in Table XIX.

Table XIX Probabilities for Ortho and Para Attack of Alkyl Radicals on the Cyclohexadienyl Radical calculated on the basis of the Kerr and Trotman-Dickenson Model

R	$\triangle(R, Cyl)$	k_{6c}^{I}/k_{6c}^{II}	ω^{b}	π^{c}	x^{d}
$CH_3^{\cdot}$	0.27	0.76	0.276	0.448	0.385
$C_2H_5^{\cdot}$	0.38	0.81	0.300	0.400	0.460
$C_3H_7^{\cdot i}$	0.52	0.85	0.322	0.356	0.530
$C_4H_9^{\cdot t}$	1.35	0.0^{a}	0.288	0.424	1.0
		0.8^{a}	0.382	0.236	0.753

[a] Assumed values for $C_4H_9^{\cdot t}$ where k_{6c}^{I}/k_{6c}^{II} measurement impossible.

[b] ω is the probability that R· will initially associate with ortho position.

[c] π is the probability that R· will initially associate with para position.

[d] x is the probability that ortho attack will lead to disproportionation.

The evidence seems to favour separate, distinct associations of the alkyl radical with either the hydrogen atoms of the cyclohexadienyl system or with one of the ring positions leading to recombination. The favouring of the para position must be due to more fundamental causes than the necessity of passing through

four centre configurations in the disproportionation step.

The Kerr-Trotman-Dickenson model of the transition state has been criticized by Benson,[30] especially on the grounds that the expected pressure dependence of the $\triangle$(Et, Et) values was not observed in the experiments of Matsuoko et al.[40] where the pressure was varied over a wide range. In a later publication, Dixon et al.[41] suggested that the pressure dependence requirement may be avoided if the dissipation of the energy is an intramolecular process in nature, and that when the energy is dispersed throughout the newly formed molecule, the system has a negligible probability of disproportionation. Only in the first phase of the reaction, when the liberated energy is concentrated in the newly formed C-C bond is there any likelihood of the tranfer of a hydrogen atom taking place, according to this modified picture.

If this is the case, then one would intuitively expect that the probability of disproportionation would be dependent upon the amount of exciting energy liberated into the system by recombination. Also, the number of oscillators available to accept this energy leading to a successful combination process should be important in determing the $\triangle$ ratio of a given system. However, we see from Tables XVII and XIX that the reverse is true. The methyl-cyclohexadienyl system has the most excitation energy and the fewest vibrational oscillators, yet displays the least tendency towards disproportionation. In view of the available evidence, the model of Kerr and Trotman-Dickenson, whether or not modified to account for the lack of pressure effects, seems untenable.

Separate transition state models   While Kerr and Trotman-Dickenson suggest that a single transition state governs the

formation of both combination and disproportionation products,
separate transition states have been proposed by Bradley and
Rabinovitch,[136,53] and by Benson.[30] Neither of these proposals
includes an excited molecule intermediate, and differs fundamen-
tally from the Kerr-Trotman-Dickenson model.

The Bradley-Rabinovitch disproportionation transition state
is intermediate between a completely loose, freely rotating struc-
ture (that only constrains the reactants from independent trans-
lation) and the rigid, low entropy structure typical of hydrogen
atom metathesis from molecules. These authors do not specify the
precise structure of the transition states of either combination
or disproportionation, but say only that the bonding is "loose",
thus characterized by little loss of entropy. Rice[31] has suggest-
ed the presence of three centre hydrogen bonding in the transition
state complex of methyl radicals and Bradley and Rabinovitch
suggest such structures may be general. The terms "head-to-head"
and "head-to-tail" are often used to describe the configuration
of radical interaction systems; these terms lose their meaning
if applied to the models of the transition state proposed by
Bradley, Rabinovitch and Rice.

Benson[30] agrees that loose binding in separate transition
states is essential to explain the observed disproportionation
and combination rate constants, but does not believe that the
very low vibrational frequencies required to explain the high
entropy of the transition state complexes are consistent with
normal covalent bonding. On the basis of estimates of the ener-
getics of charge transfer between alkyl radicals separated by
distances typical of transition states of recombining radicals,
he concludes that ionic forms may make significant contribution

to the Valence Bond description of the bonding. Such forms, representing non-directional bonding, would be expected to lower force constants opposing rocking and bending motions of the reactants with respect to one another explaining the high entropy of the transition states.

As the ionization potential of the participating radical is the largest energy term opposing charge transfer, and is quite sensitive to the structure of the radical, the ratio of disproportionation to combination may be influenced profoundly by ionization potential changes. Such influence is apparent in the mutual termination behavior of ethyl, iso-propyl and tert-butyl radicals which favour disproportionation very much more for the higher homologues. The ionization potentials have a wide variation with values[56,140] 10.0, 8.8, 7.9 and 7.4 eV. respectively for methyl, ethyl, isopropyl and tert-butyl radicals. The electron affinities are probably constant within the range 1.1 ± 0.1 eV.[141] The application of this idea to the present results would seem attractive. The cyclohexadienyl radical has the low ionization potential of 8.0 ± 0.2 eV.[59] in the gas phase, and likely has an electron affinity larger than is common for alkyl radicals since the extra electron can be accomodated in a delocalized orbital. Similarly, the polarizability of this radical would exceed that of an alkyl radical, contributing to the stability of charge transfer structures. One would imagine that if transfer of charge should occur at all, it would occur in this system, and that the change in $\triangle(R, C_6H_7^{\cdot})$ is due to the pronounced variation in the ionization potential of $R\cdot$. Benson[30] suggests that the ionization potential variation may be generally important in controlling the extent of disproportionation.

On the other hand, application of the model of Bradley and Rabinovitch leads to the suggestion[29] that entropy differences between the products of disproportionation and of combination determines their distribution. Holroyd and Klein[54] have successfully tested this suggestion. They find that $\triangle$ values of a wide variety of simple alkyl radicals are satifactorily correlated by the equation

$$\log k_d/k_c = 0.131\left(\sum s_d^o - s_c^o\right) - 5.47$$

This equation also predicted the pattern of interaction between the allyl and the ethyl radicals,[55] a system substantially different from those studied by Holroyd and Klein. We shall see below that the trends in the $\triangle(R\cdot, C_6H_7\dot{}\,)$ results are also consistent with this entropy correlation.

Since the Holroyd-Klein relation and the ionization potential patterns of alkyl radicals predict similar results, no test of the models of Benson and of Bradley and Rabinovitch is conclusive within alkyl systems.

Recently, Dorer and Rabinovitch[32] have studied the chemically activated decomposition of alkenes according to the equation

$$RCH_2CH=CH_2^* \longrightarrow R\cdot + CH_2CHCH_2$$
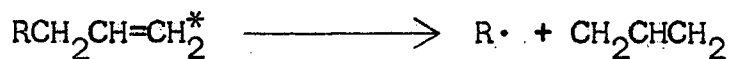
for alkyl radicals R = methyl, ethyl and n-propyl. Their studies reveal that activated complexes for the recombination of alkyl radicals and allyl radicals are significantly tighter than those common for alkyl radical mutual combination. Thus the steric factor for methyl-allyl combination is 5×10^{-3} whereas 10^{-1} is common for alkyl systems. Rabinovitch believes this behavior is typical of delocalized systems.[34] Since ionization potentials, electron affinities and polarizabilities of delocalized radicals are more favourable to charge tranfer than they are in alkyl

systems, we might have anticipated a high efficiency for alkyl-allyl recombination. If Rabinovitch's suggestion is correct and low recombination efficiencies prevail, ionic forms are apparently unimportant in delocalized systems. The trend in values of $\triangle(R, C_6H_7^{\cdot})$ is similar to that observed for alkyl radicals as R is varied, (Figure 22); the same factors apparently control both systems.

We can easily show that the present alkyl-cyclohexadienyl results are consistent with the entropy correlation within the bounds of certain assumptions. Holroyd and Klein's equation can be written

$$7.63 \log \triangle(R, C_6H_7^{\cdot}) = (S_{RH}^{o} - S_{RC_6H_7}^{o}) + 22.6 \tag{30}$$

if $S_{C_6H_6}^{o}$ = 64.34 cal./mole.deg. We assume the $-C_6H_7$ group contributes a constant amount of entropy to the compound $R-C_6H_7$. This is supported by the constant values of k_{6c}^{I}/k_{6c}^{II}, regardless of the attacking radical. Any statistical correction for the multiplicity of sites for recombination in the cyclohexadienyl radical should be constant for our systems. Equation (30) becomes

$$7.63 \delta \log \triangle(R, C_6H_7^{\cdot}) = \delta S_{RH}^{o} - \delta S_{RC_6H_7}^{o}$$

where $\delta \log \triangle(R, C_6H_7^{\cdot}) = \log \triangle(R, C_6H_7^{\cdot}) - \log \triangle(CH_3^{\cdot}, C_6H_7^{\cdot})$

$$\delta S_{RH}^{o} = S_{RH}^{o} - S_{CH_4}^{o}$$

$$\delta S_{RC_6H_7}^{o} = S_{RC_6H_7}^{o} - S_{CH_3C_6H_7}^{o}$$

Table XX shows that the values predicted for $\delta S_{RC_6H_7}^{o}$ compare favourably with those for $\delta S_{RPr^n}^{o}$, $\delta S_{RPr^i}^{o}$ and $\delta S_{RC_6H_5}^{o}$ calculated from the appropriate standard values.[55] This means that the values of $\triangle(R, C_6H_7^{\cdot})$ must lie close to a line having the gradient

TABLE XX

Distribution of the Products of Combination and Disproportionation of Alkyl Radicals with the Cyclohexadienyl Radical - Dependence on the Standard Entropy

R	S^o_{RH} [a]	$\Delta(R, C_6H_7^.)$	7.63 logΔ	$\delta S^o_{RH} - \delta S^o_{RC_6H_7}$ [b]	δS^o_{RH}	$\delta S^o_{RC_6H_7}$	$\delta S^o_{RPr^n}$	$\delta S^o_{RPr^i}$	$\delta S^o_{RC_6H_5}$
Me	44.50	0.27	- 4.34	0	0	0	0	0	0
Et	44.85	0.38	- 3.20	1.14	10.35	9.21	9.28	11.70	9.73
iso-Pr	64.51	0.52	- 2.17	2.17	20.01	17.84	16.83	17.00	16.45
<u>tert</u>-Bu	70.42	1.33	-.0.95	5.29	25.95	20.63	19.73	21.16	-

[a] Entropy values taken from American Petroleum Institute Res. Proj. #44 (Carnegie Press, Pittsburgh, 1952) pp. 466 et seq.

[b] The symbol $\delta S^o_{RX} = S^o_{RX} - S^o_{CH_3X}$

predicted by Holroyd and Klein, and to this extent the results
are consistent with their equation. Complete identification is
not possible as the lack of appropriate standard entropies pre-
vents evaluation of the corresponding intercept.

Bates et al.[107] have found the free energy of cyclohexadiene-
1,4 to be only 0.58 kcal./mole greater than that of cyclohexadiene-
1,3 at 95°, in solution. An estimate of the enthalpy difference
can be made as follows. Kistiakowsky found the heat of hydrogen-
ation of cyclohexene to be 28.59 kcal./mole at 82°.[108] The heat
of hydrogenation of cyclohexadiene-1,4 will probably be at least
twice as great, since some ring strain will likely exist in the
diene molecule. The heat of hydrogenation of cyclohexadiene-1,4
at 82° will be at least 57.18 kcal./mole, which is 1.81 kcal./mole
larger than the similar value found for the heat of hydrogenation
of cyclohexadiene-1,3. Assuming that the same difference exists
at 95° in solution, the entropy of cyclohexadiene-1,4 must exceed
that of cyclohexadiene-1,3 by 3.34 eu./mole. Now Holroyd and
Klein's relationship for the disproportionation to combination
ratio can be applied to the alternative combinations k_{6c}^{I} and k_{6c}^{II};
we readily derive

$$\log k_{6c}^{II}/k_{6c}^{I} = 0.131 \ (S_c^{II} - S_c^{I})$$

If we approximate $S_c^{II} - S_c^{I}$ as $S(C_6H_8-1,4) - S(C_6H_8-1,3) = 3.34$,
then $k_{6c}^{II}/k_{6c}^{I} = 2.74$. Correcting for the statistical factor of
two which favours the compound I, we find that $k_{6c}^{II}/k_{6c}^{I} = 1.37$,
precisely what is experimentally observed here, and very nearly
equal to the results of Eberhardt[10] ($k_{6c}^{II}/k_{6c}^{I} = 1.6$) for the inter-
action of the methyl and the cyclohexadienyl radical in liquid
cyclohexadiene-1,4, substantiating the use of the liquid phase

results of Bates et al.[107] for the free energy estimate. All the aspects of disproportionation and combination of $R\cdot$ and $C_6H_7^{\cdot}$ fall into place in the entropy correlation of Holroyd and Klein. Similarly, the favouring of the process $2\ C_6H_7^{\cdot} \longrightarrow C_6H_8\text{-}1,4 + C_6H_6$ over the process $2\ C_6H_7^{\cdot} \longrightarrow C_6H_8\text{-}1,3 + C_6H_6$ is reasonable if $S^o(C_6H_8\text{-}1,4)$ is greater than $S^o(C_6H_8\text{-}1,3)$.

The Bradley-Rabinovitch model is compatible with most experimental studies. The low primary isotope effects measured for alkyl disproportionation reactions at liquid nitrogen temperatures indicate very little C-H bond breaking in the transition state; k_H/k_T has been measured for disproportionation of ethyl-$\underline{t}$ ($k_H/k_T = 2$ at $63^o K.$)[44] and for isopropyl-$\underline{t}$ ($k_H/k_T = 1.7$ at $77^o K.$)[142] radicals.

Careful study of the temperature dependence of the values of $\triangle(C_2H_5^{\cdot}, C_2H_5^{\cdot})$[40,41], $\triangle(CH_3^{\cdot}, C_2H_5^{\cdot})$[43] and $\triangle(\text{iso-}C_3H_7^{\cdot}, \text{iso-}C_3H_7^{\cdot})$[42] has indicated that combination becomes more important than disproportionation as temperature rises; all cases are compatible with an activation energy difference $E_c - E_d = 0.3$ kcal./mole. Such a difference is difficult to reconcile with a single transition state model. The difference in energy, $E_c - E_d$, is small, however.

Such activation barriers provide a plausible explanation for the failure of the cyclohexadienyl radical to remove a hydrogen atom from alkyl radicals which otherwise donate them efficiently. Removal of hydrogen from the alkyl radical without an activation energy means strong bonding must occur between the cyclohexadienyl radical and the reactive hydrogen to compensate for the energy required to break the original C-H bond. A sufficiently strong C_6H_7-H bond may not be possible until a substantial degree

of localization of the free valence in the ring occurs. This
would impose a barrier not present for the recombination process
where concerted bond formation-electron localization could more
easily occur. Furthermore, we have seen that the free valence
may be extensively located on the methylenic hydrogen atoms of
the cyclohexadienyl radical by the operation of exceptionally
efficient hyperconjugation. This may render these hydrogens more
reactive than those of the alkyl radicals and the transfer of
hydrogen from the alkyl system to the cyclohexadienyl system
becomes most unlikely relative to the transfer to the alkyl rad-
ical from the cyclohexadienyl radical. In the case where the
cyclohexadienyl radical donates the hydrogen atom, dispropor-
tionation is assisted by the release of additional, benzene
resonance energy. In fact, when the reactive hydrogen atom is
weakened in this way the cyclohexadienyl radical is able to re-
move it; the value $\triangle(C_6H_7\cdot, C_6H_7\cdot) = 0.45$ is similar to
$\triangle(\text{iso-Pr}\cdot, C_6H_7\cdot)$ and indicates that any barriers opposing dis-
proportionation are overcome.

B. Metathesis between Alkyl Radicals and Cyclohexadiene-1,4

The experimental systems studied in this work have provided
rate constants for the metathesis reaction between the methyl,
isopropyl and tert-butyl radicals and the cyclohexadiene-1,4 mol-
ecule. Results for the ethyl radical are available from previous
work.[1] The following Arrhenius parameters result for the reac-
tion of alkyl radicals, R·, with the cyclohexadiene-1,4 molecule:

$$R\cdot + C_6H_8\text{-}1,4 \xrightarrow{\quad 6 \quad} RH + C_6H_7\cdot \qquad k_6 = pZ_6\exp(-E_6/RT)$$
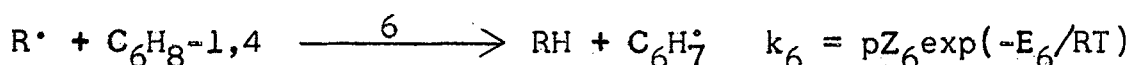
R	E_6 (kcal.)	$10^3 p$	$\log_{10} A_6$ (cm^3/molecule sec.)	$\log_{10} k_6 (60°)$
$CH_3^{\cdot}$	5.52 ± 0.35	0.9	-12.2 ± 0.2	-15.8
$C_2H_5^{\cdot}$	5.7 ± 0.1	0.6	-12.5 ± 0.1	-16.3
iso-$C_3H_7^{\cdot}$	6.4 ± 1.1	2.4	-12.0 ± 0.6	-16.1
tert-$C_4H_9^{\cdot}$	5.3 ± 0.8	0.9	-12.3 ± 0.5	$\underline{-15.8}$
				-16.0 ± 0.2

Errors quoted for $\log_{10} A_6$ are those measured for $\log_{10} A_6/A_2^{1/2}$, and do not account for the error of measurement of A_2, which is much greater, but is not known. The great similarity of the various radicals in their reactivity towards the cyclohexadiene-1,4 molecule is indicated in the constancy of the activation energies and the fact that, at 60°, the metathetical rate constant for each reactant radical lies in the range $k_6 = 10^{-16.0 \pm 0.2}$ cm^3/molec.sec.

Measurements of metathetical rate constants have been made for a single radical over a series of substrates, but studies of a variety of radicals with a common substrate are rare. Unfortunately, this particular substrate, while necessary to provide the cyclohexadienyl radical, is a poor choice for comparative study of the attacking radicals. The molecule is so very highly activated towards metathesis that the individual radicals are not selective in attacking it. The activation energies measured are all about the same, considering the experimental error. The similarity of the steric factors is expected at least within the accuracy to which it can be determined.

Trotman-Dickenson[38], in a study of the rates of the reactions $R^{\cdot} + RCHO \longrightarrow RH + R\overset{\cdot}{C}O$ for alkyl radicals, $R^{\cdot}$, found activation energies that dropped from $E(R^{\cdot} = CH_3^{\cdot}) = 7.6$ to $E(R^{\cdot} = $ tert-Bu$) =$

4.3. Rate constants at 182° were all about the same however. As the RCO-H bond is weak, he suggested a comparison of these results to those measured for the systems R· + C_6H_5-CH_3; however, results for such a study are not, at present, available. The present results with C_6H_8-1,4 are for a similarly activated system. The constancy of the measured activation energies contradicts the aldehyde system results, and would seem to be more expected.

A simple relationship[125,126] has been used to correlate activation energies with bond energies, the so called Evans-Polanyi relationship:

$$\triangle E_{act} = \alpha \triangle^2 H \qquad (31)$$

$\triangle^2 H$ is the difference in the heats of two related reactions, for example, two of the hydrogen abstraction reactions studied here. $\triangle E_{act}$ is the difference in the activation energies of these reactions, and α is a constant; typically $\alpha = 0.25$.[126]

Applying the Evans-Polanyi relationship to the reactions of this work, where alkyl radicals R· remove hydrogen atoms from C_6H_8-1,4, consider two radicals R· and R'·:

$$R· + C_6H_8\text{-}1,4 \xrightarrow{\quad E_6 \quad} RH + C_6H_7·$$

$$R'· + C_6H_8\text{-}1,4 \xrightarrow{\quad E_6' \quad} R'H + C_6H_7·$$
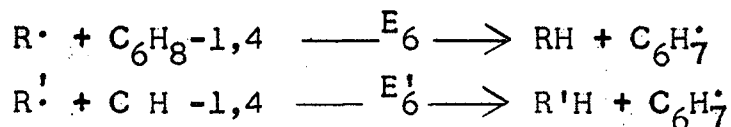
In this case, $\triangle^2 H = D^o(R\text{-}H) - D^o(R'\text{-}H)$. For R = $CH_3·$, R' = tert-butyl, $\triangle^2 H = 104 - 91 = 13$ kcal./mole.[143] So we may have expected that an activation energy difference $\triangle E = 13/4 \sim 3$ kcal./mole would have existed between the methyl and tert-butyl cases, on the basis of the Evans-Polanyi relationship. Certainly the results are not consistent with such a conclusion. This is really quite surprising since, assuming 71 kcal. for the C_6H_7-H bond energy, the exothermicities of the reactions vary from 20 kcal./mole

(tert-butyl) to 33 kcal./mole (methyl). A 65 % increase in the
reaction exothermicities would normally be reflected in the act-
ivation energies.

Inspection of Figure 23 shows that the maximum value of
consistent with the errors of measurement at the 5 % probability
level is α = 0.017. The tert-butyl and methyl results strongly
suggest that α is, in fact, zero.

Johnson and Parr[143] have recognized that the Evans-Polanyi
relationship (31) is not sufficient when $\triangle$H is large and have
proposed a more complex correlation of activation energies to
bond energies. They obtain considerable success in predicting
activation energies by treating the reacting system as having
three separable energy terms; the attraction between R_1 and H,
and between R_2 and H and repulsion between R_1 and R_2.

$$R_1 \cdots H \cdots R_2$$
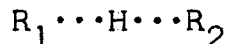
Applying this calculation to the alkyl radical-cyclohexa-
diene-1,4 systems leads to activation energies that are too low
(lying around 3.5 kcal./mole rather than the observed 5.5 kcal./mole)
but which do show a definite increase of 40 % from the methyl case
to the tert-butyl case. Figure 23 indicates that such a trend is
not present in this system; the lack of this expected trend in-
dicates that the energetics of the transition state are deter-
mined entirely by the cyclohexadiene-1,4 species.

The extensive resonance energy of the cyclohexadienyl radical
is probably responsible for this effect. At a certain point dur-
ing stretching of the C_6H_7-H bond by the attacking alkyl radical
a sufficient change in the hybridization of the methylenic car-
bon atom occurs to allow effective conjugation to occur to the
π system. After this, very little further increase in energy is

required. The activation energy is therefore set by conditions at the methylenic carbon atom and is not dependent on the attacking radical. It may very well be that constant activation energies are characteristic of all hydrocarbon substrates with activated hydrogen atoms.

These ideas can be illustrated with the simple diagram at the head of the next page. Curves A, B, and C represent attack of tertiary, secondary and primary radicals respectively on a normal, non-activated secondary hydrogen atom, showing the usual dispersion of activation energies. Curve D is the value of the cyclohexadienyl resonance energy as a function of the extension of the methylene C-H bond. Curves E, F and G represent the sums of A, B and C with D. In this case, the dispersion of activation energies is negligible.
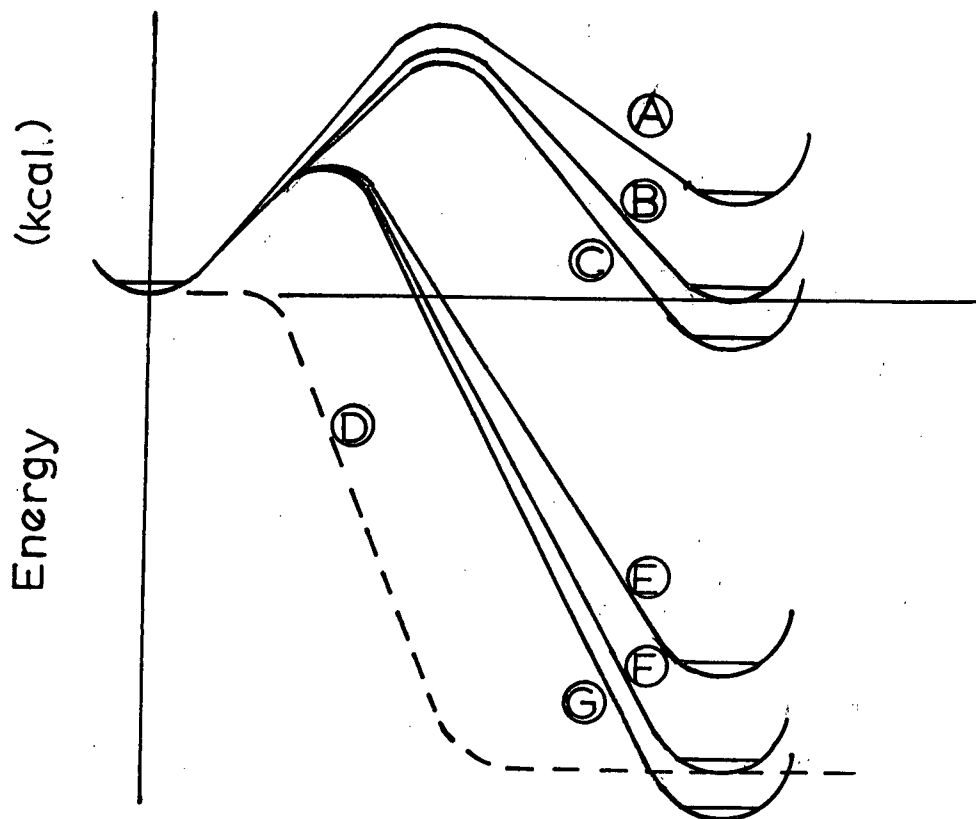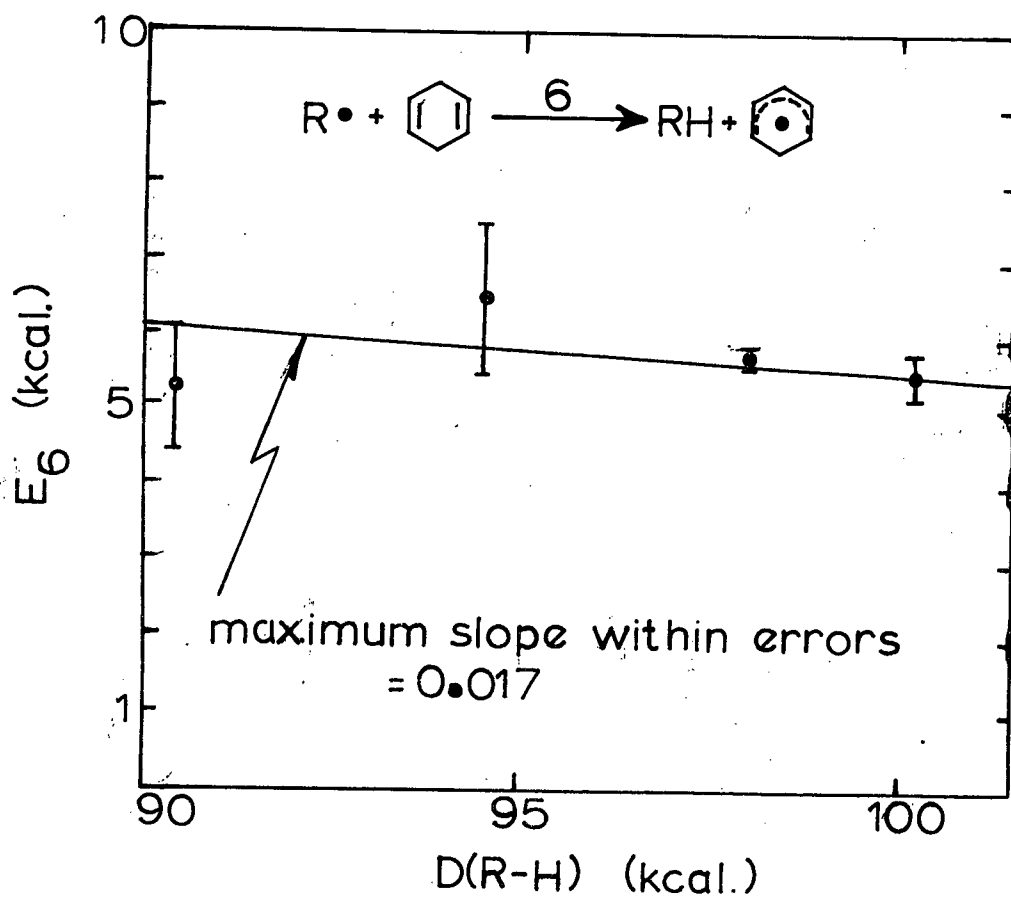
Figure 23. The Dependence of E_6 on the Bond Dissociation Energy
of the Attacking Radical.

CONCLUSIONS

Examination of the distribution of the products of the inter-
actions of the cyclohexadienyl radical with the alkyl radicals
$\cdot CH_j(CH_3)_{3-j}$ and with another cyclohexadienyl radical has indicat-
ed that generally these products are distributed preferrentially
amongst those of maximum entropy. The pattern of the ratios
$\triangle(CH_j(CH_3)_{3-j}, C_6H_7^{\cdot})$ is similar to that of the ratios
$\triangle(CH_j(CH_3)_{3-j}, R^{\cdot})$, for alkyl radicals, $R^{\cdot}$; in all systems the
effectiveness of $CH_j(CH_3)_{3-j}$ as a hydrogen acceptor decreases
as j increases. Such behavior is predicted by the transition
state proposals of Bradley and Rabinovitch and suggests that
reacting radicals pass through distinct configurations for each
mode of reactivity which are weakly bound, resembling the reac-
tants. The probability of attaining configurations leading to
a particular product is related to the entropy of the product
when no energy barriers exist to influence the reaction course.

Confirmation has been obtained for the suggestion that
activation barriers may exist to oppose termination reactions
that involve the disruption of conjugated π electron systems.
Thus the transfer of a hydrogen atom to the cyclohexadienyl rad-
ical does not occur unless the donor radical is also a cyclo-
hexadienyl radical; here the gain of the benzene resonance energy
compensates the loss of the cyclohexadienyl resonance energy.
The distribution of the cyclohexadienes produced in the reaction
of two cyclohexadienyl radicals favours the unconjugated, 1,4-
diene. As evidence suggests that this has the greater standard
entropy, this result accords with the maximum entropy principle.

The magnitude of the cyclohexadienyl resonance energy has

been estimated as 24 kcal./mole, substantially larger than the value of 15.5 kcal./mole measured elsewhere for the straight chain pentadienyl resonance energy. A simple explanation for such a discrepancy assumes a pronounced, hyperconjugative inter-action in the cyclic system across the methylenic carbon atom. Since the benzene resonance energy ($\sim$37 kcal./mole) is still greater than the cyclohexadienyl resonance energy, the expulsion of a hydrogen atom from the cyclohexadienyl radical is more favourable, energetically, than it is from alkyl radicals.

The considerable resonance energy of the cyclohexadienyl system makes it sluggish in reactions with molecules, but makes vigorous those reactions which generate it. This combination of circumstances provides that the free radical homopolymerization of cyclohexadiene-1,3 shall be severely retarded by degradative chain transfer. The rate of generation of the cyclohexadienyl radical by metathesis from cyclohexadiene-1,3 is slower than by metathesis from cyclohexadiene-1,4; this supports the contention that the free energy of the 1,4-diene exceeds that of the 1,3-diene in the gas phase, just as it has been found to do in liquid amyl alcohol. The rate of hydrogen abstraction by various alkyl radicals from cyclohexadiene-1,4 is independent of the attacking radical, although a considerable variation in the reaction heat is experienced. Features of the cyclohexadiene-1,4 molecule are responsible for control of the reaction rate; the release of the resonance energy probably sets a limit on the energy required to attain the transition state, about 5.5 kcal./mole.

The reactions of the methyl radical with azomethane have been studied. Addition to the nitrogen-nitrogen double bond

occurs with a low activation energy (5.9 kcal.) and a low steric factor (0.7×10^{-4}), but at an overall rate comparable to the rate of attack of methyl radicals upon mono-olefins. The activation energy for the abstraction of a hydrogen atom from azomethane, when compared to that measured for abstraction from acetone and from 2-butene, suggests that the resonance energy varies in the order $\dot{C}H_2\text{-}C\text{=}CH_2 > \dot{C}H_2\text{-}C\text{=}O > \dot{C}H_2\text{-}N\text{=}N\text{-}$ for each of the allyl resonance stabilized residues.

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