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THE STUDY OF HIGHLY STRAINED CYCLOPROPYL ADAMANTANE COMPOUNDS WITH EMPHASIS ON THEIR RADICAL COPOLYMERIZATIONS WITH OXYGEN

BY

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ABSTRACT

The synthesis of a new type of highly strained cyclopropyl group between the two remaining bridgehead positions in 1,3-dimethyladamantane was accomplished by an internal coupling reaction involving the removal of two bromines with sodium-potassium alloy in ether. The product, 5,7-dimethyltetracyclo[3.3.1.$1^{5,7}$.$0^{1,3}$]decane, commonly named 3,5-dimethyl-1,3-dehydroadamantane (DMDHA), formed a polymer on heating the pure material to a temperature above 90°C. The polymer's properties were studied by X-ray analysis and differential scanning calorimetry.

The previously reported parent compound to DHDMA, tetracyclo-[3.3.1.$1^{5,7}$.$0^{1,3}$]decane, commonly named 1,3-dehydroadamantane (DHA), was synthesized and studied to determine the properties of the cyclopropyl bond between the bridgehead carbons. Reactions with several stable free radicals and other known reagents with affinities for radicals indicated a very high degree of radical character present at the bridgehead positions. From kinetic studies of the reaction of DHA with molecular oxygen at approximately 1 atmosphere and 22°C, first order kinetic plots were obtained which yielded the rate constants of $k = 15.0 \times 10^{-5} sec^{-1}$ in octane and $32.8 \times 10^{-5} sec^{-1}$ in xylene. Oxygen was absorbed to an extent slightly greater than one mole per mole of DHA. The reaction was without ambiguity shown to be of radical nature through the use of several free radical inhibitors to retard the reaction rate.

The initiation mechanism of the DHA-oxygen copolymerization could not be determined with certainty. The spontaneous reaction was either

initiated by oxygen radicals attacking the highly strained, highly p-orbital-charactered carbon atom from its unprotected back side or else by the internal bond of the cyclopropyl group spontaneously ring opening to form an adamantane diradical. In the latter case the radical formed would sometimes capture an oxygen before the equilibrium shifted back to the closed form. All that is known for certainty is that the 1,3-carbon bond in DHA is very highly strained and is either in equilibrium between an open and a closed form or else is at least very radical-like in nature.

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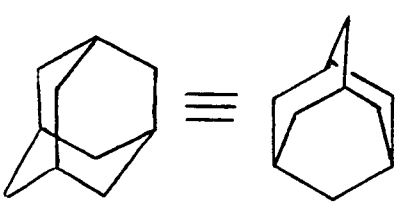
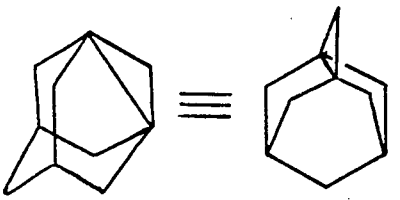
INTRODUCTION

The chemistry of adamantanes has been a field of intensive interest within the last 15 years. Another field of great interest is the study of cyclopropanes. To date the two studies have crossed paths very little in the literature; those few times have usually involved studying the effect of various cyclopropyl substituents on adamantane reactivities. To study a system such as the dehydroadamantane (DHA) system which has properties of both molecules, a background study into the two separate fields is necessary.

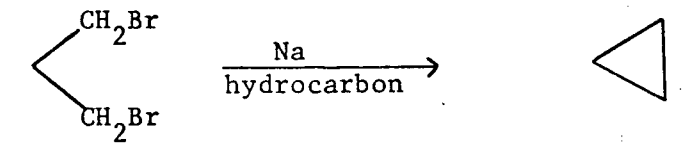


Adamantane



DHA

Cyclopropanes, due to their unusual geometry, bonding, and reactivity, have provided a basis for vast numbers of both theoretical and synthetic studies. Cyclopropanes themselves have been known and synthesized by numerous methods for many years. Reactions (1) through (6) in Figure 1 are some of these syntheses. By making use of one of these methods or others unmentioned, a wide variety of cyclopropyl compounds or compounds with cyclopropyl substituents have been made.



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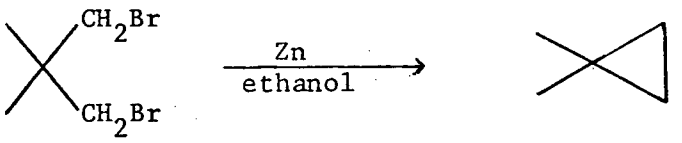

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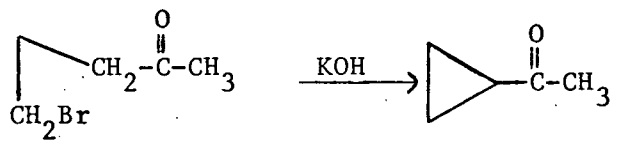

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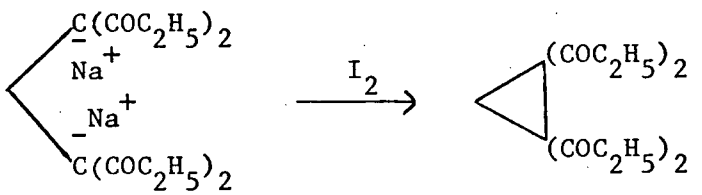

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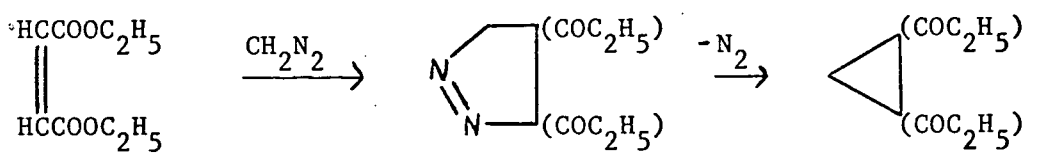

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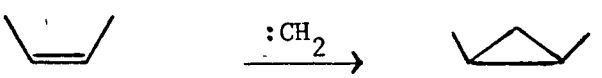

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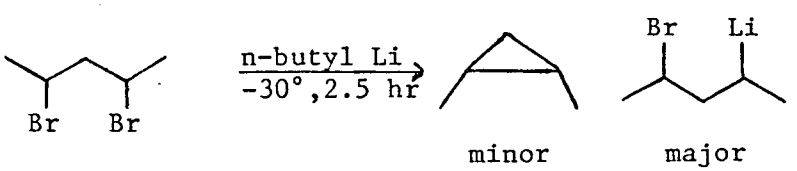


(6) ref. 7

Figure 1. Classical Synthesis of Cyclopropyl Compounds.

The chemistry of cyclopropane reactions is in general similar to olefins. Cyclopropanes are unstable to acid, degradation occurring with ring opening, but are extremely stable to base. Radical attack is generally a favourable reaction, excepting in the reactions of radical polymerizations, which are very difficult to induce, as will be discussed later.

The problem of bonding in cyclopropane is as yet a very open discussion. In general, at least two models for bonding may be drawn with variations in these, depending on the type of calculations used. These are the Walsh model (Figure 2a) and the bent bond model (Figure 2b). The Walsh model involves carbon sp^2 hydridization with p orbital overlap of the three carbons. One sp^2 lobe from each carbon is directed toward the center with the other two bonded to hydrogens. The overlapping p orbitals contain four electrons while the central sp^2 orbitals contain two electrons. The bent bond model is described in different ways, but is generally thought to consist of approximately sp^5 C-C bonds and sp^2 C-H bonds.[8] Calculations concerning bent bond

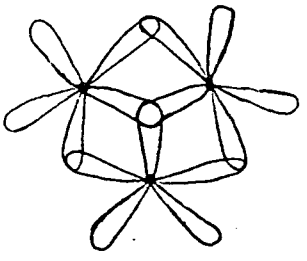


Figure 2a. Walsh Model

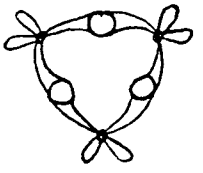


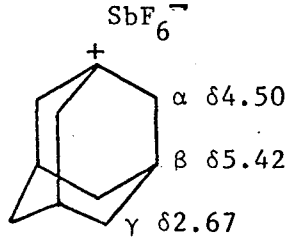
Figure 2b. Bent Bond Model

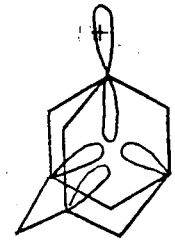
models have yielded degrees of p character (written in the form sp^n) varying from C-C $sp^{3.86}$, C-H $sp^{2.40}$ (Clemente)[9] and C-C $sp^{4.12}$, C-H $sp^{2.28}$ to C-C $sp^{4.91}$, C-H $sp^{2.02}$ (Slater).[10,9] All these calculations at least agree that carbon-carbon bonds have an unusually high

degree of p character for alkanes, whereas the carbon-hydrogen bonds have much more s character than usual. This bonding character, along with the strain energy of 27 Kcal $mole^{-1}$, is a strong factor in cyclopropyl reactivity and in directing the types of reactions cyclopropanes undergo.

Adamantane, because of its rigid, almost strain-free tricyclic structure, has been subject to intensive study and several reviews in the last 15 years.[11-13] Due to the high degree of symmetry of the molecule, only two types of carbons are present: 6 secondary and 4 tertiary carbons. These two types of carbons react somewhat as expected to both carbonium ions and carbanions. Tertiary carbonium ions are stabilized to the order of 10 kcal more than secondary carbonium ions,[11] a sometimes complicating factor in adamantane reactions.[14] Tertiary carbanions of adamantane have not been reported; however, recently a synthesis of secondary carbanions has appeared.[15]

Several other interesting properties of the adamantane structure are due to its symmetry and rigidity. Among these are its inability to form olefins and the n.m.r. spectrum of the 1-adamantyl carbonium ion. The n.m.r. spectrum was studied by Olah and Schleyer and found to be of interest because the hydrogens β to the carbonium ion were shifted substantially downfield from the α hydrogens. The authors explain the observations as resulting from back lobe sp^3 stabilization of the carbonium ion. This stabilizing effect would draw electron density more from the tertiary β hydrogens than from the secondary α hydrogens, causing the three bridgehead hydrogens to be shifted further





Back lobe sp^3 stabilization

downfield.[16] The lack of ability to form olefins within the adamantane structural body is due to the geometrical requirement of an olefin being located at a bridgehead position. This placement of a double bond at a bridgehead is a clear violation of Bredt's rule. Bredt's rule in its modern form says that a double bond at a bridgehead position may only occur in an isolatable compound if the ring containing the trans portion of the double bond is eight or more membered. Transitory species may occur with the trans portion of the double bond in a seven membered ring.[17] A double bond in adamantane by necessity must be placed trans in a six membered ring. This rule has been shown to hold in the adamantane case despite several attempts to disprove it.*

With this brief background into cyclopropane and adamantane chemistry, attention may be directed toward the main aim of this thesis, namely the synthesis of a highly strained cyclopropyl adamantane compound and the study of its radical nature as determined by radical

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* Two such attempts that failed involved either the elimination of HBr from 1-bromoadamantane[18] or the use of the photochemical Norrish Type II elimination using 1-adamantylacetone.[19]

type reactions, in particular, its radical polymerizations. Previous work in this area has been quite limited; therefore, to study the radical properties of the system, both the properties of adamantyl radicals and the radical properties of cyclopropyl compounds should be investigated.

Studies of adamantyl radicals, though not as numerous as carbonium ion studies, are quite common. Much of the information resulted from studies directed toward determining the geometry of alkyl radicals. The earliest of these was a study of the relative rates of decarbonylations from t-butyl, adamantyl, and two bicyclic aldehydes.[20] The authors concluded that 1-adamantyl radical was just slightly more stable than t-butyl radical, the relative rates being 2.5:1. Other similar studies were carried out on t-butyl and adamantyl peresters of t-butyl carboxylates.[22,23] All three studies indicated that 1-adamantyl radical is just a normal tertiary radical with no unusual properties and reacts in a similar manner as t-butyl radical. More recent studies using carbochlorination in CCl_4 led to final conclusions concerning adamantane radicals.[24] These were that 1-adamantyl radicals formed more readily than the secondary radical in accord with normal tertiary versus secondary radical stability, but that the secondary radical was more stable after formation due to its ability to rehydridize to sp^2. The tertiary radical would be less stable, and hence more reactive, because the carbon cannot rehydridize to sp^2.

Much information concerning the radical nature of cyclopropanes may be obtained from studies concerning their halo reactions, ring openings, and isomerizations. Halo reactions have been shown to proceed

by radical attack and ring opening as shown below. This addition of

$$Cl\cdot + \triangle \xrightarrow[\text{step 1}]{} ClCH_2\text{-}CH_2\text{-}CH_2\cdot \xrightarrow[\text{step 2}]{Cl_2} ClCH_2\text{-}CH_2\text{-}CH_2Cl + Cl\cdot$$

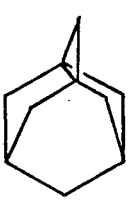
two halo atoms instead of the exchange of a halogen for a hydrogen is typical of olefins or other molecules which have carbon-carbon bonds with a high degree of p-character. Molecular isomerizations of cyclopropanes were studied extensively to determine whether the preferred mechanism was biradical or concerted ring opening and closing as seen in cases of conjugated olefins. The isomerizations of concern were only those resulting in cyclopropane products and not the minor side reactions of hydrogen shifts to form propene. Bergman studied the isomerization of a single diastereomer of 1-ethyl-2-methyl cyclopropane thermalized at 400°C.[25] If isolation of only starting material, material with one center inverted, (the other retained), or material with both centers inverted occurred, then the concerted (con and/or disrotatory) mechanism would have been operating. When the reaction was complete only totally racemic material was obtained. Since this result could not have occurred by any process other than freely rotating biradicals, he concluded that the concerted mechanism was not operating and that biradicals were operating at least in this example. Benson has gone further to say that all cyclopropyl ring openings during isomerization are by the biradical mechanism with the exception of cis-1,2-divinyl cycylopropanes.[26] These observations of biradical ring openings indicate that formation of radicals in cyclopropane reactions is a reasonably favorable process, at least at high temperatures. As the temperature decreases,not enough energy is

available to overcome the activation barrier of 27 K cal/mole.[27]

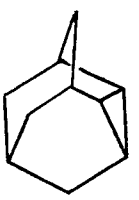
Reactions to form polymeric material by radical ring openings are relatively rare in cyclopropane chemistry. In general, cyclopropanes that are not either highly stabilized by groups such as vinyls or highly strained, are poor homopolymerization materials and form at best short chain polymers.[28a,b] Examples of highly strained cyclopropane homo-polymerizations have been reported by Wiberg[29] and by Hall et al.[28] Wiberg found that 1-carbomethoxybicyclobutane polymerizes either readily when initiated or slowly when left at room temperature (bicyclobutane itself would not polymerize). The polymer was that resulting from cleavage of the 1,3-carbon bond, making polycyclobutane, and not the one resulting from cleavage of the 1,2-carbon bond, as is the usually observed diradical cleavage pathway isomerizations of bicyclobutanes. Other properties of these strained (to the order of 64-67 kcal/mole) molecules include enough stability to oxygen to allow their synthesis without excluding it, and the lack of oxidation by m-chloro-perbenzoate. Hall's group also studied substituted bicyclobutanes and their polymerizations. They found bicyclobutanecarbonnitriles to readily undergo radical initiated polymerizations to form high polymers. They concluded that the more radical stabilized the bridgehead positions were, the more facile the polymerizations were.

The strained cyclopropanes discussed above are in actuality structurally quite different from the cyclopropane in 1,3-dehydroadamantane, which is the compound involved in the research of this thesis. Two compounds which may be considered structurally much more similar have been reported in the last five years. The first is

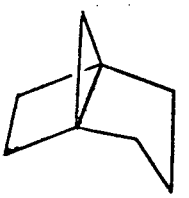
2,4-dehydroadamantane, a compound which is thermally stable to at least 203°C (m.p. 202.5-203.5°) and does not seem to react with oxygen readily.[30a,b] This molecule will, however, react readily with radical agents such as iodine or bromine. 2,4-Dehydroadamantane would not be expected to be as strained as 1,3-dehydroadamantane, however, because the bonding in the former is similar to that in bicyclo[3.1.0]hexane, a reasonably stable and normal cyclopropane,[31] while the bonding in the latter requires the inversion of two normally tertiary sp^3 centers. The other molecule similar to DHA is tricyclo-[3.2.1.$0^{1,5}$]octane. This molecule was found to have a strain energy of



1,3-Dehydroadamantane



2,4-Dehydroadamantane



Tricyclo[3.2.1.$0^{1,5}$]octane

60 kcal/mole and spontaneously reacts with oxygen to form short chain peroxypolymers.[32] No mechanism was postulated or further information concerning the oxygen reaction mentioned. Another interesting property of this compound was that it was extremely stable to thermal homo-polymerization ($t_{1/2}$ < 20 hr at 190°C).

It is therefore evident that a cyclopropyl group formed across the 1 and 3 positions of adamantane is a unique structure within the groups of both cyclopropane and adamantane chemistry. Because this adamantane compound contains an extremely strained cyclopropyl group,

it lends itself well to a study of the effects of strain on the properties and reactions of cyclopropanes. This study is aimed at determining these properties.

RESULTS

Synthesis

Preparation of 5,7-Dimethyl-1,3-dehydroadamantane

Bromination of 1,3-dimethyladamantane (Sunoco X-924-25) was done by the Friedel-Crafts reaction using aluminum bromide in bromine. The product was worked up by adding ice water and CCl_4 and neutralizing the bromine with $NaHSO_3$. The crude crystals obtained from evaporating the CCl_4 fraction were recrystallized from hexane to give the pure 1,3-dibromo-5,7-dimethyladamantane (DBDMA) which melted at 108.5-110°C and was identified by nmr and analysis.

Synthesis of 1,3-dehydro-5,7-dimethyladamantane was accomplished through the reaction of DBDMA in ether with potassium-sodium alloy while under nitrogen. Additives such as triethylamine, t-butanol, and sometimes potassium bromide seemed to initiate the reaction and improve the yield. Reaction progress was followed by vpc analysis. The product was unstable under prolonged reaction conditions and therefore must either be used immediately or stored in sealed degassed glass vessels. Several impurities including 1,3-dimethyladamantane (DMA) and 1-hydroxy-3,5-dimethyladamantane were also formed during the reaction. The former was particularly troublesome because it, as well as DHDMA, sublimed readily; thus precluding sublimation as a good

purification technique. DHDMA, purified by preparative vpc, was found to have a melting point of 44-45.5°C and an IR spectrum containing absorptions (in cm^{-1}) at 3030 (shoulder), 2900(s), 1445 (s), 1360 (s), 1280 (m), and 890 (m). The first and last absorptions are indicative of cyclopropane groups.[33,34] An nmr spectrum of DHDMA in degassed benzene showed absorptions at δ .91 (s)(6H), 1.01 (d, 10 cps)(4H), 1.47 (broad)(2H), 1.60 (d, 10 cps)(4H), and 1.93 (s)(2H). These absorptions correspond in the listed order to the methyl protons, H_{4a}, H_2, H_{4b}, and H_6 as shown in Figure 3.

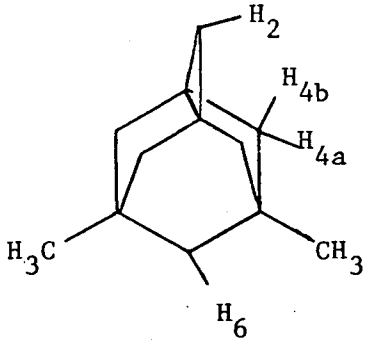


Figure 3. The DHDMA Structure and its N.M.R. Absorptions

DHDMA was found to react with many common laboratory reagents such as bromine, iodine, H_2S, CS_2, and acids, to name a few. Attempts to determine by esr if DHA were a diradical possibly in equilibrium with the ring closed system provided no evidence of radicals (this does not exclude that possibility).

The major interests in this study were two reactions to form polymers, namely the thermal homopolymerization reaction and the spontaneous co-polymerization with oxygen. To make the thermal polymer, 1,3-poly-5,7-dimethyladamantane, a capillary tube of DHDMA was collected

from the preparative vpc, sealed by flame, and heated in an oil bath to between 90 and 125°C. X-ray crystallography by powder method showed the material to be totally lacking in crystal structure. Further study using differential scanning calorimetry showed that on heating samples of polymer under nitrogen even to 500°C no phase changes occurred. However, if the samples were run in air, oxidative decomposition occurred at ca. 417°C. Analysis confirmed the composition to be $\{C_{12}H_{18}\}_n$. These techniques all indicate the material is a true long chain amorphous polymer consisting of a chain of units of DMA joined through carbons 1 and 3.

The other polymer studied, poly-1,3-peroxy-5,7-dimethyladamantane forms spontaneously at room temperature when DHDMA contacts air. When an ethereal solution of DHDMA had air passed through it for several hours, the white co-polymer formed. Side products were mainly 1,3-dihydroxy-5,7-dimethyladamantane. The polymeric material was only slightly soluble in benzene and insoluble in any other solvent tried.

Preparation of 1,3-Dehydroadamantane

Several of the numerous literature descriptions of the bromination of adamantane using bromine and boron bromide with or without varying quantities of aluminum bromide, were previously tried in the laboratory.[35-37] All failed to give the results desired. The best bromination technique of adamantane was finally found to be the use of bromine without boron bromide and with a trace of aluminum bromide.[38] Twenty grams of adamantane (Aldrich 10,027-7) and 40 ml dried bromine when cooled on ice and reacted with 100 mg of aluminum bromide formed

1-bromoadamantane. Repeat of the cooling process and addition of 200 mg of aluminum bromide followed by careful heating to 45-50°C gave 78.4% yield of 1,3-dibromoadamantane melting at 108.5-110°C. IR, nmr, and analysis agreed with literature values.

1,3-Dehydroadamantane was successfully synthesized by two methods. The first was by modification of the basic procedure previously reported[39] and consisted of reacting 2 g DBA and 2.5 g sodium-potassium alloy in ether while stirring under nitrogen. A maximum purity of about 90% was possible with this method. The major impurities were adamantane, 1-bromoadamantane, and 1-hydroxyadamantane.

The second and better synthesis was subsequently developed in the lab.[38] This synthesis consisted of reacting under nitrogen a precooled to -30 to -40°C reaction mixture containing 2 g DBA, 100 ml anhydrous ether, and 3.5 ml of hexamethylphosphoramide with n-butyl lithium. At the end of the dropwise addition of butyl lithium, the flask was warmed to room temperature and the solution washed with degassed water. The resulting solution contained about 95% DHA and very little 1-bromoadamantane or 1-hydroxyadamantane. This method also virtually eliminated all adamantane, a previously very troublesome impurity. Purification was accomplished by washing while under nitrogen with water and vacuum sublimation at -70°C.

DHA was found to react with nitric oxide radical at -78°C while under nitrogen. The products of the warmed system could not be purified or analyzed to any extent by vpc on Carbowax or SE-30 or eluted from a column of alumina or Florisil. The ir spectrum providing the only information concerning the few products that could

be obtained, indicated a possibility of nitrogen-oxygen bonding in the products ((in cm^{-1}): 1600 (s), 1500 (s), 1300 (s), 860 (s)).

Radical Studies

Galvinoxyl (Aldrich G30-7), a very dark bluish-purple stable free radical which does not react with oxygen in air, was thought to be a potential radical polymerization inhibitor. It, however, reacted quickly with DHA in heptane under nitrogen to produce a lightly purple coloured solution. Controls without DHA remained unchanged. No product isolation was attempted.

DHA reacted readily with atmospheric oxygen to form the peroxy co-polymer. Pure DHA is well stirred solutions in a 100% oxygen atmosphere were found to have half lives of reaction of 50 minutes in xylene and 125 minutes in octane. In these reactions, a white cloudiness rapidly formed which turned to a white precipitate. When a radical inhibitor was added to the DHA solutions, the rate of reaction decreased and the white cloudiness and precipitate never formed, indicating that no polymer was produced. By measuring the rate of oxygen uptake with time and converting that value to the amount of DHA remaining, first order plots were possible. These standard plots of the logarithm of the initial concentration of DHA divided by the concentration of DHA remaining at time t versus time, gave generally straight lines. These plots indicate that the rate for at least the major portion of the reaction is first order with respect to DHA. Some deviations in the straight line plots were observed after 2 half lives, becoming more pronounced, especially after 4 half lives.

Table I. Results of DHA-O_2 Reaction Kinetics

Solvent	Inhibitor	[DHA]	$\frac{\text{Moles Inhibitor}}{\text{Moles DHA}}$	$\frac{\text{Moles } O_2}{\text{Moles DHA}}$	K sec^{-1} x 10^5
n-Heptane	-	.086	-	1.38	11.3
"	DBPC	.056	.80	1.46	3.63
n-Octane	-	.231	-	1.17	15.0
"	DBPC	.081	4.00	1.29	3.58
"	"	.158	1.00	1.22	4.22
"	"	.188	.50	1.19	4.10
"	"	.205	.25	1.26	3.98
"	"	.125	.159	1.24	3.98;22.4[a]
"	"	.238	.139	1.21	3.38
"	"	.254	.086	1.32	3.10;18.7[a]
"	"	.262	.042	1.35	2.75;18.2[a]
"	HMBP	.174	.475	1.20	3.38
"	DBHQ	.174	.50	1.52	3.52
"	1-dodecane-thiol	.198	.50	1.25	6.68
Xylene	-	.484	-	1.20	32.8
"	DBPC	.185	.333	1.23	12.7
"	"	.278	.167	1.29	12.5
"	"	.345	.083	1.25	13.3;26.3[a]
"	HMBP	.246	.80	1.24	13.8
"	"	.326	.167	1.20	15.3
"	"	.345	.083	1.23	16.2
"	p-quinone	.088	.289	.96	209.3
"	"	.326	.307	.90	20.8
"	1-dodecane-	.246	.504	1.11	16.5
"	"	.169	.980	.96	17.8

[a] The first figure is the rate constant of the reaction while under the influence of inhibitor, the second figure is the rate constant after all inhibitor is consumed.

[b] DBPC = 2,6-di-t-butyl-p-cresol, HMBP = 4-hydroxymethyl-2,6-di-t-butyl phenol, DBHQ = 2,5-di-t-butyl-4-hydroquinone, p-quinone = 1,4-benzoquinone.

This deviation was, however, not surprising because it was in the region where kinetic measurements are not nearly as accurate as the initial measurements; therefore the deviations had no real significance. The initial slopes of the plots, taken as soon as they got under way, were used to calculate the rate constants of reaction. Table I shows the values for each kinetic run of the experimental rate constant, the solvent in which the run was made, the identity of the inhibitor used (if any was used), the molar ratio of inhibitor with DHA, and the molar ratio of oxygen absorbed with DHA. Table Ia shows the mean values from Table I in the cases where several runs using the same solvent and inhibitor were made.

Table Ia. Some Mean Values from Table I.

Solvent	Inhibitor	$k \times 10^5$	$\frac{\text{Moles } O_2}{\text{Moles DHA}}$
Octane	-	15.0	1.17
"	DBPC	3.67 ± .85	1.25 ± .1
Xylene	-	32.8	1.20
"	DBPC	12.8 ± .5	1.26 ± .03
"	HMBP	15.2 ± 1.4	1.22 ± .02

In general, DHA polymerizations were found to be about twice as rapid in xylene as in octane. The inhibited rates using DBPC dropped to 25% in octane and about 40% in xylene. The difference in the two solvents may have been due to the greater stabilization of the

adamantyl radical by the aromatic system than by the saturated hydrocarbon system. The process of forming the more stabilized radical would require less energy than the corresponding process for the less stabilized radical; hence, the more stabilized radical would be formed more readily. If this formation were the rate controlling step of the reaction, that reaction would have a slightly greater rate as a result. This stabilization would, of course, be expected to be small as was observed because radical reactions are affected only slightly by solvents. The explanation of the greater inhibiting effect of DBPC in octane than xylene can be explained in a similar manner. The aromatic solvent would tend to associate with the aromatic inhibitor slightly more than the saturated solvent will. As a result the enhibitor will be less "free" and less active for blocking radical reactions in xylene.

Perhaps another explanation of the differing degrees of inhibition by DBPC in the two solvents arises from the relative rates of reaction of the chain radical with the inhibitor versus with molecules of DHA. Since the DHA chain polymerization reaction is slower in octane than xylene, the inhibitor would have more time in that solvent to trap the radical. If the trapping rate was somewhat comparable with the chain propagation rate, such a time factor could certainly account for the observed differences in the ability of DBPC to inhibit the reaction in the two solvents.

The molar ratio of oxygen to DHA consumed in the reaction was approximately 1.25. If the reaction formed pure polymer of the type $\{O\text{-}Ad\text{-}O\}_n$ the ratio would be 1; if all of the reactions were stopped

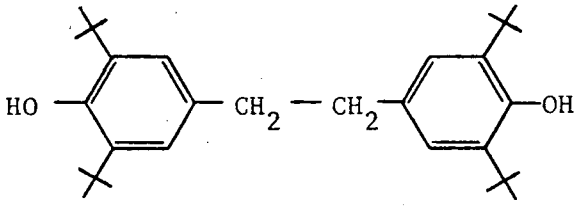
immediately the product HOO-Ad-OOH would be formed and the ratio would be 2. A ratio of 1.25 indicates that some polymerization was occurring and that short oligomers were probably forming. If the oligomers were of the type HO{O-Ad-O}OH, n would equal approximately 4.

Two usual radical inhibitors, which when used were actually found to be "initiators" and co-reactants, were p-benzoquinone and 1-dodecanethiol. When used as inhibitors, they actually increased the rate of reaction. Slight decreases in the amount of oxygen were noted in the case of the mercaptan while a drop in oxygen absorption to about 75% of normal was noted in the quinone case. When controlled experiments using identical conditions to the usual kinetic runs, excepting with total exclusion of oxygen, were run, it was found that both reacted with DHA. The thiol reacted quickly to form a single product with very long vpc retention time on Carbowax at 200°. Based on the lack of any detectable products from the DHA or the thiol (excluding the large single products) and from previous work with cyclopropyls and thiols,[40] it was felt that the product was 1-adamantyl-(1-dodecane)-sulfide. The quinone reacted to form an insoluble mud-like material which was not analyzed but which is probably several products, possibly polymeric.

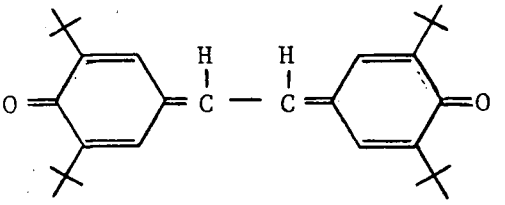
Products of Inhibited Reaction

The study of DHA reaction products when reacted with oxygen in the presence of a true inhibitor was accomplished by analyzing the products of the combined residues of all the kinetic runs using DBPC as the inhibitor. The products were separated from the residue

first by column chromatography on Florisil and then by either recrystallization or preparative vpc on 3/8" x 10' Carbowax columns. Four products were obtained which could be seen on vpc; two of these being the products of the inhibitor and the other two the products of DHA. The two products of DBPC were identified as the dimers 1,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)ethane and 3,3',5,5'-tetra-t-butyl-stilbene-4,4'-quinone. Since these dimeric compounds have been reported in the



1,2-bis-(3,5-di-t-butyl-4-hydroxy phenyl)ethane

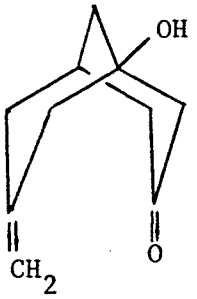


3,3',5,5'-tetra-t-butyl-stilbene-4,4'-quinone

literature as the products of reactions with DBPC, their identification was made with that knowledge and was based to a large extent on the superimposability of their n.m.r. spectra with those reported.[41-43]

One of the adamantane products was easily confirmed as being 1,3-dihydroxyadamantane. This was accomplished by superimposing vpc recordings and ir spectra of the isolated material and an authentic sample of 1,3-dihydroxyadamantane and noting their complete agreement. The other adamantane derivative was considerably smaller in quantity than the dihydroxide, a problem which hindered identification attempts. The purified material gave a melting point at 217-218°C with what appeared to be slight decomposition beginning at 210°C. N.m.r. gave a spectrum with approximately 14 protons, 8 between δ 1.85 and 2.0,

3 at δ 2.3, 2 at δ 3.6, one varying in location with solvent but centering around δ 2.8. This latter was removed with D_2O. IR absorptions at 3500 cm^{-1}(m), and 1145 cm^{-1}(s) indicated very strongly a tertiary hydroxyl group, at 1715 cm^{-1}(s) indicated a carbonyl, probably on a six membered ring, and at 900 cm^{-1} (m) and 885 cm^{-1}(w) indicated possibly an exocyclic methylene group (literature for these groups: t-OH 1150 cm^{-1}, 6 membered ring carbonyl 1715 cm^{-1}, exocyclic methylene 890 cm^{-1}).[60] Analysis of a sample of probably 99% purity (by vpc) gave values of C, 73.76; H, 8.36, as compared to the predicted $C_{10}H_{14}O_2$ values of: C, 72.26; H, 8.49. The mass spectrum of the material unfortunately provided little information. A final piece of information concerning the compound's identity was a comparison of the IR of 7-methylene-bicyclo[3.3.1]nonan-3-one with the IR of the isolated material. The spectra were essentially identical except for the very strong hydroxylic absorptions at 3500 cm^{-1} and 1145 cm^{-1}, which were present in the isolated material. A speculative structure based on this data could be 1-hydroxy-7-methylene-bicyclo-[3.3.1]nonan-3-one.



1-Hydroxy-7-methylene-bicyclo[3.3.1]nonan-3-one

In order to help understand the reaction of DHA with oxygen, product studies on the reaction residues resulting from the reaction run with the addition of 1-dodecanethiol were made. Even though the thiol reacted with DHA as has been previously discussed, it was not the exclusive reactant when oxygen was present. This was shown by the isolation and identification of 1-hydroxyadamantane and 7-methylene-bicyclo[3.3.1]nonan-3-one in addition to the thiol-DHA product. The DHA products were obtained from the residues in the benzene fraction from a Florisil column separation and were separated from each other and purified by use of preparative vpc on a 3/8" x 10' Carbowax column. The 1-adamantanol was identified by its ir, its n.m.r. (which was superimposible with Stadtler Standard Spectrum N.M.R. 4544 for the same compound), and by analysis. The methylene bicyclic ketone melted at 163-163.5°C; literature: 160-164°C,[44,45] and gave correct analysis for $C_{10}H_{14}O_2$. It was further confirmed by the ir: absorptions at 1710 cm^{-1} (s), indicating carbonyl, and 895 cm^{-1} (s) and 885 cm^{-1} (m), indicating exocyclic methylene; and by its n.m.r. which gave singlets of ratio 1:5:1 at δ 1.95, 2.40, 4.78.

The relative ratios of the products of reaction were determined for one example using a 9:2 ratio of DHA to DBPC. This ratio was chosen to be as close as possible to the experimentally determined proportions of the two needed for complete inhibition. By doing this there would not be large excesses of either polymeric material or of unreacted DBPC. The product ratios were determined by vpc using the cut-out-and-weigh technique. Any products which were peroxides (i.e., polymeric material) or hydroperoxides would decompose

on the column and could not be detected. The remaining 27% of the products were determined to be 1,3-dihydroxyadamantane 63%, the still somewhat uncertain bicyclic hydroxyketone 16%, and three minor peaks totalling 21%. Because 1-dodecanethiol was not a true inhibitor, no quantitative study was done on the reaction products obtained when it was used.

DISCUSSION

Preparative Reactions

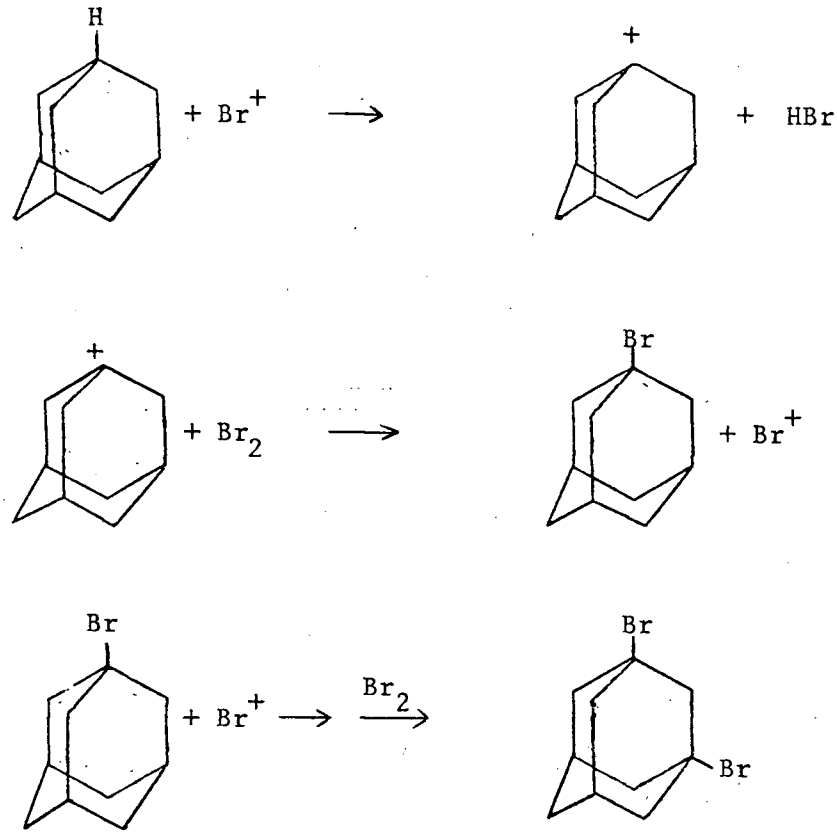
Previous authors have come to considerable disagreement as to the best method to selectively place two bromines on bridgehead positions of adamantane. Many of these same workers have also come into disagreement as to the correct melting point of 1,3-dibromoadamantane. The first reported synthesis[46] involved making the di-silver salt of 1,3-adamantane dicarboxylate and then adding bromine in carbon tetrachloride and heating to 70°C. The product was purified by sublimation to give an 18% yield and found to have a melting point of 108°C.[46] Stetter and co-workers reported selectively brominating by use of boron bromide and in refluxing bromine. The dibromide product obtained in 12.5% yield was also found to have a melting point of 108°C.[47] Later, using his same synthesis, Stetter reported the melting point to be 112-3°C.[35] Baughman later refuted Stetter's work, saying that when they tried his synthesis with bromine and boron bromide, no dibromide product was obtained, the major product being the monobromide.[36] He experimented with ratios of aluminum bromide and boron bromide in bromine and found the best results occurred with a 1000:1 molar ratio of catalysts. A yield of 74% with a melting point of 112-3°C was obtained. A final group of workers

following Baughman's method found that they obtained only the monobromide when using the 1000:1 ratio of catalysts. They found 125:1 molar ratio to be the best, yielding 86% dibromide product.[37] No melting point was reported. The last two authors could give no mechanism or explanation of the function of the co-catalysts in the reaction.

This laboratory had followed previous suggestions on the synthesis of the dibromide without the best success in terms of yield or ease of purification. Therefore the method developed was to eliminate the boron bromide entirely and simply use small amounts of aluminum bromide under very carefully controlled conditions. By this method a yield of 78.4% was obtained with a melting point of 108.5-110.0°C. It is felt that this synthesis may not be the best possible synthesis, but to date it appears to be the most convenient in terms of experimental ease and yield.

The mechanism of the reaction appears not to involve any complicated undetermined co-catalysis schemes, but rather the ordinary accepted Friedel-Crafts mechanism. It probably involves formation of bromine cations and aluminum tetrabromide anions, the former abstracts a tertiary hydrogen from adamantane to form the 1-adamantane carbonium ion. The carbonium ion would then abstract a bromide from bromine and generate another bromine cation as shown below.

$$Br\text{-}Br + AlBr_3 \longrightarrow Br^{+}AlBr_4^{-}$$



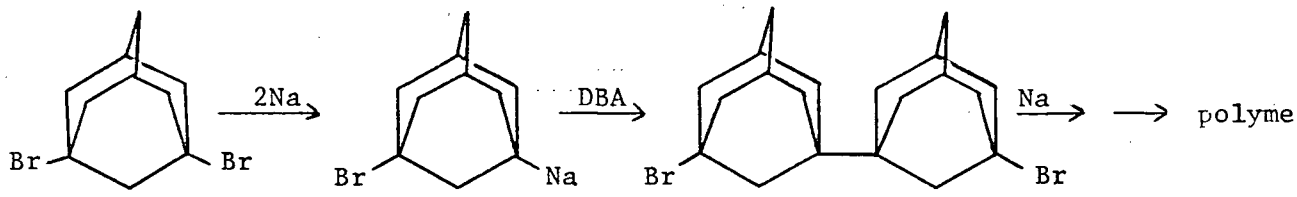
The process would be repeated to place a second bromine on the molecule. A possible explanation for the need for aluminum bromide instead of boron in the placement of the second bromine may be found in the relative strength of the two as Lewis acids. Aluminum bromide, being more acidic than boron bromide, will form the more stable tetra-bromide anionic complex, and therefore, allow the bromine cation to be "freer". A freer bromine cation would be a stronger acid for the removal of a hydride from the adamantane. The previously shown experimental fact that the addition of subsequent bromines to adamantane becomes progressively more difficult as more bromines are added[35] is reasonable on the basis of the stability of the resulting

carbonium ion as each hydride is abstracted by a bromine cation. Olah and Schleyer have shown through acid media n.m.r. studies that 1-adamantane carbonium ion is stabilized by the back lobes of the three tertiary sp^3 hydrogens in adamantane.[16] Since an electron withdrawing bromine on a tertiary position decreases the electron density of the back lobe of one of the sp^3 orbitals, the carbonium ion would not be as stabilized. Further addition of bromines successively decreases the back lobe stabilization, accounting for the experimental observations.

Bromination of 1,3-dimethyladamantane was straightforward since excess bromination was impossible, baring extreme conditions which may have caused some secondary position bromination or decomposition.

Syntheses of 1,3-dehydro-5,7-dimethyladamantane and 1,3-dehydro-adamantane by the alkali metal technique proceeded with a great deal of hit or miss results. In general, the total synthetic method was not reproducible in any of the variations tried in hopes of improving the yield. It was found that lithium metal instead of sodium or potassium was not a strong enough reagent to abstract the bromines. Therefore, neither zinc or magnesium, other common metals used for Wurtz couplings and similar reactions, were tried. Another method hoped to work was the use of phenyl lithium. With the knowledge that 1-adamantene is a violation of Bredt's rule, it was hoped that the phenyl lithium might react in a concerted mechanism to abstract both bromines, forming DHA, LiBr, and bromobenzene. The results in fact, appeared to be the synthesis of phenyl adamantane, a novel but not practicable synthesis.

Since only alkali metals seemed to work for the reaction, it was felt that the reaction was in some respect similar to the Wurtz coupling. It could not have been the ordinary Wurtz reaction, for if it was the reaction would have proceeded by the following mechanism,



Rhinehard, in fact, reacted DBA with sodium at elevated temperatures and obtained polymeric material.[48] Since the results from this lab confirmed the existence of DHA and since this study confirmed the thermal polymerization of DHA, it was felt that Rhinehard's reaction was also not a simple Wurtz coupling but instead was the same reaction as ours. It was felt that perhaps the reaction was a modified Wurtz mechanism which coupled the alkyl sodium and the alkyl bromide together by an internal Sn2 type of mechanism. Assuming this mechanism and knowing that alkyl sodium compounds readily attack diethyl ether,[49] it was felt that hydrocarbon solvents such as heptane, hexane, pentane, and toluene would be necessary for the reaction. Using these solvents, the reaction would indeed produce DHA or DMDHA; however, it was very slow and gave very poor yields, rarely over 70% DHA. The product also seemed to rapidly decompose into adamantane. Therefore despite the possibility of solvent decomposition, the solvent was changed to ether. It was found that the reaction went much smoother, more rapidly,

and in better yield than in hydrocarbons. The ether also did not decompose and was easier to remove. The lack of solvent decomposition indicated that either no 1-adamantanyl sodium was formed or else that if it was formed, it was so transitory that it did not get a chance to react with solvent. In other words, the reaction was essentially concerted. The ether may have improved the reaction by helping to solvate the sodium.

In pure ether solvent it was found that the reaction was often very slow to start. Once started it would react very rapidly until completion. Although the reason for this was not understood, it was felt that if perhaps a catalyst could be found, the time to initiate the reaction could be shortened and the yield could be improved. "Initiators" used for this purpose included trace quantities of methyl iodide or n-butyl iodide (in hopes of cleaning the alloy surface to expose reactive metal surfaces), potassium bromide and copper bromide (to help expose surfaces by breaking up the metal under stirring, as well as to provide positive metal ions which may facilitate the elimination of bromide), and t-butanol and DBPC (in hopes of cleaning the surface of the alloy). No improvement was found by use of methyl iodide, butyl iodide, copper bromide, or DBPC. However, potassium bromide did in several reactions drastically improve the reaction time and yield. The effect was not reproducible and was felt to be caused in some systems because these systems were too "clean". The addition added impurities, perhaps oxygen, which appeared necessary to initiate reaction. t-Butanol had the same effect as KBr had of improving many reactions, and was generally used in reactions to give better success.

These results were also non-reproducible, the reason for improvement was not understood, though perhaps again the addition of impurities may have been the reason.

A final experimental modification which improved the reaction was the addition of anhydrous triethylamine to the solvent. The improvement which resulted may possibly be explained by better solvation of the metal by the amine than by ether or hydrocarbons.

The exact mechanism of the elimination is not known. However, two possible mechanisms are illustrated in Figure 4a.

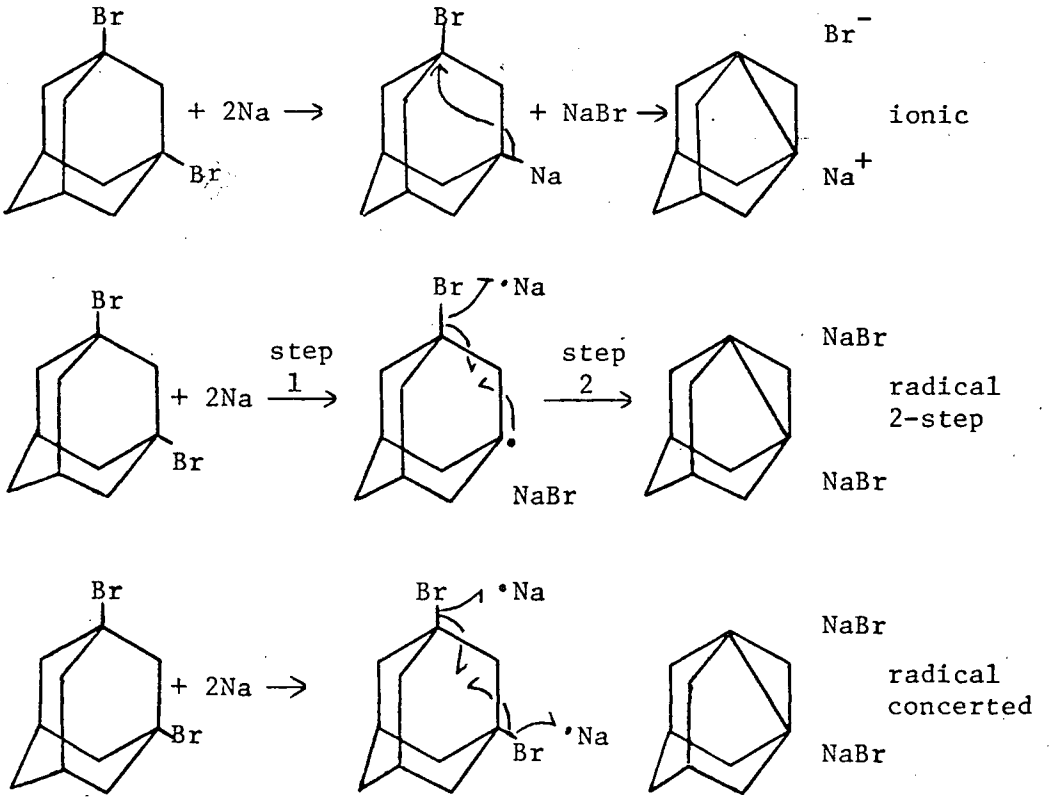


Figure 4a. Possible Debromination Mechanisms Yielding DHA from DBA.

The ionic mechanism is appealing in light of the precedence of the Wurtz reaction. However, it has the disadvantage that alkali metals have never been known to exist at bridgehead positions on adamantane.[50,51] The second reaction is radical in nature and may either involve a two step reaction or else be the concerted abstraction of both bromines by two sodium atoms. Another way to consider the reaction is shown in Figure 4b. If the alloy emcompasses the molecule and by concerted

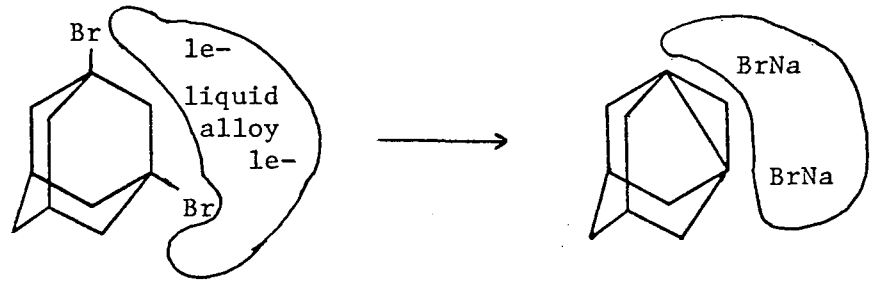


Figure 4b. Potential Role of Na°-K° Alloy in Formation of DHA.

mechanism joins one electron from the metal electron cloud with an electron from each C-Br bond to make NaBr, the two remaining electrons from the C-Br bonds will join to form a molecule of DHA. A similar ionic mechanism could perhaps also be drawn using electrons from the metal electron cloud. Whether the mechanism is ionic or radical is not known, but it is felt that the lack of coupling reactions to form biadamantane or polyadamantane indicates that the reaction is concerted.

The reaction of DBA with n-butyl lithium in ether to produce DHA is a much better synthesis. It reacts more rapidly, eliminates the hazards of alloy, reduces adamantane as a side product, gives a better yield, and is much easier to handle.

Mechanisms of organo lithium reactions are not well understood at present. It has been suggested that a mechanism consistent with the experimental results of lithium couplings could be the following slow 2-step process.[52] This mechanism could not be the major pathway

$$R'\text{-}X + Li\text{-}R \xrightarrow{\text{slow}} \begin{cases} R'^{+} \xrightarrow[\text{fast}]{R\text{-}Li} R'\text{-}R + Li \\ X{:}Li{:}R^{-} \end{cases}$$

operating in the case of DBA because, if it was, one would expect the major product to be the product of electrophilic attack of the 1-adamantyl carbonium ion on butyl lithium. This would give 1-bromo-3-(n-butyl)-adamantane and 1,3-di-(n-butyl)-adamantane as the products. These are not observed as major products.

Synthesis of 1-adamantyl-lithium has not been accomplished due to its instability.[15] This report, along with the fact that the carbon on butyl lithium is primary as opposed to being tertiary on adamantane, tends to make direct metal-halo exchange seem improbable. Yet this type of mechanism seems to be operating. The addition of HMPA to the reactants holds some key to the mechanism, although its exact function is not known. Previous published work on 2,4-dibromopentane indicated that the major product was 2-lithium-4-bromo-pentane (in this case direct metal-halo substitution) with some 1,2-dimethyl cyclopropane.[7] This reaction was run without HMPA and had a very long reaction time in comparison. The authors formulate that the metal-halo replacement is with retention and the intramolecular displacement is most probably

with inversion of both centres. The elimination of bromine from DBA may be somewhat similar to elimination reported from 2,4-dibromopentane. However, the lack of stability of 1-adamantyl lithium and the necessity of HMPA indicate that the mechanism is somewhat more complicated.

Polymerization Reactions

Thermal polymerization of DHDMA was a simple process once the monomer was sealed in a tube. Since the capillary tube only had a small amount of DHDMA, small traces of oxygen which may have been sealed inside would be expected to form peroxypolymer. Since the peroxypolymer would be at most just a few percent of the product, it could possibly explain the fact that the total C-H analysis only added up to 99% despite the fact that the carbon:hydrogen ratio was almost exact. Oxygen radicals would co-polymerize with DHDMA but, due to the low polymeric reactivity of the monomer to self-polymerization at room temperature, the presence of traces of oxygen could not initiate self-polymerization. Self-polymerization at above 90°C may be due to spontaneous cleavage of the carbon 1,3 bond. Once initiated by this cleavage the temperature is high enough to make the energetics of propagation feasible. The lack of an esr spectrum at low temperature does not exclude the possibility of ring opening to form biradicals. Rather, it indicates that the radicals, if they exist, must be in concentrations of less than 10^{-8} molar. If an equilibration of ring-open and ring-closed forms were occurring, the esr observations could be realistic if the equilibrium strongly favoured the ring-closed form at room temperature.

The calorimetric studies of the thermal polymer indicated the polymer was stable in air to a temperature above 400°C (in the absence of oxygen the polymer appeared completely stable to 500°C). Also during the heating process no phase changes were detected. Since the polymer was also found to be almost totally insoluble in organic solvents, this property combined with its thermal stability could make the polymer potentially very useful for industrial applications.

DHA seemed a useful intermediate in the synthesis of 1,3-nitrogen derivatives of adamantane. Nitric oxide was known to readily react with radicals or olefins forming nitroso compounds. While the very reactive primary and secondary nitroso compounds often give rearranged and degradation products,[53] tertiary nitroso compounds are much more stable. A major problem of all nitroso compounds, including tertiary ones, is the side reaction illustrated below.[54] It was hoped that

$$R\text{-}N{=}O + 2NO \longrightarrow R\cdot + N_2 + NO_3 \qquad \text{rate} = K[RNO][NO]^2$$

$$NO_3 + NO \longrightarrow 2NO_2$$

by exluding air and running at low temperature that this reaction as well as other side reactions could be prevented. The dinitroso could then be reduced under nitrogen at room temperature and the diamine formed. If this synthesis worked it would, in addition to indicating the reactivity of DHA, be a new synthesis of the diamino compound. If NO_2 was formed at any time and nitrato compounds resulted, the adamantane system would be open-ringed and numerous products could be

formed. When the reaction was run, decomposition did occur extensively, yielding at least four products. After attempts to isolate some of the products failed, the study was abandoned.

Radical Studies

Galvinoxyl free radical is extremely stable to oxygen (no decomposition of crystals took place in air in three months or in benzene solution in three days).[55,56] It is, indeed, best known for this oxygen stability plus the fact that it is the only known case of a radical product of hindered phenols which is stable to oxygen.[56] It does not in general react readily with any heteroatomic radical, reacting much more slowly with t-butoxy radical than with any carbon radical. It does, however, react very rapidly with carbon radicals, reacting with them ten times more rapidly than does the iodine radical (iodine is also a compound which is non-reactive to galvinoxyl).[57] Knowing these properties and assuming it does not react with DHA, galvinoxyl would make an excellent trapping agent to study the oxygen-DHA reaction. By competing with oxygen for adamantane radicals, it could perhaps be an effective inhibitor by stopping the radical propagation. Isolation of even very minor amounts of digalvinoxyl adamantane product would be convincing evidence that the reaction was caused by the spontaneous ring-opening of DHA to form a biradical. As the situation turned out, galvinoxyl was very reactive with DHA even while under nitrogen and therefore was of no use for that purpose. It does, however, indicate that DHA does either form radicals itself or is at least very radical-like in nature.

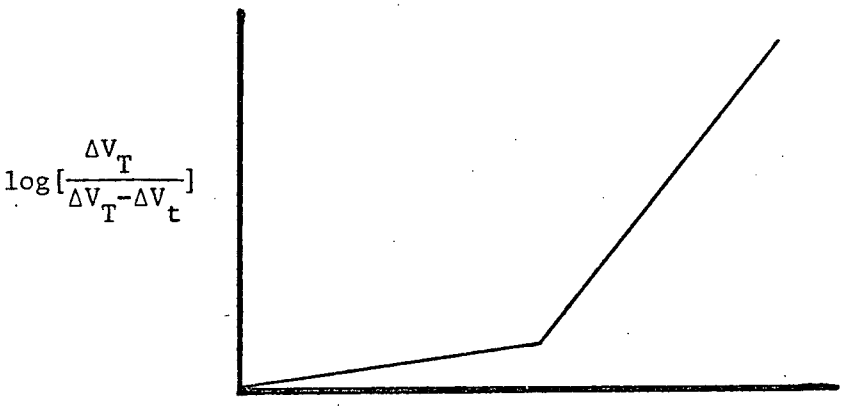
The measurements of the kinetics of the DHA reaction with oxygen was relatively routine once the bugs of the system were eliminated. The solvents chosen were generally high boiling, saturated, or aromatic compounds which did not either react with DHA or have the same retention time as DHA on the vpc. Olefins were specifically excluded by thoroughly purifying to prevent any possibilities of olefinic co-polymerization or other complication of products. The solvents were chosen to be high boiling to insure low solvent vapour pressure in the system, thus requiring no correction factor in case the temperature of the system were to fluctuate a small amount during the reaction. All solvents were shown by blank runs to be nonreactive with DHA. The actual volume measurements were exact to within about 0.1-0.2 ml, these being due to the human error of equilibrating the mercury levels in the manometer. Also most runs were continued for approximately 1400 minutes to make all the end points consistent. The uncertainty of the individual points in the first order plots of log $[\frac{\Delta V_T}{\Delta V_T - \Delta V_t}]$ versus time may be considered negligible when the concentration of DHA is still high. This is apparent when the precision of the measurements and the scale of the graphs are noted. As the DHA concentration becomes more dilute, the precision of the points becomes less as is the usual case with kinetic plots. The real error in the graphics arose from the exact determination of the end point. If it was off by as little as 2% of the total volume, the later points would curve significantly off the line. The early points however should be reasonably good up to at least the half-life of the reaction. As has been observed in numerous radical reactions, there is frequently an induction

period at the beginning of the run. Those points taken during this induction period were omitted from the determination of the slope of the plot. The slope, due to considerations above-mentioned, was taken simply from the more exact points of the initial reaction. The accuracy of the slopes of the curves may be taken as within about 30%. This approximate value is obtained by drawing the extremes of reasonable lines through the initial points and noting their deviation from the drawn line.

If the reaction of DHA and oxygen were entirely stopped by inhibition after the first step of the chain, one would expect to observe

$$\text{DHA} + 2O_2 \xrightarrow{\text{step 1}} \cdot\text{OO-Ad-OO}\cdot \xrightarrow{\text{inhibitor}} \text{HOOAdOOH}$$

a slow uptake of oxygen as seen on the graph by a straight line of low slope. When the inhibitor is entirely consumed the reaction would become a chain propogation with a greatly increased reaction rate. A straight line of much great slope would result. The graph below shows a hypothetical idealized reaction which is inhibited initially and then consumes the inhibitor to return to the polymerization reaction.



Mechanisms of radical reactions, in general, must involve three separate types of reactions: initiation, propagation, and termination. In this case the reaction is an autoxidation. Almost all autoxidations of hydrocarbons involve, at least during the propagation steps, the abstraction of a hydrogen radical. A typical autoxidation once initiated has propagation and termination reactions as shown below.

$$R\cdot + \dot{O}=\dot{O} \longrightarrow R\text{-}O\text{-}O\cdot \quad (1)$$

$$R\text{-}O\text{-}O\cdot + HR \xrightarrow{\text{slow}} R\text{-}O\text{-}O\text{-}H + R\cdot \quad (2)$$

} propagation

$$2R\text{-}O\text{-}O\cdot \longrightarrow \text{often non-radical products} \quad (3)$$

$$R\text{-}O\text{-}O\cdot + R\cdot \longrightarrow \text{non-radical products} \quad (4)$$

$$2R\cdot \longrightarrow \text{non-radical products} \quad (5)$$

} termination

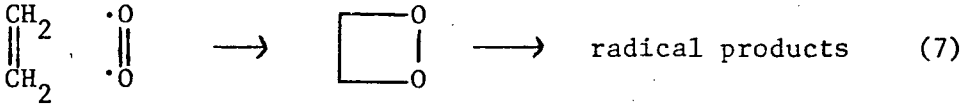
In this reaction scheme, reaction (1) is extremely fast, being in the order of k(first order) = $10^6 sec^{-1}$ with an activation energy of $E_{act} \leq 2$ kcal.[58] Reaction (2) varies considerably in rate, depending on the structure of R and the strength of the R-H bond, but often has a E_{act} of 8-12 kcal. Step (2) is therefore the slow step. Termination reactions depend on the exact system studied; however, the combination of any of the two radicals has a rate constant of approximately $k = 10^{10}$ liter-mole^{-1}sec^{-1} [58] and usually forms non-radical products.

The use of inhibitors or "retarders" in autoxidation is based on the non-reactivity of the material with either of the reactants and the fact that it can break either step (1) or step (2) of the chain and form stable non-reactive products. It breaks the chain by reacting

with a chain radical more quickly than the co-reactant. Since step (1) is so rapid, usual inhibitors such as quinones, tertiary amines, thiols, phenols, etc. are often used to block the second step. By blocking this step the rate is decreased almost to zero until all the inhibitor is consumed after which time the reaction resumes at normal rate.

In the DHA-O_2 reaction, it is immediately apparent that the previous pathway cannot be operating. DHA contains no hydrogens to extract from the 1 and 3 carbons, and abstraction from the secondary position would involve a violation of Bredt's rule. The two remaining tertiary hydrogens could perhaps be removed, but at room temperature this certainly could not occur in a chain. It should also be noted that the reaction occurs without any radical initiators added. This brings up the problem of the source of initiation. Is the reaction initiated spontaneously in the same manner as other oxidations, or is the mechanism different? The two postulations for the spontaneous initiation of usual autoxidations are reactions (6) and (7).

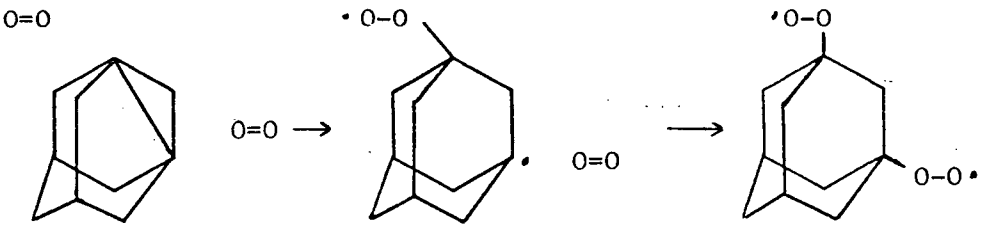
$$R\text{-}H + O_2 \longrightarrow R\cdot + \cdot OOH \qquad (6)$$

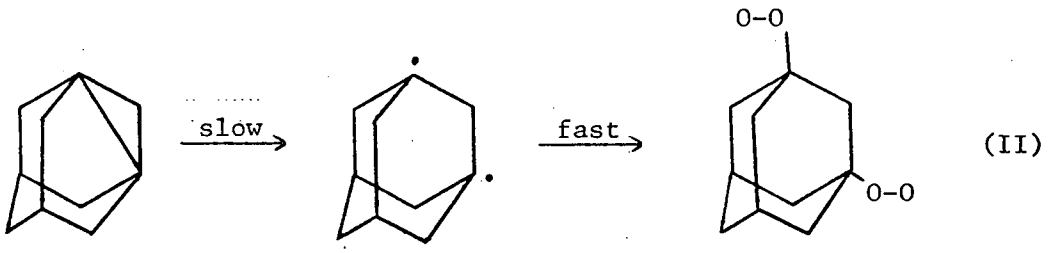


(7)

Reaction (6) is the usually accepted mechanism at high temperatures and is believed to occur heterogeneously, perhaps with assistance of the wall of the container. Reaction (7) has little support but has been mentioned several times as a potential initiator.[59]

Clearly, at room temperature, reaction (6), the usual mode of initiating, cannot be occurring. This leave two possible mechanisms of initiation (I) and (II). Possibility I involves the oxygen radical





directly attacking the back lobe of the C_1-C_3 bonds, bonding with one electron of the central bond and displacing the other to the remaining carbon. This mechanism essentially means that the DHA molecule remains in its original form throughout its existence until its strain is relieved by an attacking radical. Possibility II involves the DHA strain being great enough that the molecule spontaneously ring-opens to the biradical and then closes rapidly again. If, however, oxygen is present, the biradical will at least sometimes successfully attack the oxygen before it closes again. The two mechanisms I and II are in some respects like the debate over classical versus non-classical carbonium ions. DHA may be thought of as having two resonance forms or else as having an equilibrium. Both possibilities are shown in Figure 5. The resonance forms in (A) indicate that DHA has substantial

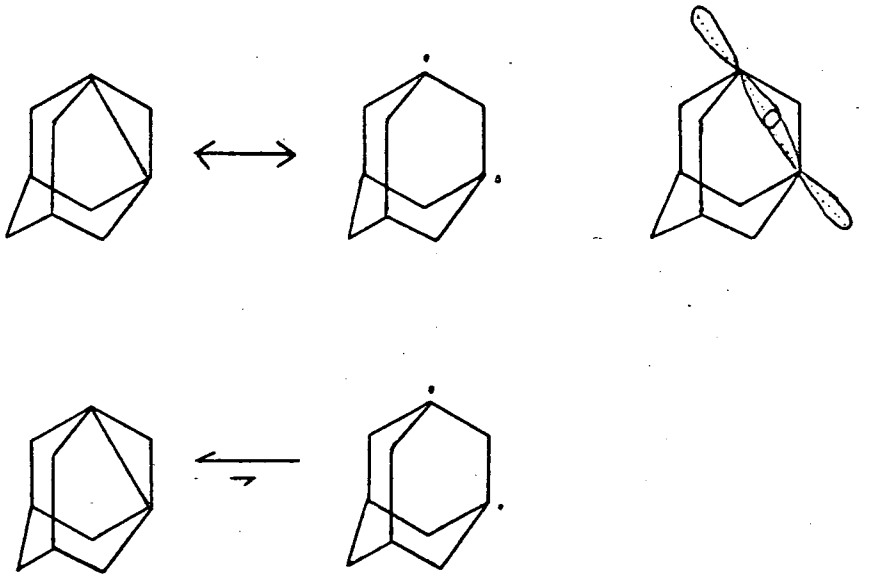


Figure 5. Two Possible Respresentations of the DHA Molecule.

radical nature but that it is not a biradical. Form (A) may be illustrated as the hybrid formed by carbon p orbitals overlapping endwise in the centre to form the structure shown above. Form (B) is an actual equilibrium in which two distinct species are present. In this case, DHA would be an outright biradical at times. The results of this study cannot determine which is the true case.

Once the reaction of DHA and oxygen is initiated, the propagation steps are:

$$\text{O-Ad-O}\rangle_n\text{O-Ad}\cdot + O_2 \longrightarrow \text{O-Ad-O}\rangle_{n+1}\text{O}\cdot \qquad (8)$$

$$\text{O-Ad-O}\rangle_n\text{O}\cdot + \text{DHA} \longrightarrow \text{O-Ad-O}\rangle_n\text{O-Ad}\cdot \qquad (9)$$

In light of the fact that 1-adamantyl free radical has very similar stability and reactivity as does t-butyl radical, it would be expected that it would react about equally well with oxygen. Assuming this, the rate constant k_8 would equal approximately 10^6 liter-mole^{-1}sec^{-1} as indicated earlier for radicals with oxygen. The slow step therefore must be step (9), the peroxy attack on DHA.

Termination of the chain would probably occur by the usual mechanisms illustrated in reactions (3), (4), and (5) with R being adamantyl or polymer. It might be noted, however, that diradical chain propagations are in general very poor and inefficient, due partly to the entropy effects of forcing two radicals to remain in the same proximity.[61,62] This would cause substantial chain self-termination.

The addition of inhibitor to the reaction system should terminate the reaction by trapping the first radicals as they are produced. Due to the lifetimes of the hydroperoxy radicals, presumably the trapping in this system would involve blocking their propagation, usually by the radical abstracting a hydrogen.

The various inhibitors tried in the reaction were all known for inhibiting qualities in various radical reactions. The different types of inhibitors were chosen to prove that many common radical inhibitors inhibited the reaction and that the inhibition was not due to a specific interaction with the particular inhibitor. The results of changing inhibitors also proved interesting in light of indicating the reactivity of DHA. In octane solutions the inhibitors DBPC, HMBP, and DBHQ showed essentially the same inhibiting effectiveness. The last had plots which were somewhat irregular, particularly in initial rates, and seemed to cause the reaction to absorb about 25% more oxygen

than usual. 1-Dodecanethiol and p-quinone were not inhibitors, but instead initiators and co-reactants. In xylene solvent, DBPC and HMBP showed very similar inhibitory properties.

Another interesting aspect of the inhibition concerns the number of radical chains inhibited per molecule DBPC. In the study of the rate of loss of DHA versus the rate of loss of DBPC using concentrations of .294 and .039 molar, respectively (see appendix for graph) it was found that $-\frac{d[DHA]}{dt} = .966 \times 10^{-3}$ mole/ℓ min and $-\frac{d[DBPC]}{dt} = .244 \times 10^{-3}$ moles/ℓ min. The inhibition, therefore, seems to be operating in a consistent ratio of 4 moles of DHA consumed per mole of DBPC. The reactions of DBPC as an inhibitor have been studied previously in detail to determine both the number of radical chains inhibited per molecule DBPC and the actual inhibition mechanism. Various workers making these studies have shown the reaction to be quite variable as well as mechanistically interesting.[41,42] Their work showed the reactions of the inhibitor to be those shown in Figure 6. The reactions in Figure 6 are self-explanatory. DBPC radicals react with each other forming the end products V and VI with regeneration of some DBPC. If DBPC is in excess, product V is formed in largest quantity. Formation of V involves the overall consumption of two DBPC with the liberation of two H·. If DBPC is not in great excess, more of product VI is expected. The degree to which V may react with radicals and ultimately form VI was not discussed. It may be mentioned however, that for each molecule of VI formed, six hydrogens were liberated, meaning six radical chains terminated. The number of radicals captured by DBPC can therefore vary from one to three per molecule. Since at most three

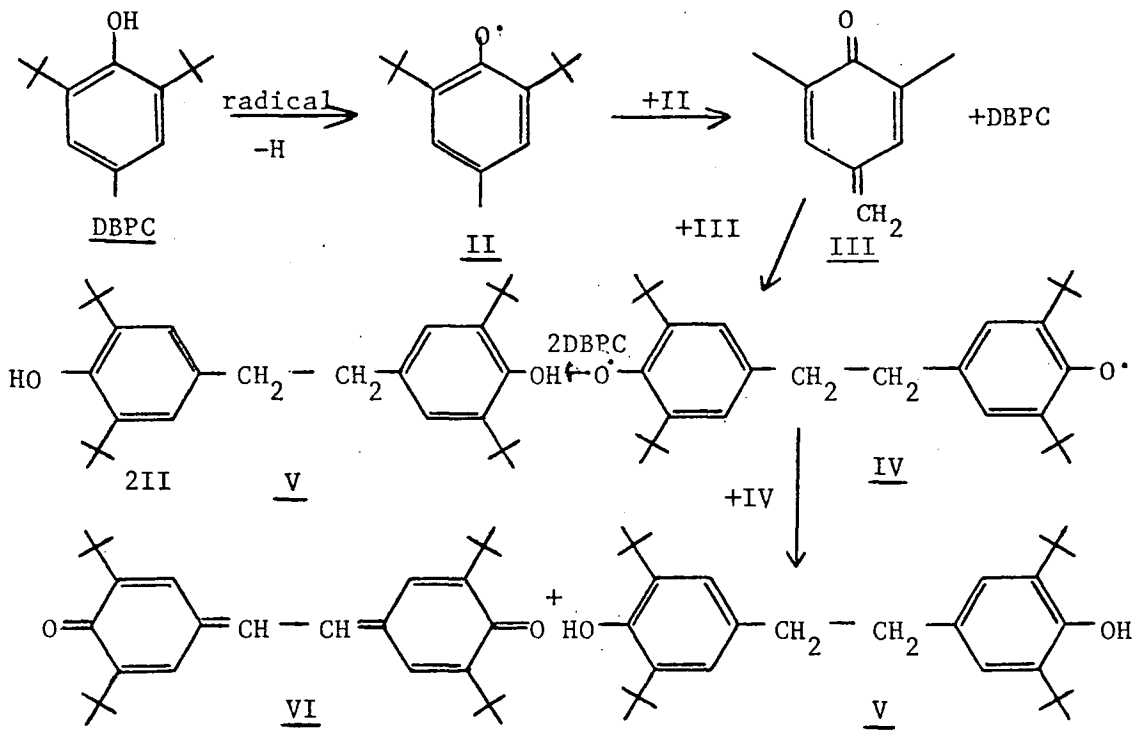


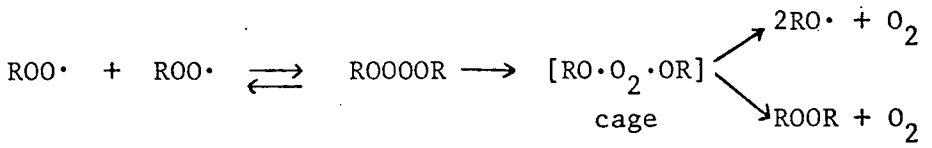
Figure 6. Mechanism of Radical Inhibition by DBPC

chains are stopped per inhibitor molecule, the termination of all the radical chains produced by the four DHA molecules per molecule DBPC certainly cannot be due entirely to the inhibitor.

The inherent difficulties in studying the products unfortunately led to less useful information concerning the nature of the reaction than desired. The major problem with the product studies was the fact that the methods of purification and detection of the products caused product decomposition. These involved the passage of the crude material through a Florisil column during the purification. This step

probably did not cause any decomposition of peroxy material because Florisil has been shown to be mild and has been used before to separate t-butyl peresters from t-butyl hydroperoxide (fate of the latter material not mentioned).[63] Since peresters are less stable than peroxy compounds, the latter surely survived the process; however, hydroperoxy compounds are much less stable than either, and may have decomposed on the column. The critical factor concerning peroxy material came with the detection of the products. This involved passage through a v.p.c. Carbowax column at 200°C. Polyperoxyadamantane has been shown to explode at 160°C and surely could not have survived the high temperature.[39] Once hydroperoxy or peroxy material decomposes on the column it was seen to be mainly absorbed irreversibly on to the column.

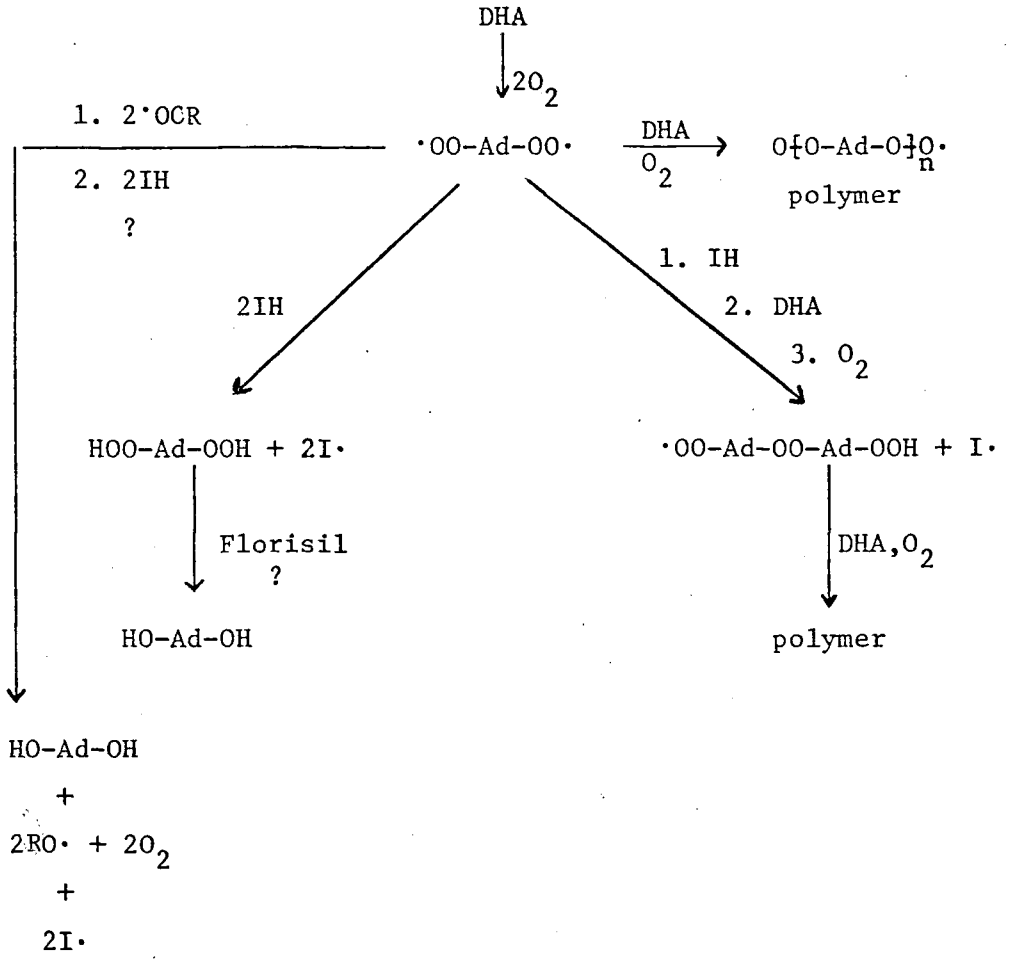
Because of peroxy and hydroperoxy decomposition on the columns, the product study was less informative than desired. The few remaining products which were stable turned out to be the expected reaction products from DBPC plus some 1,3-dihydroxyadamantane and a small unidentified bicyclic compound. The exact origin of the adamantane products cannot be known. The 1,3-dihydroxy compound may have been formed in the reaction flask by the reaction of two hydroperoxy radicals followed by hydrogen abstraction, or else by hydroperoxide decomposition on the Florisil column. A third possibility, the decomposition of hydroperoxide in the reaction flask itself can be pretty well ruled out at room temperature as has been well confirmed several times.[64] The first possibility, the reaction of hydroperoxy radicals, has been studied in detail by Ingold.[65a,b] He has shown the reaction to occur via the tetroxide and its decomposition to the two caged radicals.



The radicals formed quite frequently escape the cage to become free alkoxy radicals. If adamantane alkoxy radicals were formed, they could abstract hydrogens from DBPC to form the dihydroxy product. The possibility of decomposition of 1,3-dihydroperoxyadamantane on Florisil could also be very likely in light of the fact that the very polar solvent acetone was required to elute the column.

The evidence concerning the mechanism of DBPC inhibition of the DHA-O_2 reaction is not conclusive, but does allow some speculation. Figure 7 shows some possible explanations of the observations. If the inhibitor was actually inefficient and could not trap all of the peroxy radicals, then significant amounts of polymer would form despite the inhibitor. The polymeric chain would of course be smaller as expected and the rate would be decreased. The ratio of four DHA molecules reacted per DBPC would be a result of the incomplete inhibition. The observation of 1,3-dihydroxyadamantane as a product would arise from one or both of the pathways shown with question marks.

The observations of the reactions of DHA and oxygen in the presence of thiol or quinone may be partially explainable in light of the various reactions which occur subsequent to initiation of the reaction. It was observed that in both cases the initial rate of oxygen absorption shot up drastically and stayed at a rapid rate until

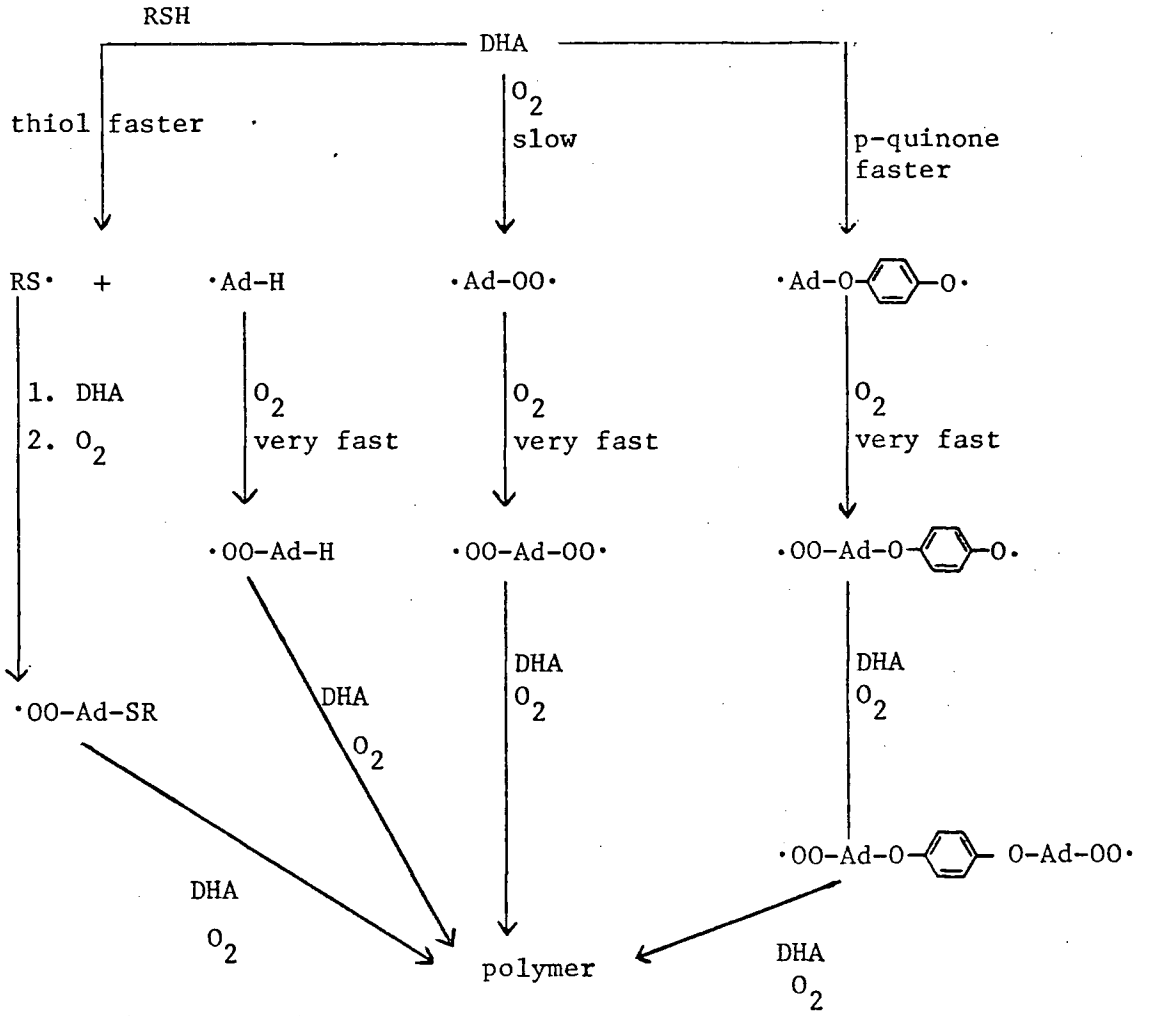


IH = DBPC, R = 1-adamantyl or polymer chain

Figure 7. DHA-O_2 Reactions Occurring in the Presence of DBPC.

the thiol or quinone was consumed. After that the reaction became more normal. This factor of up to six-fold rate increase (k_1 = 32.8 x 10^{-5}_{xylene} versus 209 x 10^{-5}_{xylene}) in the case of quinone could be due to the quinone reacting with DHA to form radicals. These radicals in turn prefer reaction with oxygen over reaction with quinone. Due to this competition most of the initiator only reacts with one of the DHA radicals, the other radical absorbs oxygen to give the rapid rate observed.

With this mechanism it would be expected that somewhat less oxygen would be absorbed, as is the observation. Figure 8 indicates qualitatively what may be occurring. The quinone reaction would most likely form

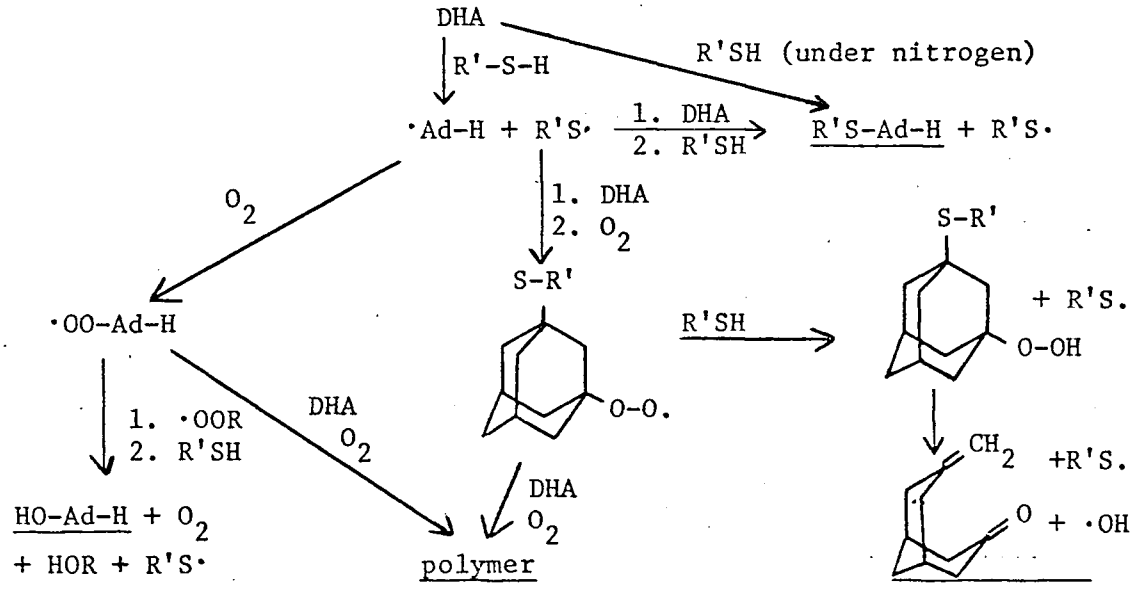


R = 1-dodecane

Figure 8. DHA-O_2 Reactions in the Presence of 1-Dodecanethiol and p-Quinone.

the complex of adamantane bonding to the oxygen of quinone,[66] leaving a molecule with two radical ends which can only react with further DHA. The thiol reaction would probably occur by donation of a hydrogen to DHA and thereby initiating one chain. The RS· would then attack another DHA, initiating the second chain. This somewhat oversimplified argument shows how essentially the same end products result in all cases and that the major difference in the rate is caused by the rapid initial reaction of DHA with thiol or quinone rather than with oxygen.

The product studies using thiol with DHA and oxygen also tend to support the pathway in Figure 8. The products (other than polymer or hydroperoxide) that were formed were 1-hydroxy adamantane, 7-methylene-bicyclo[3.3.1]nonan-3-one and the same product as that observed in the reaction of DHA and thiol under nitrogen (or one very similar). The products would arise by the scheme in Figure 9. The major products



R = adamantyl or polymer

R' = 1-dodecanyl

Figure 9. Possible Explanation of DHA-O_2 + RSH Reaction Products.

are underlined. As expected, because they follow secondary routes, the quantities of 1-hydroxyadamantane and the bicyclononane were small. Apparently the competition for hydrogen transfer from thiol to adamantyl radical versus oxygen addition is fairly good because substantial quantities of the sulfide were found in addition to the major polymeric product.

In analyzing the potential of the DHA system it is seen that the material may be suited for several practical uses. First of all the thermal polymer could if industrial techniques are perfected find wide use in the plastics field. Perhaps the liquid material could be squeezed into a cold mould, then heated to 150° quickly and removed as an extremely hard and rigid, highly temperature stable, solvent resistant material. These properties would result from the inherent rigidity and stability of the parent adamantane monomers in the polymer. The other potential of the system is for studying radical ring openings and closings in cyclopropane systems. If there is a true equilibration of two distinct species (ring opened biradical and ring closed) this would be unique among 3 membered rings. The system does, however,have numerous complicating factors in studies of this type which must be overcome first.

EXPERIMENTAL

Infrared spectra were taken on a Perkin-Elmer 137 Sodium Chloride Spectrophotometer. Any special methods of sample preparation and solvents used will be mentioned. Symbols referring to stretch intensity are (s), strong; (m), medium; and (w), weak.

Proton Nuclear Magnetic Resonance Spectra were obtained by a Varian A-60 spectrometer unless otherwise specified.

Differential Scanning Calorimetry was carried out using a Perkin-Elmer model DSC-1B.

Analytical vapour phase chromatography (vpc) was carried out on a Perkin-Elmer 900 Gas Chromatograph using either a 1/8" x 6' OV-17 8% AW-DMCS, Chromosorb W, 80/100 mesh column (abbreviated OV-17), a 1/8" x 6' K-20M 20% Carbowax, Chromosorb W 80/100 mesh column (abbreviated as Carbowax), or a SE-30 1/8" x 6' 8% AW-DMCS Chromosorb W 80/100 mesh column (abbreviated SE-30). All programs were run at a flow rate of approximately 50 ml/min. Vpc specification will be written shorthand: an example is (80°/6 min $\xrightarrow{32°/\text{min}}$ 200°C), which means that the column is at an initial temperature of 80°C for 6 minutes and then is heated at a rate of 32° per minute until it reaches 200°C, where the temperature is maintained.

Preparative vpc was done on a Varian Aerograph, Model 90-P using either a 1/4" x 5' 10% Carbowax 20M, Chromosorb W 80/100 column

or a 3/8" x 10' Carbowax 20M 60/80 Chromosorb W column.

Synthesis

Synthesis of 1,3-Dibromo-5,7-dimethyladamantane*

Vpc analysis of the filtered products gave a yield of 95% DBDMA, less than 2% monobromination product, and the rest as small impurities. Recrystallization from hexane yielded the white crystalline product in excellent purity. M.p. 115-116 °C. IR (in CCl_4) (cm^{-1}); 2940 (s), 2880 (shoulder), 1450 (s), 1160 (s); (in nujol): 830 (s), 715 (s); n.m.r. (benzene): 0.65 (s)(6H), 0.77 (s)(2H), 1.75 (s)(8H), 2.70(s)(2H).

Anal. Calcd. for $C_{12}H_{18}Br_2$: C, 44.75%; H, 5.63%. Found: C, 44.69%; H, 5.54%.

Synthesis of 1,3-Dihydro-5,7-dimethyladamantane

A 250 ml 4-neck flask was fitted with a nitrogen inlet, a $CaCl_2$ drying tube, a mechanical stirrer, and a dropping funnel for slow addition of liquids. The flask was then charged with 125 ml of untreated (Mallinckrodt) absolute diethyl ether, 3.2 g of 4:1 Na°-K° alloy, and 20 ml of dry triethylamine (dried over $CaCl_2$ and distilled from sodium pellets). 1.5 g of DBDMA in 10 ml ether were added dropwise over a period of 10 minutes. After stirring for 2 1/2 hours, qualitative vpc analysis using carbowax (80°/6 min $\xrightarrow{32°/min}$ 200°) showed the reaction to be complete with a product distribution of

* The preparation of the crude dibromide was done by K. Waldman, a summer undergraduate research assistant. For the basic procedure of synthesis see the section under Synthesis of DBA.

85% DHDMA, 5 to 10% DMA, and 5 to 10% for the combined minor impurities. No DBDMA was remaining.

Characterization of DHDMA was accomplished via first purification on preparative vpc using the 1/4" Carbowax column and a temperature of 150°C. The center fraction coming off the column was trapped in a long open-ended capillary tube which was packed on the outside with dry ice. Immediately upon completion of collection, the ends of the tube were drawn out and sealed by flame. Corrected melting points of these samples ranged from 41° to 45.5°C, with the best melting at 44.0-45.5°C. Several samples were then collected, dissolved in benzene, and placed in an n.m.r. tube. Successive freeze-thawing, followed by flame-sealing preserved the sample for analysis on the Varian HA-100 N.M.R. The spectrum obtained gave: δ 0.91 (s)(6H), 1.01 (d, 10 cps)(4H), 1.47 (broad)(2H), 1.60 (d, 10 cps)(4H), 1.93 (s)(2H). Due to rapid reaction of DHDMA in solution the infrared spectrum was obtained by dissolving the material from the melting point capillaries in CCl_4 and immediately running one-quarter of the spectrum. The process was repeated three times to obtain an entire spectrum. Absorptions were (in cm^{-1}): 3030 (shoulder), 2900 (s), 1445 (s), 1360 (m), 1280 (m), 890 (m). The absorptions at 3030 cm^{-1}, 1280 cm^{-1}, and 890 cm^{-1} quickly disappear if the material was allowed to sit in air or allowed to remain for several minutes in CCl_4. A sample for mass spectral analysis was prepared by collecting a capillary from the vpc, checking its melting point, and then breaking off the capillary ends and placing it in a special evacuated attachment for the mass spectrograph. The analysis showed peaks at m/e^+ of 485 and 324,

indicating the presence of dimers and trimers. Other fragments fell at m/e^+ of 164, 163, 162(parent), 149, 107, 93, and 44.

Ultraviolet analysis was attempted in heptane on the Bausch & Lamb Spectronic 502, but showed no absorptions above 210 mμ as expected. An electron spin resonance analysis was also performed on a sample of DHDMA in thoroughly degassed hexane. The e.s.r. (Varian E-3) failed, however, to show any signs of a radical.

Thermal Polymer of 1,3-Dehydro-5,7-dimethyladamantane

Sealed capillaries collected from the vpc and melting at above 41°C were thermally polymerized in the oil bath of a melting point apparatus. The liquid DHDMA would begin to irreversibly polymerize at 90°C as indicated by a whitening which could not be reversed by cooling. By 125°C (heating at a rate of approximately 5°/min) the polymerization was essentially complete, yielding a hard white amorphous material. The polymer was extremely stable and insoluble in any solvent tried.

Crystal and phase properties of the polymer were studied by X-ray analysis and differential scanning coulometry. The X-ray study was made on powdered samples in very finely drawn glass thin-walled capillary tubing and exposed for 21.5 h on a G.E. powder camera. The powder technique was used because no single crystals could be obtained. None of the numerous samples gave any sharp diffraction lines or patterns as would be expected from a structured material. Differential scanning was done both in air and under nitrogen and at heating rates of 40° per minute and 80° per minute on ranges of 16, 8, and 4.

Blank samples of lead were used for temperature calibration. On all the above settings, the polymer under nitrogen had no deviations in the baseline up to the temperature of 773°Kelvin (machine maximum) and recorded only a gradual baseline drift. During this entire time, the sample remained visibly the same, with no melting, change of colour, etc. The polymer, when analyzed in air, again had no baseline deviations until a temperature of approximately 690°K at which time the line gradually began to curve upward, the slope increasing until a maximum of 728-735°K, after which it dropped off quickly. Visibly the samples maintained their whiteness up to 690°K where they started turning yellow, the colour deepening with heating until the material was entirely black at 750°K.

In order to obtain a microanalysis, vpc-collected and sealed samples melting at 43° and above were polymerized for 24 hours at 160°C. The ends were then broken, the samples pumped under vacuum for several hours to remove potential impurities (adamantanes generally sublime readily), and the polymer removed with great difficulty from the tube by scraping it out with stiff steel wire.

Anal. Calcd. for $(C_{12}H_{18})_n$: C, 88.82; H, 11.18. Found: (A) C, 85.98; H, 10.82, and normalized to 100%: C, 88.82; H, 11.18. (B) C, 87.94; H, 11.19; and normalized to 100%: C, 88.61; H, 11.39.

Synthesis of Poly-1,3-peroxy-5,7-dimethyladamantane

Co-polymerization with oxygen of an ethereal solution of DHDMA (prepared as previously described) was accomplished by bubbling air through the sample. Almost immediately a whitish material precipitated

After several hours of reaction the ether was driven off and the polymer's solubility checked. It proved insoluble in any ordinary solvent except benzene and other aromatics, where its solubility was limited. The material was then washed several times with pentane and ether and dissolved in benzene for vpc analysis. The polymer could not be detected either on analytical or preparative columns (Carbowax, OV-17, SE-30). The washings of the polymer were analyzed on Carbowax and found to contain the same impurities as those in the starting solution of DHDMA, plus 1,3-dihydroxy-5,7-dimethyladamantane as identified by comparison of an authentic sample (Sunoco X924-47B) and one other small unknown impurity. Because of the polymeric nature of the material and its insolubility, no spectral data were obtained. Microanalysis was omitted because the analyst claimed previous samples of poly-1,3-peroxyadamantane were difficult to analyze due to peroxide explosions. Identity was mainly based on the similarities of the polymer to known properties of the peroxypolymer of DHA.

Synthesis of 1,3-Dibromoadamantane

A 200 ml 3-necked flask was assembled with a slow mechanical stirrer, a large, efficient, water-cooled condenser, and an inlet for N_2. The flask was dried by passing a cool flame over the glass surfaces while purging with nitrogen. The flask was then charged with 20 g adamantane and 40 ml of pre-dried (with 20 ml concentrated H_2SO_4) bromine and cooled on ice for 15 minutes. 100 mg of aluminum bromide (BDH 27071) were added, causing a violent reaction as evidenced by evolution of large quantities of white HBr vapours. After 30 seconds the reactions and evolution of vapour slowed, at which time the flask

was removed from the ice bath and was stirred for 2 hours. By this time all visible evolution of HBr had ceased. The flask was then again cooled on ice and another 200 mg of aluminum bromide added. When the reaction again slowed, the flask was placed in a 35° bath and very slowly heated to 45-50°C over a period of about 1 1/2 hours. The temperature was maintained there for 1/2 hour. To work up the reaction, the flask contents were poured into 100 ml of CCl_4 and 200 ml of ice. With good stirring, $NaHSO_3$ and ice were added so as to keep the temperature at all times below 15°C. When all colouration disappeared, the CCl_4 layer was taken off, neutralized, and dried over $CaCO_3$. CCl_4 was then removed by rotatory evaporation and the dibromide recrystallized from hexane. The product was analyzed by vpc on OV-17 at 210°C. Retention times were 2.2 minutes for 1-bromoadamantane, 3.3 minutes for DBA, and 7.8 minutes for 1,3,5-tribromoadamantane. Crude vpc analysis gave 95% DBA with very little mono- or tri-substituted material. Recrystallization gave 33.9 g (78.4% yield) of very pure DBA with m.p.: 108.5-110°; literature: 108°,[46,47] 112°.[35] IR in nujol gave absorptions at (in cm^{-1}): 1335 (m), 1315 (m), 1280 (s), 1020 (s), 820 (s), 692 (s) and in CCl_4, at: 2910 (s), 1445 (s). The n.m.r. in benzene gave absorptions at: 1.22 (t)(1H), 1.70 (broad(1H), 2.06(4H), 2.85 (1H); literature[67] (benzene): 1.24 (2H), 1.88 (2H), 2.09 (8H), 2.79 (2H).

Synthesis of 1,3-Dihydroadamantane

A. 2.0 g of DBA, 250 ml of anhydrous diethyl ether, 2 g of dried KBr (200° for two hours), and 2.5 g of liquid 4:1 sodium-potassium alloy

were placed in a pre-dried and well nitrogen-purged 4-neck flask. The flask was fitted with a nitrogen inlet, a drying tube, a high speed stirrer (Lab Line Instruments, Inc., 1285 stirrer), and a stoppered neck for addition or removal of samples. Care was taken to maintain an air-free system and to keep the alloy suspension well-stirred. The reaction proceeded slowly at first, but after 2 1/2 hours analytical vpc analysis on Carbowax (80°/6 min $\xrightarrow{32°/min}$ 200°C) showed only DHA in about 90% purity with no starting material (DBA). The impurities present were adamantane (5%), 1-hydroxyadamantane (trace), 1-bromo-adamantane (trace) and several small unidentified compounds.

B. 2 g of DBA, 100 ml anhydrous ether, and 3.5 ml of hexamethyl-phosphoramide (Fisher H343), dried over 5A molecular sieves (BDH), were placed in a 200 ml 3-neck flask fitted with a magnetic teflon-coated stir bar, a nitrogen inlet, a calcium chloride drying tube, and rubber septum-capped stopper. The reaction vessel and its contents were cooled in a bath to -30°C to -40°C, 10 ml of n-butyl lithium in hexane (Foote, 1.6 Molar) were then added over a period of 10 minutes via a syringe through the rubber septum. Upon completion of addition, the flask was removed from the cold bath, allowed to warm to room temperature (1/2 hour), and washed with three 10 ml aliquots of oxygen free distilled water (boiled two hours). The final ether solution was dried while still under nitrogen over $MgSO_4$. Identity and purity were confirmed by analytical vpc retention time comparisons with results of known samples. The DHA purity by this analysis was greater than 95% with no DBA or adamantane present and only traces of 1-bromoadamantane

plus a few unknown impurities. Since DHA had been identified and well characterized in the lab previously,[39] no further identification was made.

Radical Studies

DHA Reaction with Nitric Oxide Radical

A 250 ml 3-neck flask was fitted with a rubber septum capped stopper, a gas outlet line leading to a mineral oil bath (to prevent back entry of air), and a fritted gas dispersion tube inserted below the liquid level in the flask. The system was purged with nitrogen for 20 minutes, charged with a freshly prepared ethereal solution of DHA (from 1 g DBA in 50 ml ether), and placed in a dry ice-acetone cold bath. When the vessel was cold, nitric oxide (Matheson), purified by passage through a dry-ice-acetone-cooled glass-bead-filled U tube, was passed slowly through the system for two hours. The solution rapidly became a bluish-yellow, a colour which disappeared as the flask was allowed to slowly warm to room temperature while being purged with nitrogen.

Vpc on Carbowax showed no DHA remaining after the reaction; however, no useful information concerning the products could be obtained. Changing columns to SE-30 did not make an improvement. Thin layer chromatography (TLC) in chloroform showed four major products, the two largest of which, unfortunately, could not be separated on alumina (Merck 1090) or on Florisil (Floridin Co. F-3938). The quantities of the smaller elutable products were not enough to be analyzed and were impure, while the larger products were non-elutable, being irreversibly adsorbed on the column. I.r. spectra of these smaller

products did, however, indicate the potentiality of nitrogen-oxygen bonds: Absorptions at (cm^{-1}) 1600(s), 1500(s), 1300(s), and 860(s). Several attempts to repeat the reaction by modifying it, or by adding lithium aluminum hydride (and refluxing before exposing to air) failed to give any more determinable products. The new products gave similar difficulties in separation and identification. The study was therefore discontinued.

DHA Reaction with Galvinoxyl Stable Free Radical

0.062 g of galvinoxyl stable radical (0.145×10^{-3} moles) were dissolved in 15 ml heptane and kept under nitrogen in a flask. Its reaction with DHA was followed by adding 0.36×10^{-3} moles of DHA in 2 ml o-dichlorobenzene and observing the change in the deep purple colour of the solution. The colour began to fade very rapidly, becoming a faint brownish-yellow by 26 minutes. At this time more DHA was added, affecting no further colour change. A control run in air using the same solvents retained the initial colour for the 12 hours observed.

Purification of Solvents

Benzene: Reagent benzene was shaken five times with H_2SO_4, once with $NaHCO_3$, once with water, and dried over $MgSO_4$. Final purification was accomplished by distillation and collection of the centre fraction.

o-Dichlorobenzene (Eastman 494): 2 liters of o-dichlorobenzene were shaken five times with conc. H_2SO_4, once with water, and dried overnight over $CaSO_4$ and MgO. The dried reagent was distilled, the

middle 1 liter fraction being kept and stored over 5A molecular sieves.

n-Heptane (Eastman 2215): Purification consisted of shaking three times with conc. H_2SO_4, once with 10% $NaHCO_3$, once with water, and drying over $MgSO_4$.

n-Octane (Phillips Petroleum 1454 Technical grade): Approximately 1 liter of octane was shaken three times with conc. H_2SO_4, once with Na_2CO_3, once with water, and dried over $MgSO_4$. The middle fraction of the distillate was collected for use.

Xylene: A mixture of (approximately 90% para) xylenes was shaken three times with conc. H_2SO_4, once with Na_2CO_3, once with water, and dried.

Purification of Inhibitors

2,6-Di-t-butyl-p-cresol (Eastman P5917): The crude yellow cresol was distilled at 100-105° under vacuum, removing it from the coloured materials. The distilled material was then further purified by recrystallizing twice from methanol followed by drying for one-half hour at 50° under vacuum (m.p. 69-70.5°C; literature:[68] 70°).

2,5-Di-t-butyl hydroquinone (Eastman P5681): The crude yellow hydroxyquinone was washed with a small quantity of methanol to remove most of the colour and then was recrystallized once from methanol. Final purification was accomplished by recrystallizing three times from benzene (m.p. 214-215°; literature[69a]: 213-214°).

4-Hydroxymethyl-2,6-di-t-butyl-phenol (Ethyl Corporation 754): The free sample was considered pure as given.

1,4-Benzoquinone (Eastman P220): The quinone was purified by vacuum sublimation, followed by recrystallization twice from tetrachloro-

ethylene (m.p. 112-114°; literature[69b]: 115-116°).

1-Dodecanethiol (Aldrich D22,140): The bottled reagent was used directly.

Preparation and Standardization of Solutions

All the solutions of adamantane and of the inhibitors were made by placing a precise amount of material in a volumetric flask, filling to the line and shaking. Table II lists the pertinent data and the final concentrations of these standard solutions.

The preparation of DHA standard solutions involved first the preparation of the oxygen free solvents. These were prepared by taking a 50 ml, 2-neck, clean and dry flask and fitting it with a stopcock on one joint and a stopper on the other. The flask was next filled to within 90% of the possible volume with the chosen purified solvent. With the joints well greased, the solvent was degassed (including any water present) by evacuating to just above the vapour pressure of the solvent and pumping for 1/2-3 hours. Preparation was then complete after purging the system with nitrogen and sealing it while still under nitrogen.

The next step was to prepare the DHA. This was done by the n-butyl lithium process and using 2 g of DBA to 50 ml ether. The water washed ethereal solution from this reaction was cooled in a refridgerator before its final purification by sublimation. The sublimation was carried out under vacuum in the specially designed apparatus illustrated in Figure 10. The system (as drawn minus the flask and stirbar) was

Table II Concentrations of Adamantane and Inhibitor Solutions

Solute (mole wt.)	Wt. (g)	Solvent	Volume of Flask (ml)	Molarity
Adamantane (136.24 g/mole)	1.3616	benzene	100	.100
	.4390	"	"	.030
	.1364	"	"	.010
	.4420	"	10	.324
	.8840	"	"	.648
DBPC (220.34 g/mole)	.5611	heptane	25	.1037
	2.7657	n-octane	"	.5015
	1.0954	xylene	50	.0981
	2.552	n-octane	25	.462
HMBP (236.3 g/mole)	.2383	"	100	.0101
	1.1750	xylene	50	.0994
DBHQ (222.32 g/mole)	.1360	"	2	.304
p-Quinone (108.1 g/mole)	.1340	n-octane	50	.0248
	1.0414	xylene	"	.1929
1-Dodecanethiol (220.4 g/mole)	.5524	n-octane	25	.2502
	.5579	xylene	"	.2530

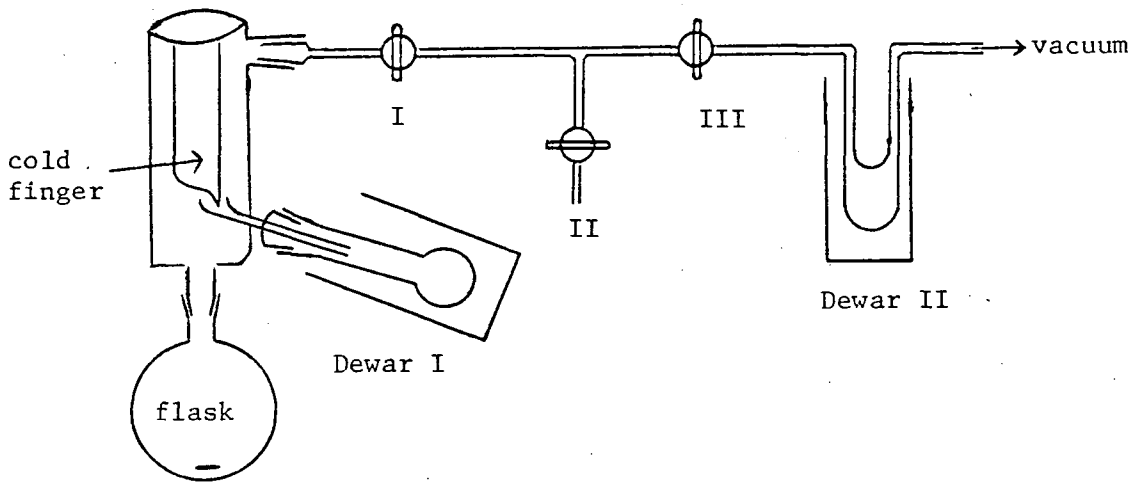


Figure 10. DHA Sublimation Apparatus.

operated by first filling dewar II with liquid nitrogen, turning on the vacuum pump, closing stopcocks I and II, opening III, and by then placing the flask (with stirbar) containing the cold freshly decanted DHA solution on the apparatus. The magnetic stirrer was then turned on and stopcock I quickly turned past the open position several times to draw out the air in the system, yet not to cause excessive bumping on the ether. Immediately after, with the stopcock closed, dry ice and acetone were placed in the cold finger and liquid nitrogen was placed in dewar I. Next the vacuum is controlled via stockcock I to draw, without bumping, the ether onto the cold finger from which it flows into the flask in dewar I and is frozen. When all the ether was frozen, about 15 minutes, the stirring was stopped, the system was opened, the collecting flask in the dewar was quickly replaced with a small flask (simply to maintain the closed system), and the system was sealed off by closing stopcock I and a hot water bath

was placed under the sublimation flask. The system was closed because sublimed DHA will also sublime off the cold finger, even at -78°C, and into the trap, if the vacuum is pumping. The water bath was heated to 70°C and maintained at that temperature until sublimation was complete (1 to 2 hours).

The transfer of the DHA to the prepared and sealed storage vessel was done by first warming the cold finger to room temperature (to prevent water condensation) and then breaking the vacuum and removing the cold finger. The transfer of the DHA from the cold finger to the storage flask was accomplished by "washing" the DHA into the storage flask, by use of a pipette, and the solvent from the flask. All during this time nitrogen was purging the system. For a typical standard solution of DHA, anywhere from four to eight preparations of DHA were required.

All DHA solution concentrations were determined by comparative vpc quantitative analysis. This was done by comparing the areas under the DHA peaks with the areas under peaks of standard adamantane solutions. For these comparisons all instrumental settings and sample injections were identical. The determination of area was done by the cut out-and-weigh method; making the assumption that 1 molecule of DHA would yield the same area under the curve as a molecule of adamantane. For each solution, anywhere from three to eight samples were compared, the number depending on the reproducibility of areas. The column was Carbowax at 80°C. Table III gives the solution concentrations of the various standard solutions obtained by this method. The error values are a reflection of the inherent non total reproducibility of the vpc technique.

Table III: DHA Standardized Solutions for Kinetics.

Solvent	Molarity	Error
Heptane	.099	3%
Octane	.273	2.5%
"	.148	3%
"	.345	7%
Xylene	.475	5%

DHA Reactions with Oxygen

The apparatus used is illustrated in Figure 11. To prepare for operation, the large neck of a 50 ml 2-neck flask containing a magnetic stirbar was connected to the apparatus, and the smaller neck was stoppered with a rubber septum capped stopper. A magnetic stirrer with a styrofoam pad holding a large beaker of ambient temperature water was then elevated from under the system. The system was then alternatively evacuated and filled with pure oxygen. An oxygen bleed off device was attached to the line to keep the system closed to air during this time. The mercury in the manometer was then leveled, the volume on the graduated column read, the desired quantity of inhibitor solution injected through the septum and the stirrer turned on. After ten minutes were allowed for equilibration (though no further volume change in the system could be detected after 30 seconds) the mercury was leveled, the stopcock on the top of the manometer was closed, the temperature and pressure were recorded, and the reading on

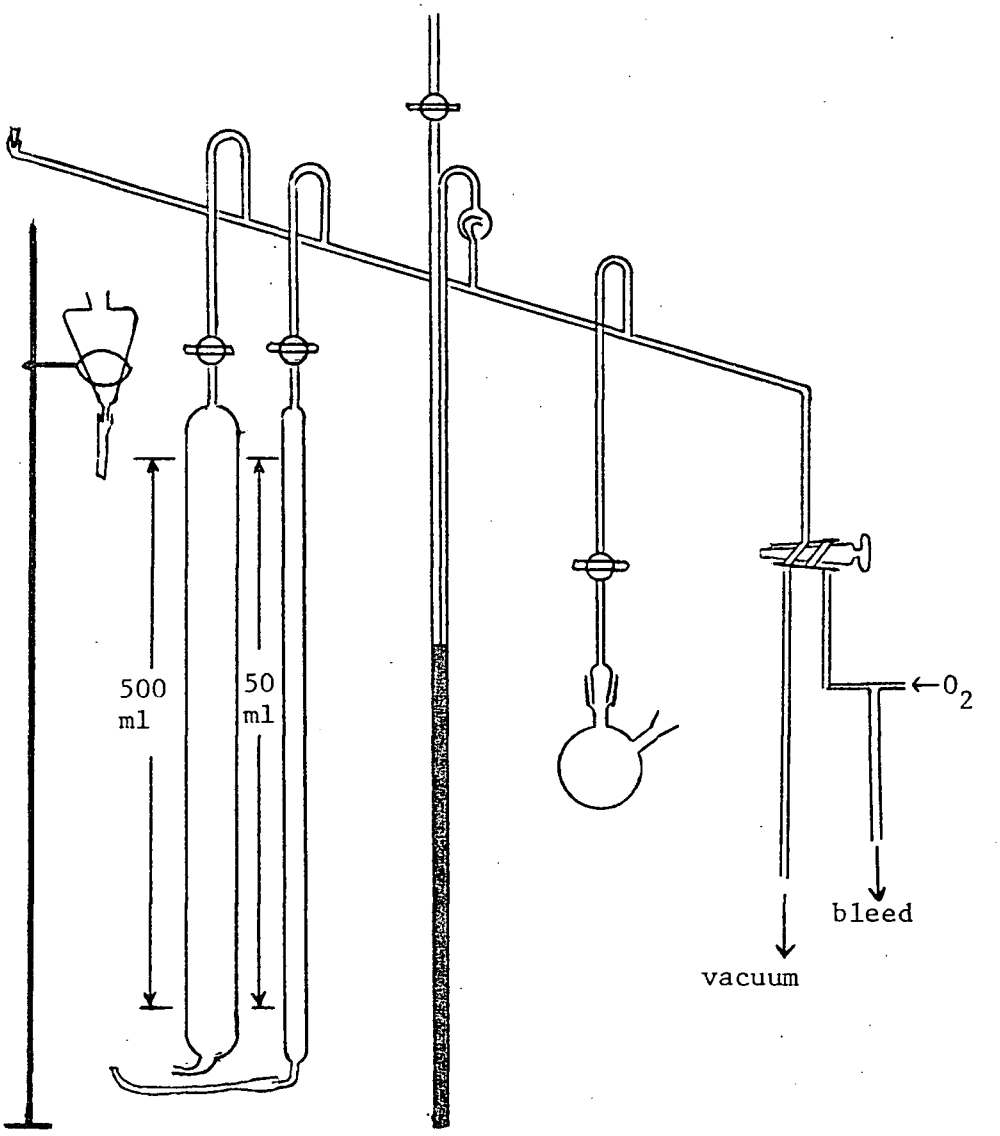


Figure 11. Kinetic Apparatus.

the graduate was taken. At this point the system was ready for the DHA which was injected into the flask while the stirring was stopped. Immediately upon removal of the syringe the timer was activated, the mercury leveled for the reading of the initial volume of the system, and the stirrer turned on. For the first half (approximately) of the reaction readings were taken every five minutes; after that, ten minutes or longer, as was necessary. Most runs lasted only 400 to 500 minutes, after which the system was left overnight for the final reading - usually at about 1300 minutes.

The technique for analysis of the kinetic data was based on the assumptions that the internal pressure of the system is constant (because stopcock D maintains the pressure in that tube of the manometer the same as the initial pressure), that the Ideal Gas Law was a suitable approximation, and that the temperature stayed constant (experimentally the water bath temperature seldom varied more than 1 to at most 2 degrees during a run). The initial reading of the volume (V_o) of the system was taken as the standard for 100% pure, unreacted DHA and the total difference (ΔV_T) between V_o and the final reading (V_∞) was taken to be the value for 100% reaction of DHA.

Vpc analysis, furthermore, showed absolutely no detectable quantities of DHA remaining after 600-800 minutes, regardless of the particulars of the run. The difference (ΔV_t) between V_o and the volume at a give time (V_t) when subtracted from the total volume change (ΔV_T), gave the amount of unreacted DHA. Kinetic first order plots were obtained in the usual manner by plotting the logarithm of the initial concentration of DHA over the concentration at time t versus time

($\log \frac{\Delta V_T}{\Delta V_T - \Delta V_t}$ vs t). The rate constant of reaction was obtained by multiplying the slope of the line by 2.303.

A second method of determining the kinetic plots was the analysis on the vpc (Carbowax 80°/6 min $\xrightarrow{32°/min}$ 200°) of the relative amounts of DHA present at time t versus the total amount of DHA initially. Because of minor deviations in sample injection sizes and the inherent non-total reproducibility of the apparatus, this technique was somewhat less precise. It did, however, allow for co-measurement of the rates of loss of both inhibitor and DHA. All these vpc comparisons were done by the cut-out-and-weigh technique (simple measurement of the peak heights was too inaccurate to be valid). Table IV lists the experimental quantities used in the individual kinetic determination.

DHA Reaction with 1,4-Benzoquinone under Nitrogen

The same apparatus that was used to measure oxygen uptake with DHA was used to totally exclude oxygen from the reaction of DHA with p-benzoquinone. The same 50 ml 2-neck flask with rubber-septum-capped stopper and containing a stir bar was again placed on the system. The system was then alternatively evacuated and filled with nitrogen for a total of eight repetitions. Ten ml of quinone in xylene (1.929×10^{-3} moles) were injected into the system, the volume was measured, and 3.1 ml of DHA in xylene (1.5×10^{-3} moles) were injected. After briefly mixing, a sample was removed and analyzed on the vpc (Carbowax 80°/6 min $\xrightarrow{32°/min}$ 200°C). By this time both the DHA and the quinone peaks had already shrunk and a new peak had appeared.

Table IV. DHA-O_2 Reaction: Experimental Quantities

Moles DHAx10^3	[DHA]	Inhibitor added	Moles inhibitor x10^3	[I]	Solvent	°C	ml O_2 absorbed (at STP)
.69	.086	-	-	-	n-heptane	19	21.4
.64	.056	DBPC	.52	.045	"	19.0	21.4
1.5	.231	-	-	-	n-octane	20	39.5
"	.158	DBPC	1.50	.158	"	20	41.2
"	.188	"	.75	.084	"	19.5	40.1
"	.081	"	6.00	.324	"	19	43.3
"	.205	"	.375	.051	"	20	42.3
1.18	.125	"	.188	.020	"	20	32.9
1.46	.254	"	.125	.022	"	22	43.4
"	.238	"	.206	.035	"	22	39.6
1.50	.262	"	.0625	.011	"	22	45.5
"	.174	HMBP	.706	.092	"	22	38.6
"	.061	p-quinone	.50	.020	"	22	43.5
"	.174	DBHQ	.743	.086	n-octane	22	45.2
"	.484	-	-	-	xylene	22	39.9
1.50	.185	DBPC	.50	.062	"	22	41.4
"	.278	"	.250	.045	"	22	43.3
"	.345	"	.125	.029	"	22	42.0
"	.326	HMBP	.25	.054	"	22.5	40.2
"	.345	"	.125	.029	"	22	41.4
"	.185	"	.50	.062	"	21	43.8
"	.326	p-quinone	.482	.105	"	21	30.1
"	.294	DBHQ	.611	.120	"	22	38.4
"	.294	DBPC	.20	.039	"	23	42.4
1.00	.088	p-quinone	2.89	.169	"	22	21.5
1.50	.246	HMBP	5.94	.195	"	22	41.6
2.14	.329	DBPC	.60	.092	n-octane	22	58.3
1.50	.246	1-dodecane-thiol	.76	.124	xylene	21	37.4
"	.406	"	.152	.041	"	21	38.5
"	.169	"	1.47	.165	"	22	32.0
1.50	.198	"	.75	.099	n-octane	22	41.1

The reaction was extremely fast and by the time the vpc could be reprogrammed, no quinone remained. A further addition of 2.4×10^{-3} moles of quinone only served to completely eliminate the DHA. During the reaction the volume of gas evolved was measured and found to be a net change of less than 1 ml.

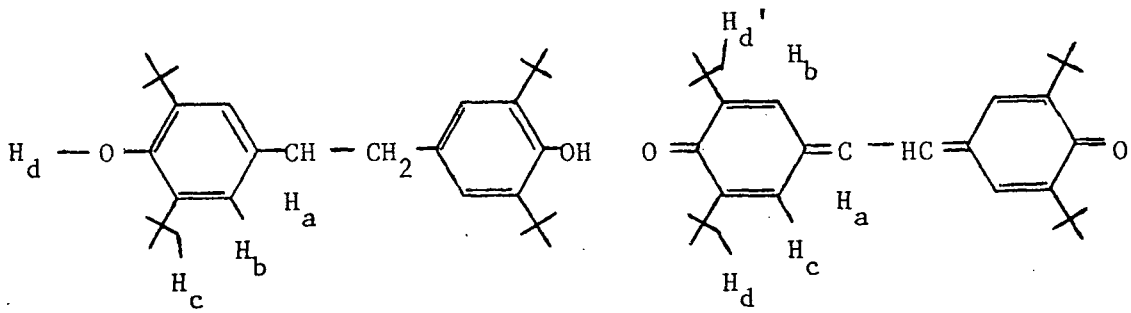
DHA Reaction with 1-Dodecanethiol under Nitrogen

Using the same apparatus and technique used to exclude nitrogen as described for the DHA-quinone reaction, 0.425×10^{-3} moles of 1-dodecanethiol and 0.275×10^{-3} moles of DHA were reacted in octane. Vpc analysis on carbowax after 2 1/2 minutes showed no trace of DHA with only excess mercaptan remaining. The reaction analysis remained unchanged for 680 minutes; the only product was seen as a large broad peak of retention time 55 minutes at 200°C.

Product Studies

The reaction residues from the kinetic runs using DBPC as inhibitor were combined and were shown by analytical vpc (Carbowax 80°/6 min $\xrightarrow{32°/\text{min}}$ 200°C) to contain four major (and several very minor) compounds, all of which were not present before reaction. The four were separated from the mixture by column chromatography on Florisil (Floridin Co. F-3938) 100/200 mesh. Elution was carried out using solvents in the order of: 1. hexane, 2. 3:1 hexane-benzene, 3. benzene, 4. 9:1 benzene-acetone, 5. 3:1 benzene-actone, 6. acetone. Most of the impurities and the unreacted DBPC eluted off with the hexane, the first two of the four compounds came in the benzene fraction,

the third compound in 9:1 benzene-acetone, and the fourth compound in 3:1 benzene-acetone. Compounds 1 and 2 were purified by allowing the crude yellow fraction to remain in the neat form for several days, during which time whitish-yellow crystals formed. When the flask was inverted and allowed to drain overnight into a dish, the crystals remained fixed to the bottom of the flask. Since these crystals themselves were almost as soluble in pentane (as well as other solvents) as were the impurities, they were washed several times quickly with cold pentane, the washing being just enough to remove the impurities with little loss of material from the crystals themselves. The crystals were identified mainly from nmr as being 1,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)ethane (I) and 3,3',5,5'-tetra-t-butylstilbene-4,4'-quinone (II). The results of the nmr run in CCl_4 are given below.



I II

Compound I: δ 1.39(s), 2.71(s)(2H), 4.8(broad)(1H), 6.83(s)(2H); Absorption at 4.8 disappears on addition of D_2O.

Compound II: δ 1.39(s), 6.91(d)(1H), 7.11(s)(1H), 7.43(s)(1H).

Literature values[43] (in CCl_4):

Compound I: δ 1.36(s)(H_c), 2.71(s)(H_a), 4.7(broad)(H_d), 6.80(s)(H_b).

Compound II: δ 1.30 and 1.33(H_d,H_d'), 7.12(H_a), 6.90 and 7.44(H_c and H_b)

The compounds were also identified as definitely not DBPC by vpc comparison with DBPC at various temperatures on Carbowax. An IR absorption band (in $CHCl_3$) at 1720 cm^{-1} also identified compound II. The fourth and largest of the products was purified as were the first 2 by crystallizing from the neat solution and rapidly washing with hexane and then acetone. Vpc (Carbowax) analysis of this compound when compared to a known sample of 1,3-dihydroxyadamantane showed the two to be identical in retention time, size, and shape. Both samples were compared as saturated solutions in acetone. The compound and the diol also appeared to have identical solubility properties in most organic solvents as well as yielding identical IR spectra (saturated solutions in $CHCl_3$). The third and smallest of the major peaks had been obtained in fair purity from the 9:1 benzene-acetone fraction from the column. It was obtained in the pure form by use of preparative vpc (3/8" x 10' Carbowax, 230°, 100 ml He flow, retention time of 15-20 minutes), melting point: 217-218°C (it turned yellow at 210° and above). N.m.r.: (> 99% purity in $CDCl_3$): δ 1.85 (shoulder) and 2.0 (8H), 2.3 (3H), 2.8 (1H), 3.6 (2H). The absorptions were all broad except a spike from the center of the 3.6 peak.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 73.76; H, 8.36.

IR (CCl_4): 3500 cm^{-1} (m, sharp), 2930 cm^{-1}(s), 2850 cm^{-1}(m), 1715 cm^{-1} (s), 1670 cm^{-1}(m), 1145 cm^{-1}(s), 900 cm^{-1}(m), 885 cm^{-1}(m).

The reaction residues from kinetics using 1-dedecanethiol as "inhibitor" when analyzed on vpc carbowax gave three new peaks and several very minor peaks. Because two of these peaks occurred in the

region where unidentified impurities resulting from DHA synthesis were concentrated, the task of isolation was made more difficult. Column chromatography using Florisil and eluting with first hexane, and then benzene gave these two in moderate purity in the benzene layer. Separation of the two from each other was accomplished using the preparative vpc (3/8" Carbowax 150°C, He flow: 100 ml/min). The first compound was completely purified by again using preparative vpc with the same column and flow rate, except at 125°C. Retention time was approximately three hours. The compound was identified as 1-adamantanol. M.p. (sealed tube): 265° (sublimes); literature: (300° (sublimes))[70], 288.5-290°.[71,72]. N.m.r. (20% $CDCl_3$ and 80% CCl_4): δ 1.37 (s)(1H), 1.70 (multiple)(12H), 2.15 (broad)(3H); add D_2O and δ 1.37 disappears. Literature (in $CDCl_3$): δ 1.70 (multiplet)(12H), 2.15 (broad)(3H).[70] IR (saturated CCl_4): 3560 cm^{-1} (w, sharp), 2920 cm^{-1} (s), 2850 cm^{-1} (m), 1450 cm^{-1} (m), 1110 cm^{-1} (s), 1085 cm^{-1} (s). Literature (KBr):[73] 3500 cm^{-1} (m), 2920 cm^{-1} (s), 1450 cm^{-1} (m), 1110 cm^{-1} (s), 1085 cm^{-1} (s).

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.69; H, 10.32.

Vpc analysis of the compound when compared to a known sample of 1-adamantanol showed the two to have identical retention times, shapes, and sizes.

After its separation from the first compound, the second compound was also purified by preparative vpc on Carbowax (125°, He flow rate 100 ml/min, retention time - approximately four hours). Its identity

was shown to be 7-methylenebicyclo[3.3.1]nonan-3-one.* M.p. 163.5°C; literature[44,45,74]: 160-164°C. IR (CCl_4): 2930 cm^{-1} (s), 1710 cm^{-1} (s), 1450 cm^{-1} (s), 1215 cm^{-1} (m), 895 cm^{-1} (s), 885 cm^{-1} (m). N.m.r. ($CDCl_3$): δ 1.95 (broad)(1H), 2.40 (sharp)(5H), 4.78 (s)(1H).

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.79; H, 9.18.

The third peak was the very long retention time product which was seen in the reaction of DHA and 1-dodecanethiol under nitrogen. Its identity was simply confirmed by inspection to be the same, but was not further identified.

A general idea of the ratios of the products of kinetic reactions was obtained by taking a selected run and determining the product ratios from that. The particular reaction taken was .24 molar DHA (0.27×10^{-3} moles) and .053 molar DBPC (0.06×10^{-3} moles) in octane solvent. The ratios of the products were determined by the cut-out-and-weigh vpc peaks method. To do this, first a sample of pure DHA solution was run, and, after the same DHA reacted to completion, another sample was run under identical conditions. In this analysis method only peaks which changed during the course of reaction were considered, and, if they were present initially, that weight was subtracted from the weight at the end of the experiment. All of the products resulting from DHA (or suspected as having DHA as their origin) were assumed to give the same relative areas under the curve. The total weights of all the peaks resulting from new compounds were summed and taken to be the 100% value for the products detectable by

* In addition to the listed properties, both IR and n.m.r. spectra, as well as vpc retention times were compared with a sample of the same material synthesized by a different method. All comparisons were identical.

vpc. Each peak was then compared to this and its percentage composition calculated. The total of the detectable products, when compared with the initial value for DHA, indicated that only 27% of the DHA was accounted for in this fraction. The remaining 63% was in the form of larger molecules probably polymeric which weren't identified.

Table V gives the data concerning the composition of the detectable fraction. No quantitative study of the products whose origin was DBPC was made.

Table V. Products of a 9:2 DHA:DBPC Reaction Mixture in the Presence of O_2.

Retention Time (min)*	Peak Growth (mg)**	% of Total Products	Identity
12.6	52.6	15.9	uncertain
14.4	28.0	8.5	?
17.1	9.9	3.0	?
19.4	207.8	62.9	1,3-dihydroxy-adamantane
29.0	32.2	9.7	?

* Carbowax 80°/6 min $\frac{32°/\text{min}}{}$ 200°C, flow rate ∿ 50 ml/min.

** Calculated by subtracting the initial wt. from the final weight of the peak.

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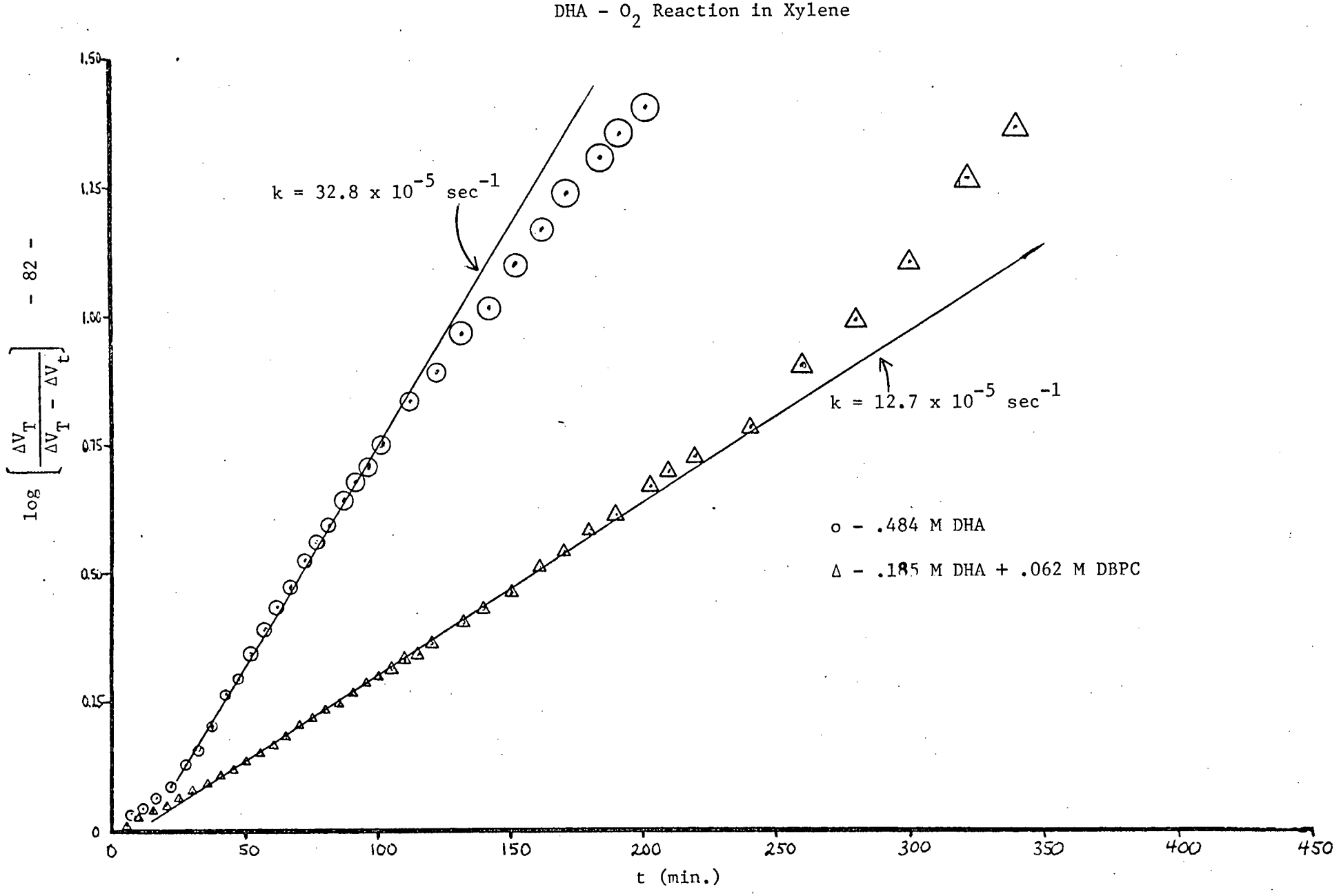
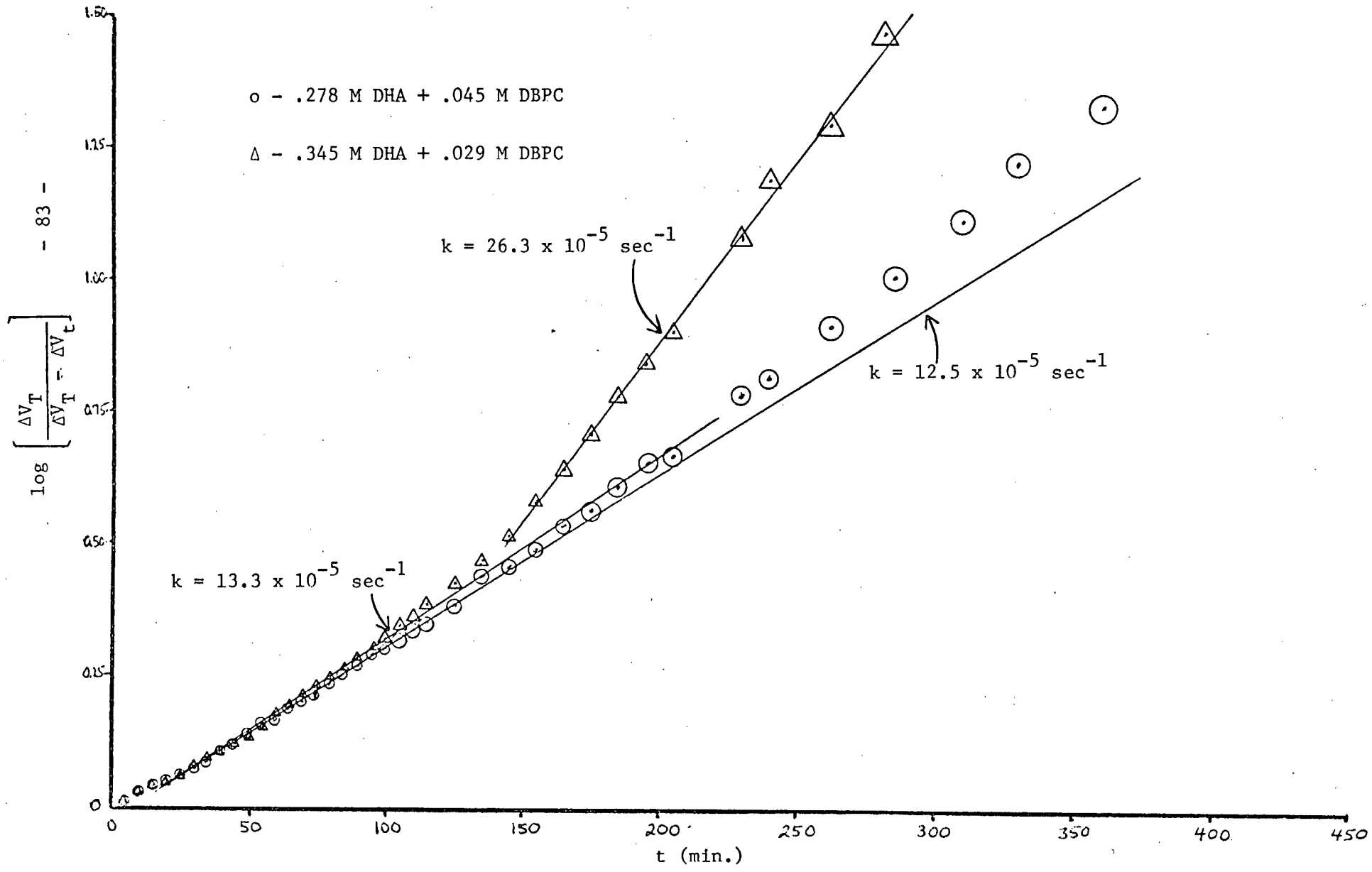
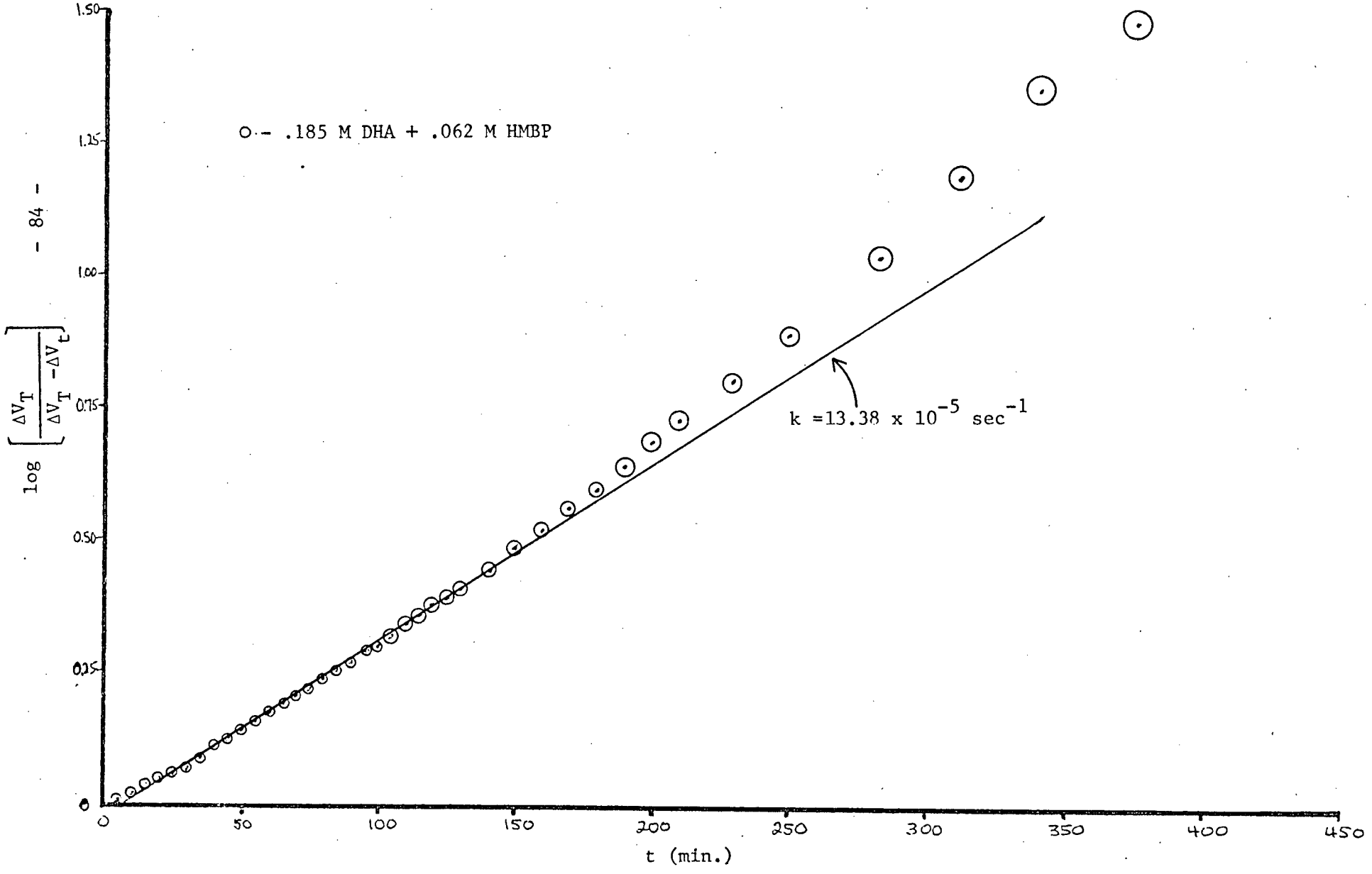
APPENDIX

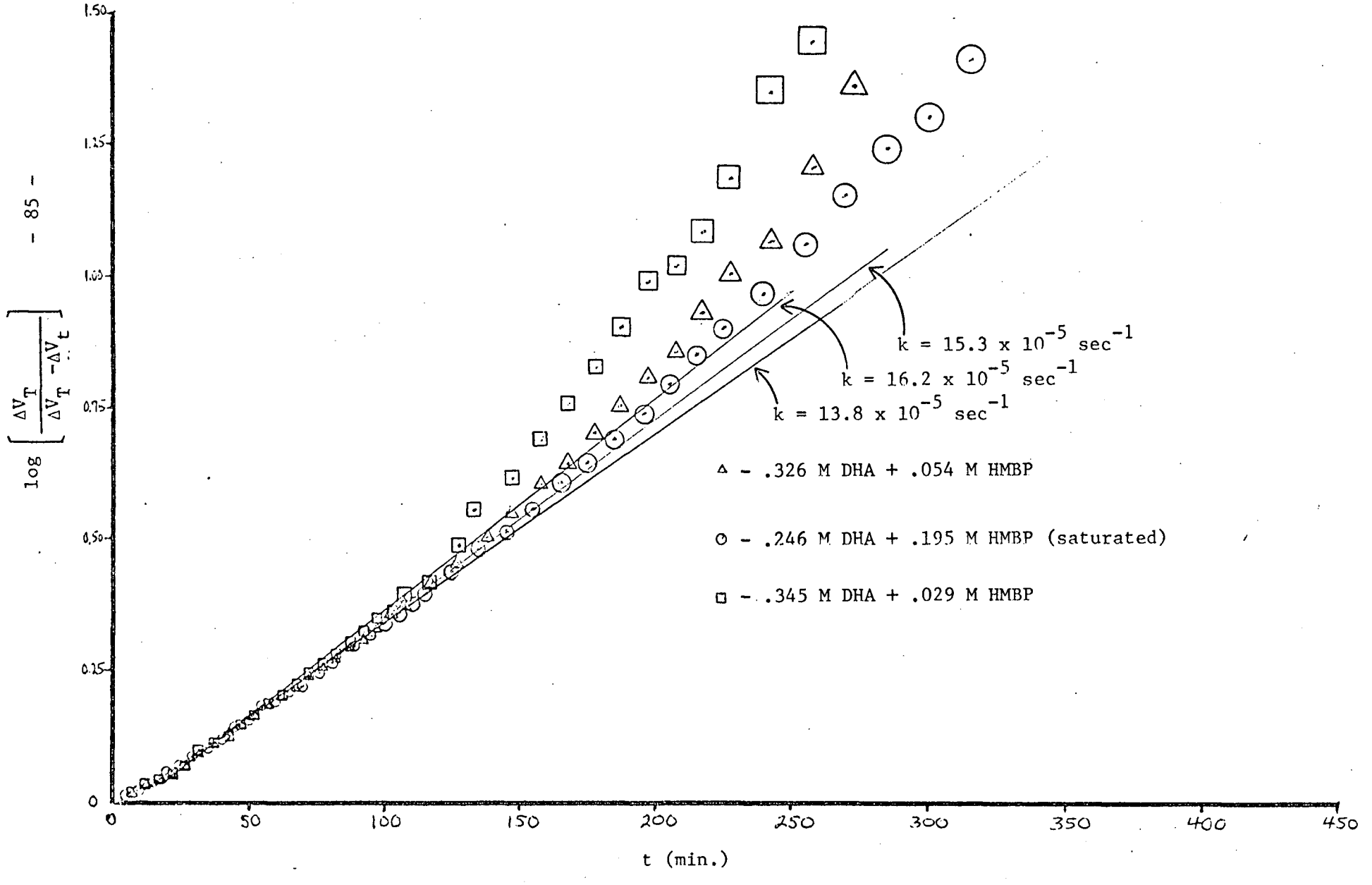

DHA - O_2 Reaction in Xylene
$\log \left[\frac{\Delta V_T}{\Delta V_T - \Delta V_t} \right]$
1.50
1.25
1.00
0.75
0.50
0.25
0
0
50
100
150
200
250
300
350
400
450
t (min.)
k = 32.8 x 10^{-5} sec^{-1}
k = 12.7 x 10^{-5} sec^{-1}
o - .484 M DHA
Δ - .185 M DHA + .062 M DBPC


DHA - O_2 Reaction in Xylene
o - .278 M DHA + .045 M DBPC
Δ - .345 M DHA + .029 M DBPC
k = 26.3 x 10^{-5} sec^{-1}
k = 12.5 x 10^{-5} sec^{-1}
k = 13.3 x 10^{-5} sec^{-1}
$\log \left[\frac{\Delta V_T}{\Delta V_T - \Delta V_t} \right]$
t (min.)
0
50
100
150
200
250
300
350
400
450
0.25
0.50
0.75
1.00
1.25
1.50

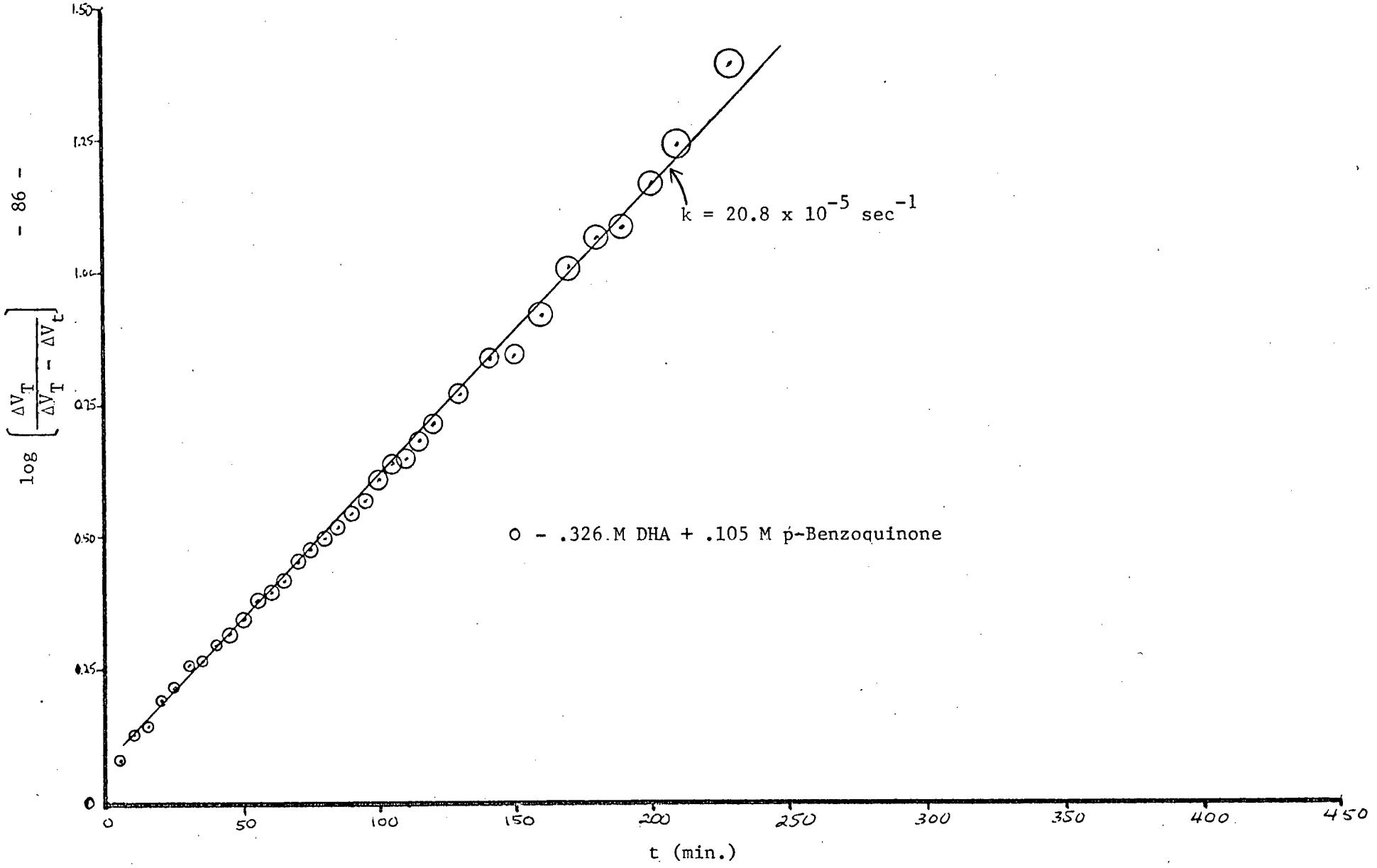
DHA - O_2 Reaction in Xylene



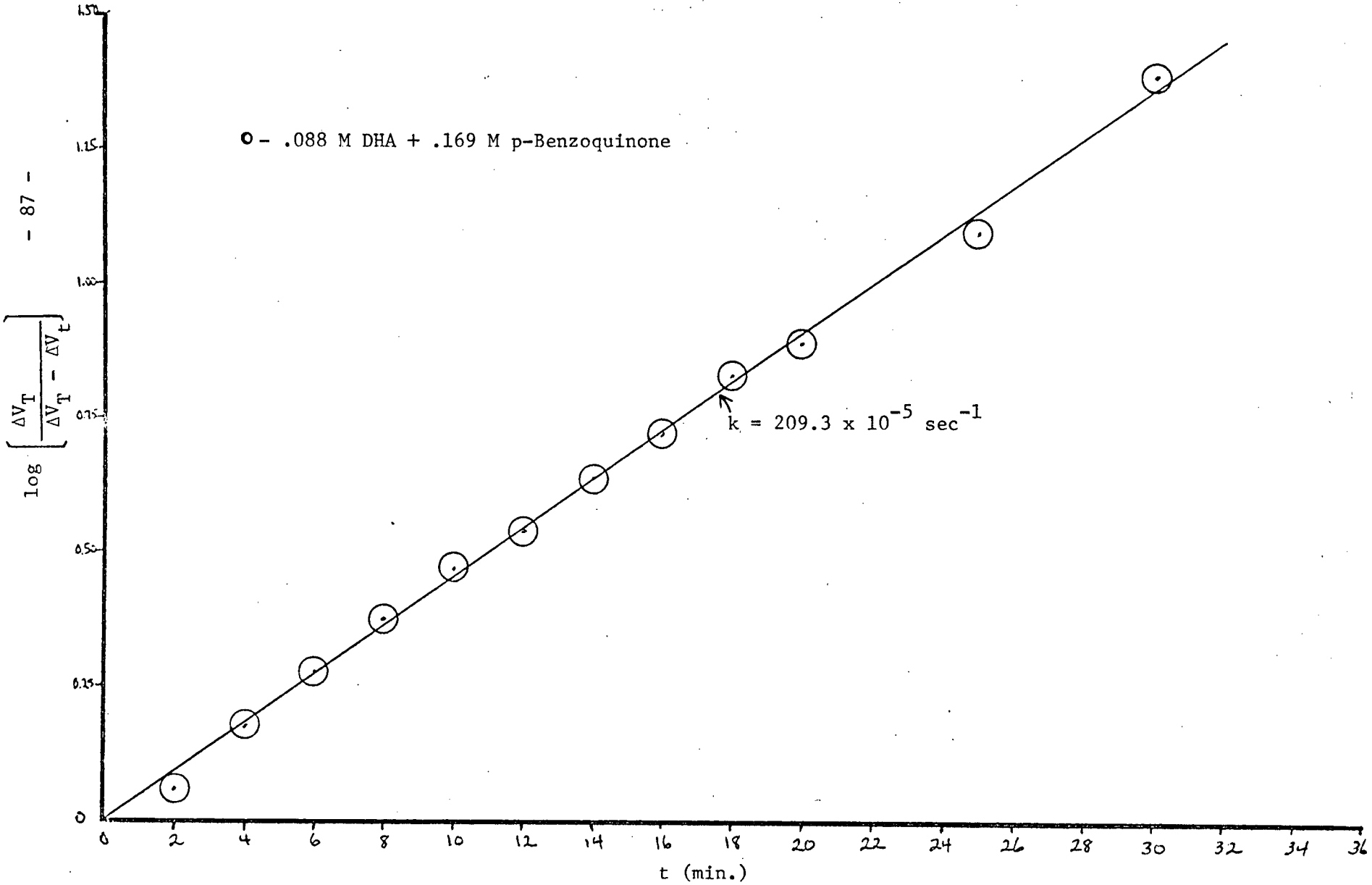
DHA - O_2 Reaction in Xylene



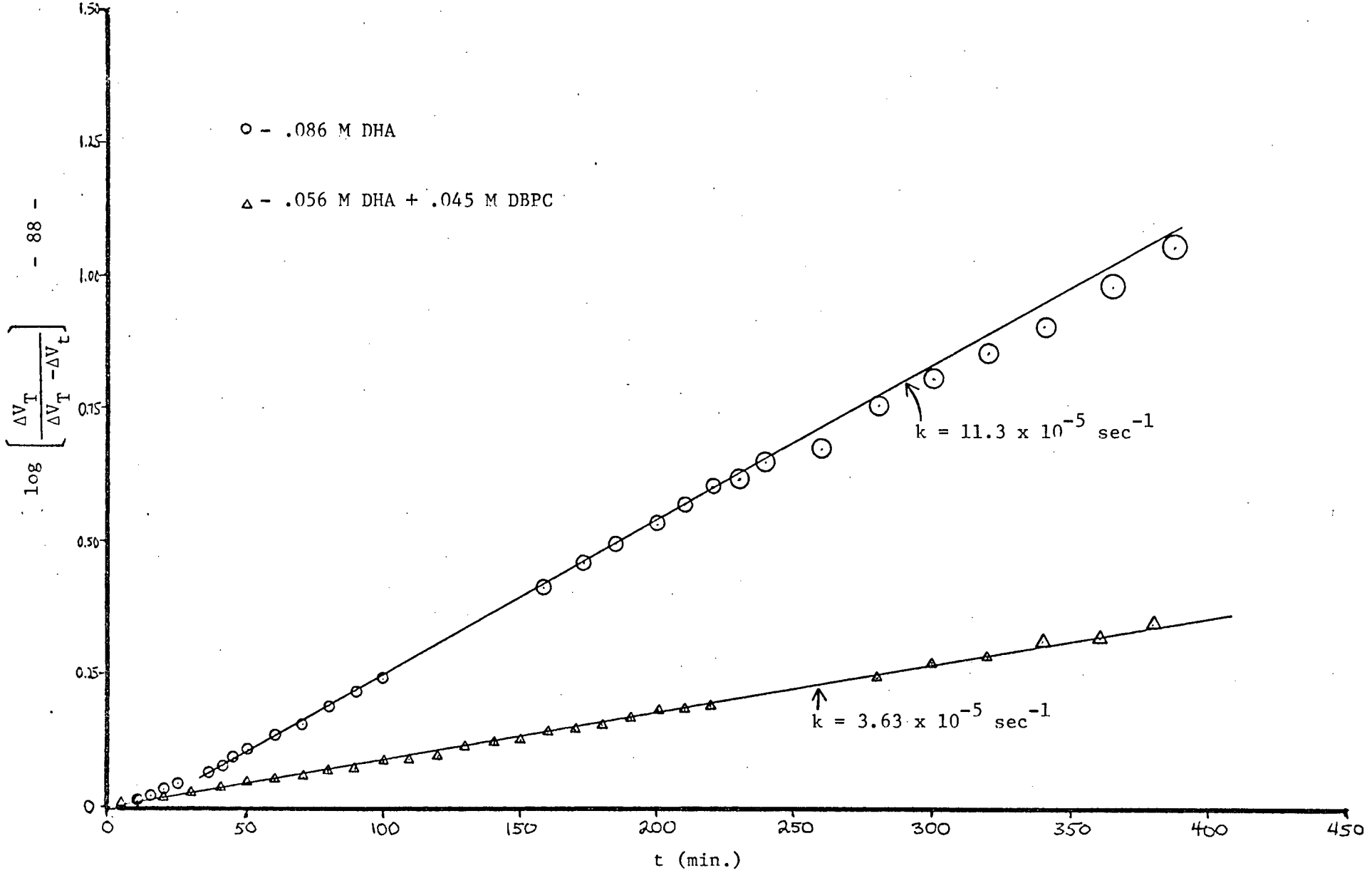
DHA - O_2 Reaction in Xylene

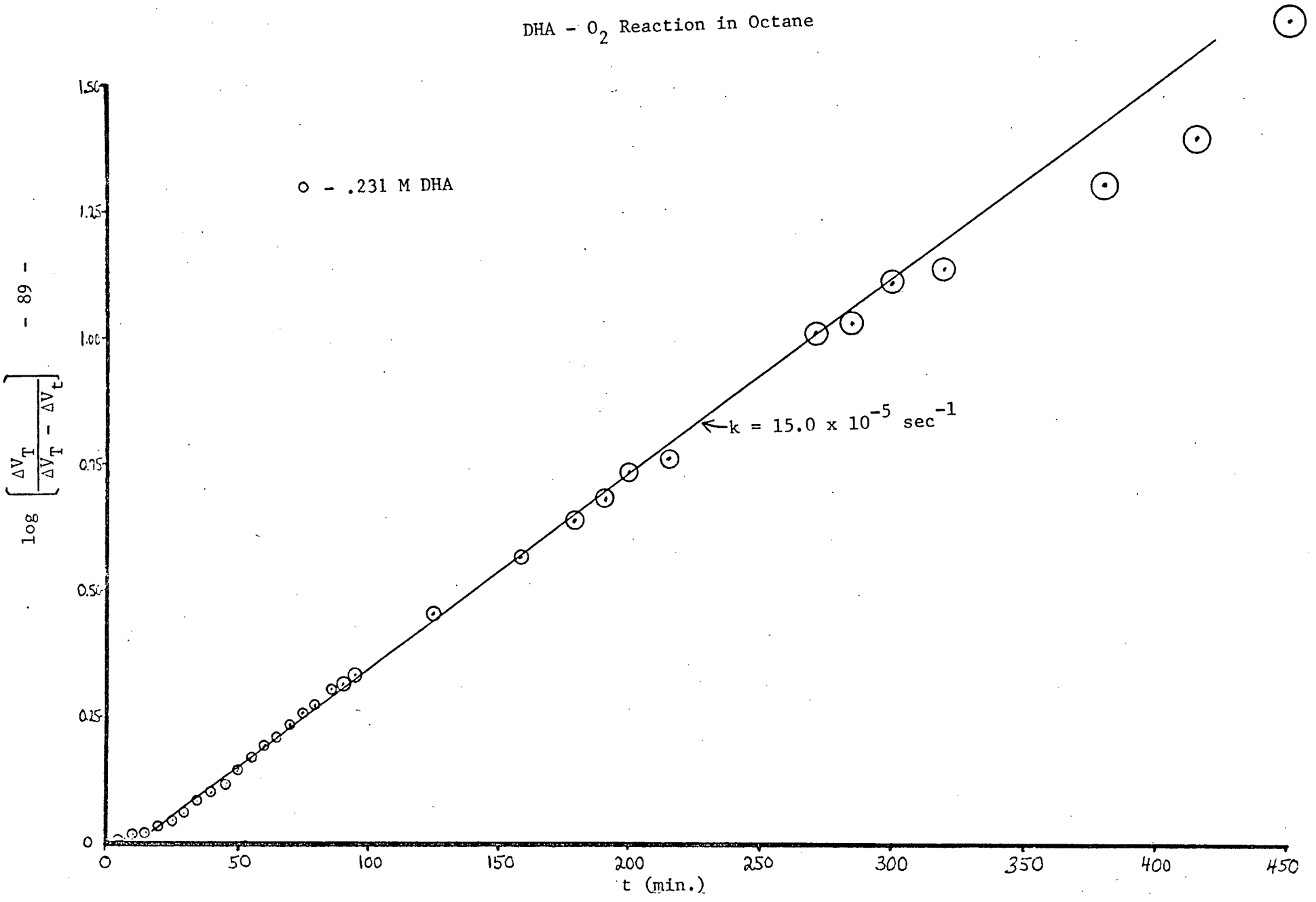


DHA - p-Benzoquinone Reaction in Xylene

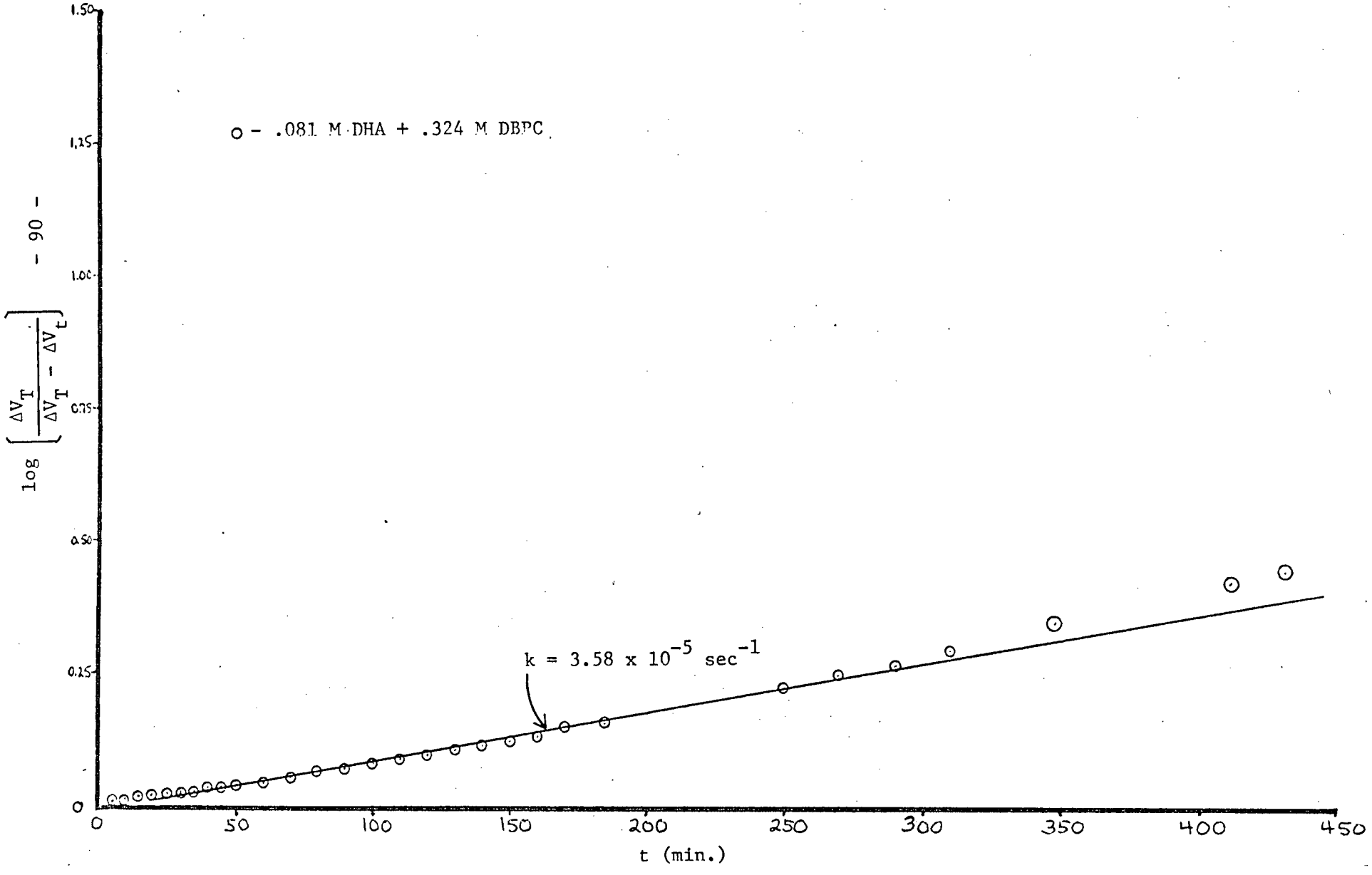


DHA - O_2 Reaction in Heptane




DHA - O_2 Reaction in Octane
o - .231 M DHA
$k = 15.0 \times 10^{-5}$ sec^{-1}
$\log \left[\frac{\Delta V_T}{\Delta V_T - \Delta V_t} \right]$
1.50
1.25
1.00
0.75
0.50
0.25
0
0
50
100
150
200
250
300
350
400
450
t (min.)

DHA - O_2 Reaction in Octane



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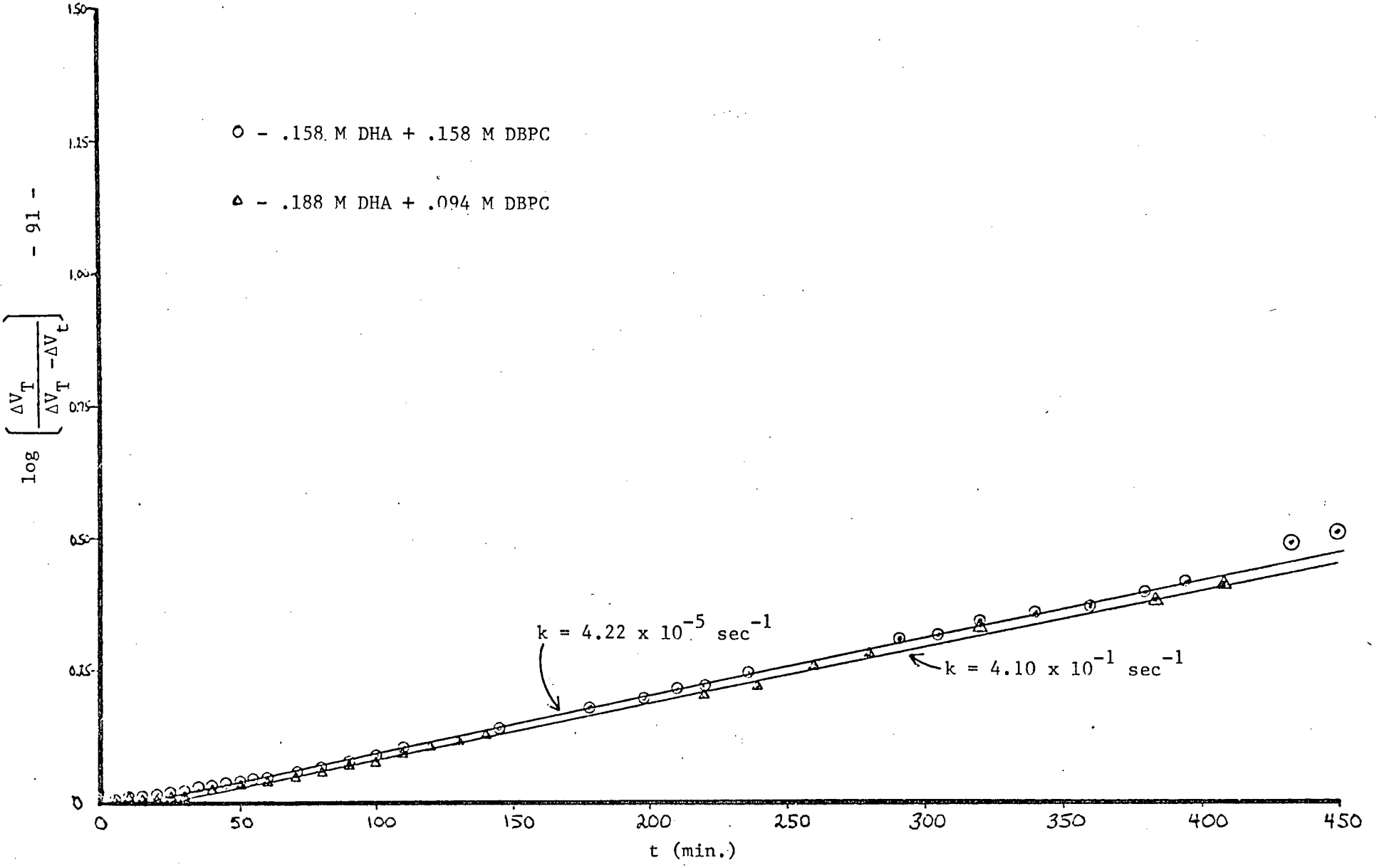
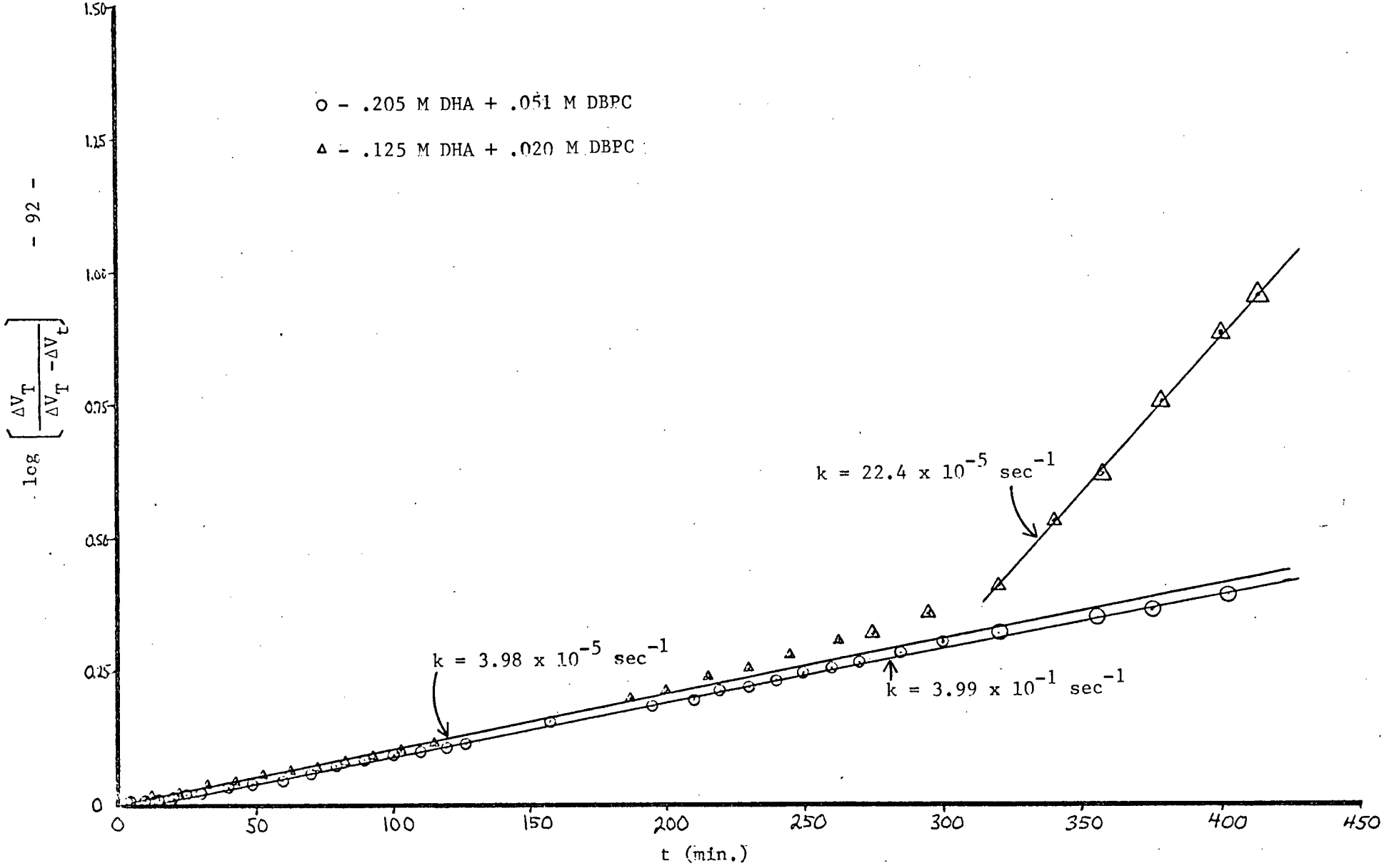


DHA - O_2 Reaction in Octane



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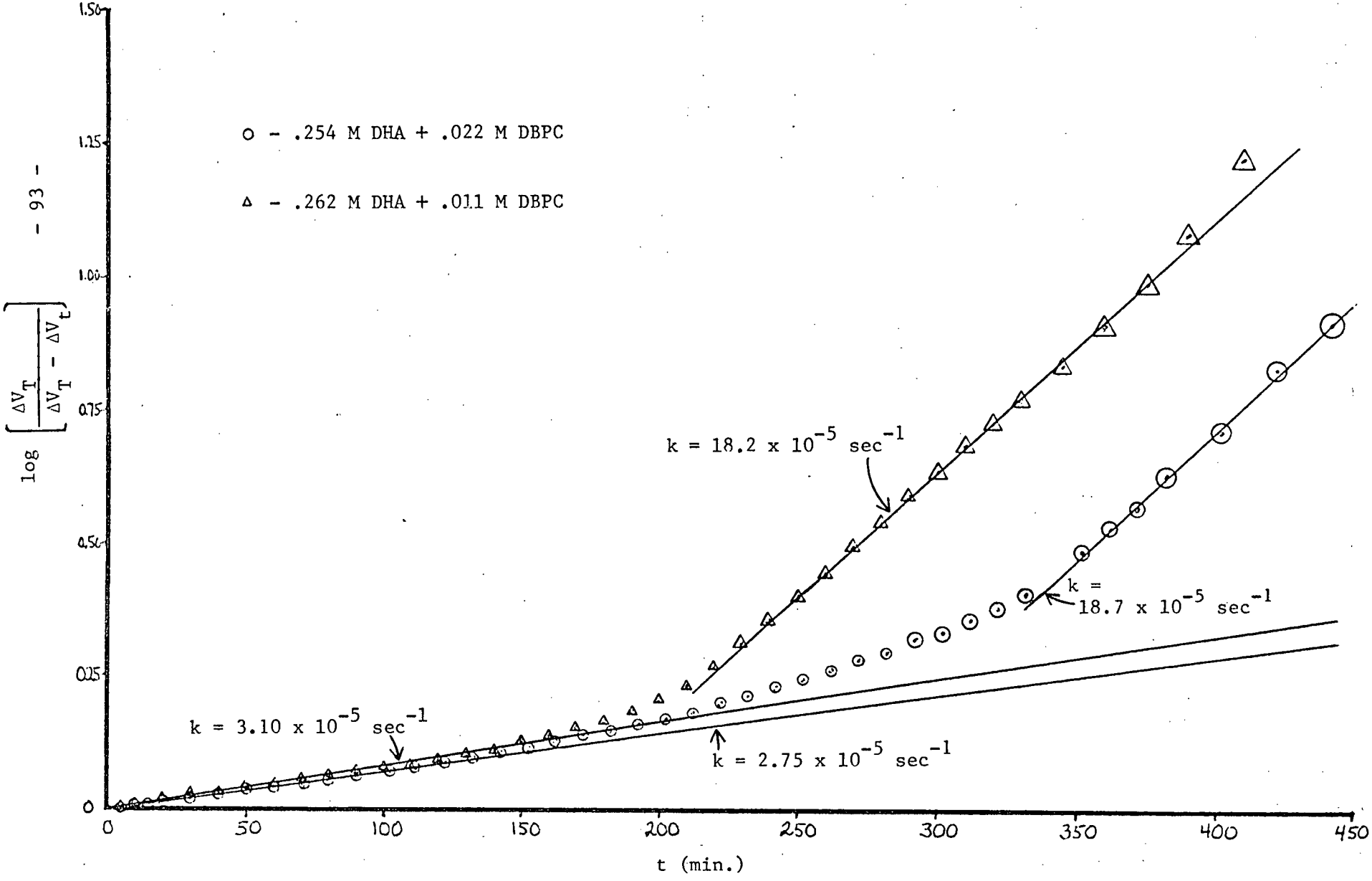
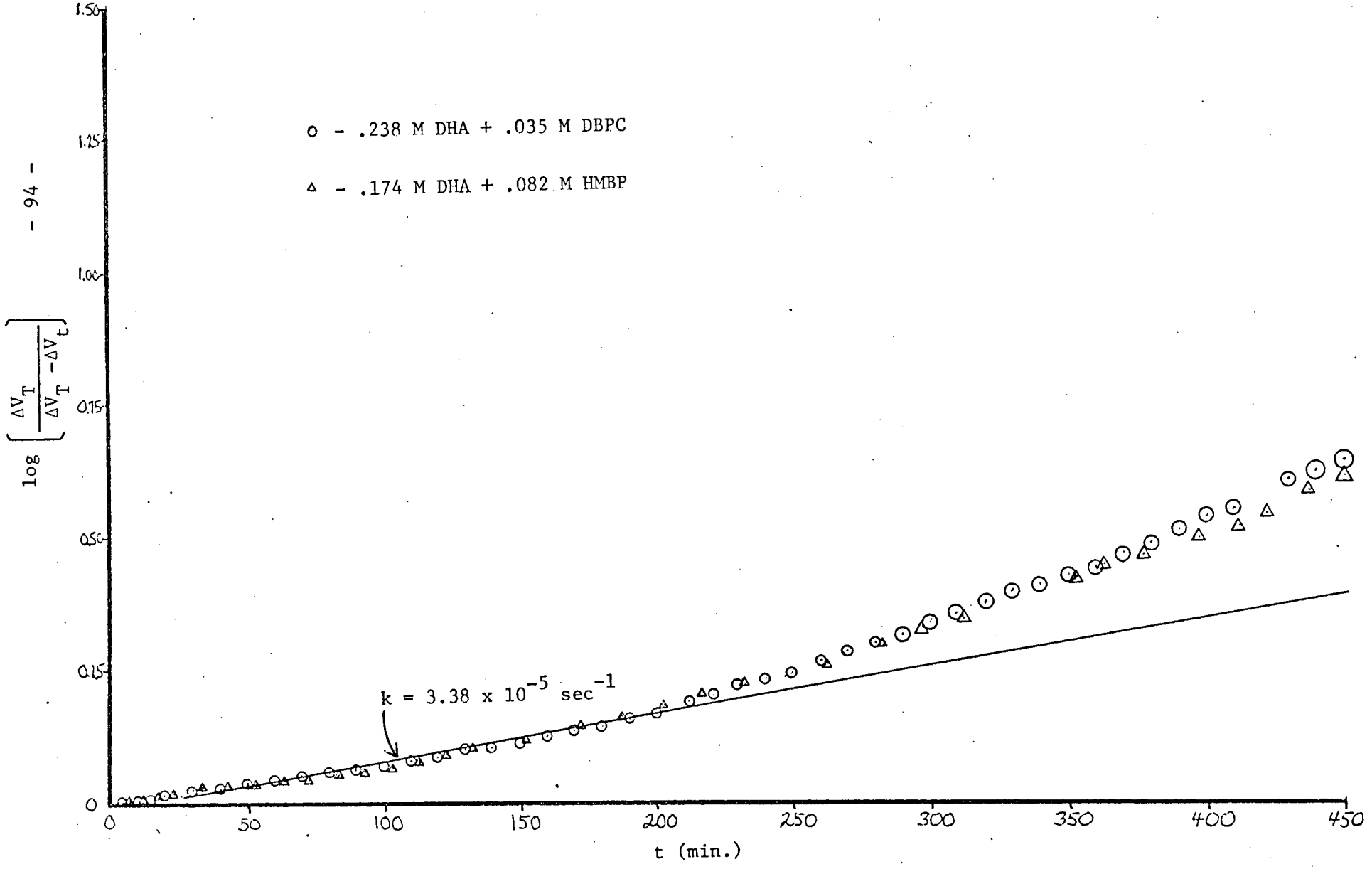


DHA - O_2 Reaction in Octane



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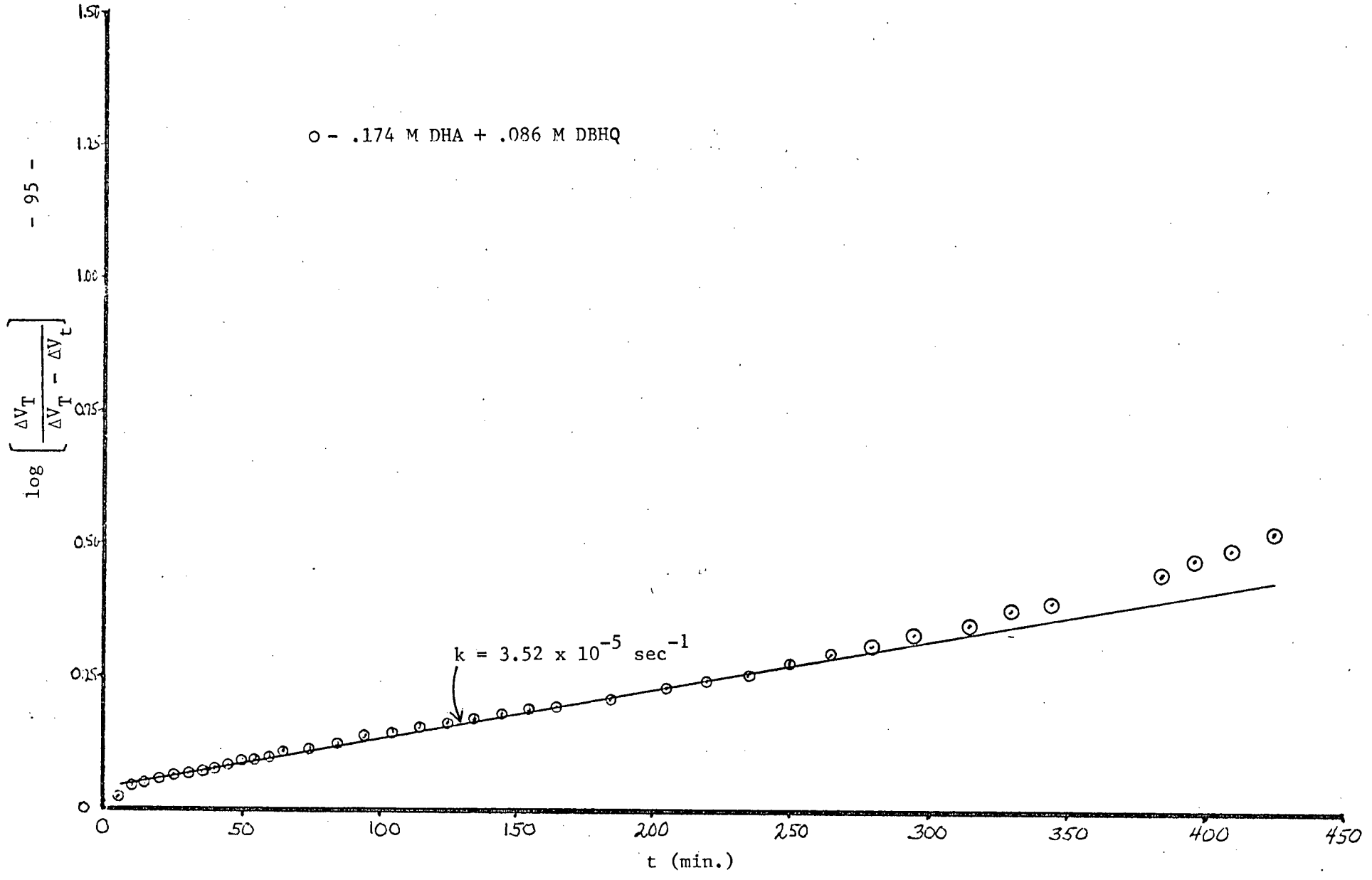
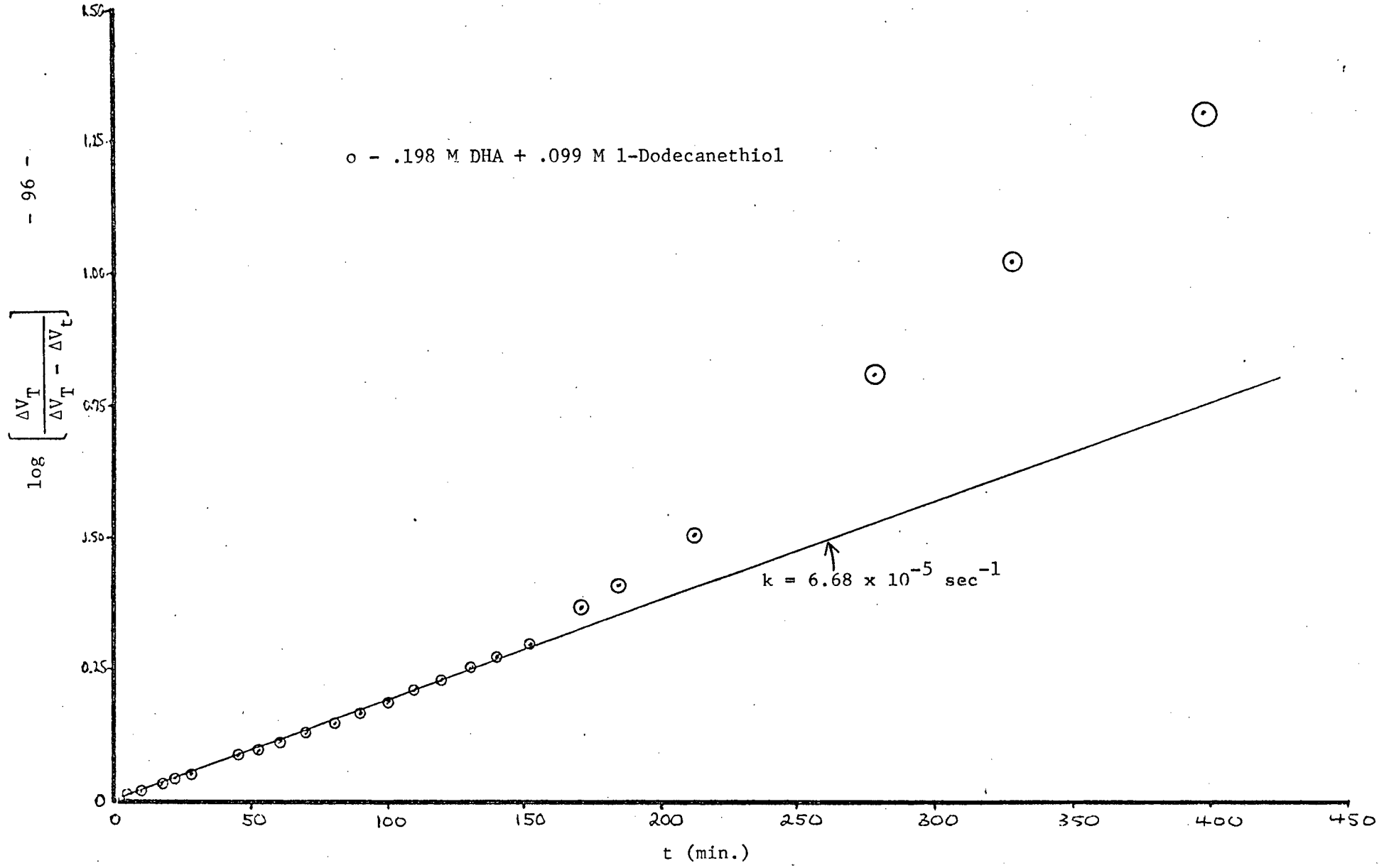
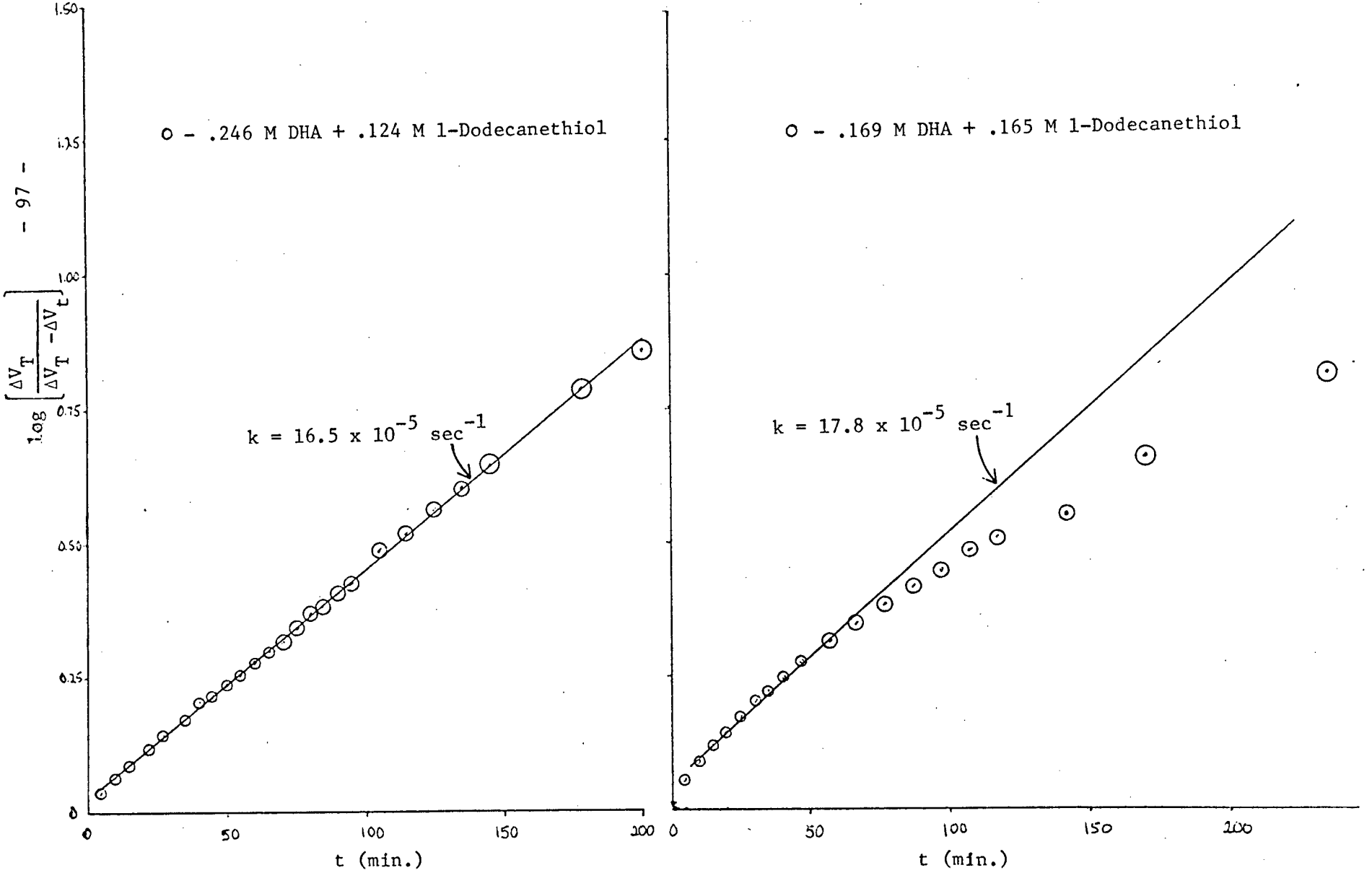


DHA - O_2 Reaction in Octane



DHA - 1-Dodecanethiol Reaction in Xylene



Concentration Changes of DHA and DBPC with Time (in Xylene)