

KINETIC STUDIES ON
THE PYROLYSIS OF PENTENE-1

by

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ABSTRACT

The thermal decomposition of pentene-1 in a static system has been investigated over a temperature range of 470 to 530°C. and a pressure range of 50 to 250 mm. The decomposition was a homogeneous first-order reaction with an average overall activation energy of 52 kcal./mole. The reaction rate was retarded by propylene and by inert gases, but was unaffected by nitric oxide. Free radicals from lead tetraethyl produced an acceleration. The activation energy exhibits a slight increase with increasing initial pressure of pentene. Evidence is presented for a composite reaction mechanism involving both a free-radical chain process and a direct intramolecular rearrangement.

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INTRODUCTION

The thermal decomposition reactions of hydrocarbons are of considerable interest from a theoretical standpoint, since a study of their mechanisms yields valuable information on the fundamental nature of chemical change. In the whole paraffin series, decomposition reactions involve the breaking and formation of only two types of linkage; only three types are involved with olefins. The nature of the problem is therefore not unduly complicated. However, the mechanism of olefin decompositions is not well understood, in spite of the fact that such thermal decompositions have been the subject of a considerable amount of study.

Thermal Decomposition of Hydrocarbons

Although the kinetics of the thermal decompositions of a variety of complex organic molecules have received much study, mechanisms are not, in all cases, fully established. It seems evident however, that each such reaction involves one or both of two primary acts of decomposition: an intramolecular rearrangement to stable products or a split into free radicals, which initiate further decomposition by a chain process.

When both mechanisms operate simultaneously in a given reaction, their relative importance depends upon two factors: (a) the relative activation energies and steric factors, and (b) the chain length. On the basis of much experimental evidence a composite reaction mechanism involving both types

of reaction has been assigned to the pyrolysis of normal paraffin hydrocarbons (1).

Evidence for the participation of free radicals in such reactions comes from experiments on sensitized decompositions at temperatures far below those at which the normal decompositions occur. Radicals from ethylene oxide induce the decomposition of propane and of n-butane (2); methyl radicals from decomposing azomethane induce decomposition of ethane and propane (3); and again the addition of 1% of mercury dimethyl to n-butane at 525°C. causes the decomposition of twenty equivalents of butane (4). Such observations indicate that free radicals produced by the decomposition of the sensitizer can react with the hydrocarbon, causing its decomposition by a free-radical chain process. Thus it is established that radicals can cause chain decomposition of paraffins, although it does not necessarily follow that a chain process occurs in the normal pyrolysis of the substance under consideration.

Nitric oxide has been found a very effective substance for inhibiting chain reactions(5). Nitric oxide, itself a free radical, combines with other radicals, so removing them from reaction systems. Very small amounts of nitric oxide have been found to inhibit reaction rates greatly; by removing one radical, a molecule of nitric oxide prevents the chain decomposition of many molecules. By means of nitric oxide inhibition, conclusive evidence has been provided for the operation of a free-radical chain mechanism in paraffin decompositions (6, 7).

As increasing amounts of nitric oxide are added to a reaction system, the rate of decomposition decreases rapidly to a constant fraction of its original value; subsequent additions produce no further inhibition; all chains appear to be suppressed. Certain other inhibitors, such as propylene, have been shown to have a similar effect. The residual reaction is believed to represent a non-chain molecular rearrangement. Nevertheless, considerable uncertainty still remains as to the precise nature of this part of the reaction. Work with isotopically labelled compounds indicates that the maximally inhibited reaction still involves free-radical chains (8).

The plot of pressure increase against time for the uninhibited decomposition of a normal paraffin shows a pronounced curvature near the origin (9), but afterwards approximates to a straight line. Analytical results show that, in most instances, olefins constitute an appreciable percentage of the reaction products. Hence the shape of the curve has been explained as due to inhibition by these unsaturates during the initial stages of the reaction.

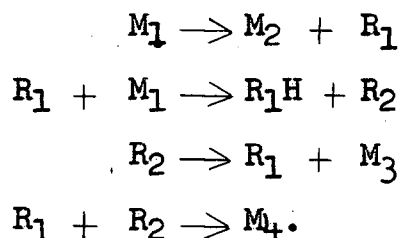
The participation of free-radical chains in such thermal decomposition reactions was greatly clarified by Rice (10), who devised mechanisms for organic decompositions. These Rice mechanisms form the basis of our understanding of free-radical chain reactions.

Rice Mechanisms

Mechanisms for the decomposition of a wide variety of

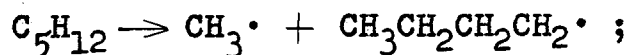
organic compounds have been proposed by Rice and Herzfeld (11). On the basis of the detection of free radicals in such decomposition reactions, Rice has suggested that these radicals play a vital role in the reaction mechanisms.

In general, the proposed steps are as follows:

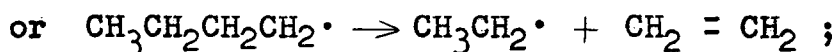
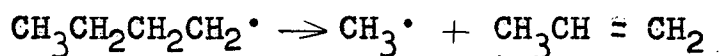


The initial step involves the rupture of a bond in molecule M_1 , yielding a smaller molecule, M_2 , and a radical, R_1 . A chain process follows. Each step in the chain involves the abstraction of a hydrogen atom from the parent hydrocarbon, yielding an alkyl radical and a molecule, R_1H . The large radicals, R_2 , are assumed to decompose readily. Chain termination takes place by radical recombination, with formation of a stable molecule, M_4 .

The mechanisms devised for the pyrolysis of paraffin hydrocarbons appear to give a fairly satisfactory interpretation of the complicated chemical changes involved, even when applied to paraffins as high as the octanes (12). Normal pentane will serve as an example: the initiating step is assumed to be a breakdown of the parent hydrocarbon to two radicals:



The large alkyl radical, assumed to be unstable, decomposes:



the chain process then proceeds by steps of the following type:



the large alkyl radical so formed now decomposes to stable products and lower radicals which perpetuate the chain. By suitable choices of the various possibilities for the chain-perpetuating and chain-terminating steps, the observed first-order overall rate can be explained. In addition, arbitrary assignment of activation energies to the various steps can lead to an overall activation energy in agreement with the low experimental value; that is, a value far smaller than the strength of the C-C bond broken in the initial step.

Survey of the Literature

A survey of the literature dealing with the pyrolysis of olefins reveals that nearly all the information available on the kinetics of such reactions has been accumulated in the last thirty years. During this period much work has been done in order to gain a better understanding of the thermal reactions - both decomposition and polymerization - of olefins. Experiments have, for the most part, dealt chiefly with the lower olefins. Dynamic methods have usually been employed; that is, the experiments have been done in flow systems, using short

contact times. A wide variety of temperatures and pressures have been used, and in few cases have comparable experimental conditions been employed.

Decomposition of Lower Olefins

Prior to 1925 very little information of a precise nature was available on olefin decompositions. It was known that at about 750°C. the pyrolysis of an olefin yielded acetylene, a considerable part of which polymerized to benzene (13). One of the earliest investigations was made by Noyes (14), who passed isobutylene through a glass tube heated to "low redness," and identified ethylene, propylene, butadiene, methane, hydrogen, benzene, toluene, and naphthalene in the reaction products. Ipatiev (15) passed isobutylene over alumina at 500°C., obtaining propylene, hydrogen, and methane. At low temperatures the chief reaction of the lower olefins was found to be polymerization, but at higher temperatures the process was found to be more complex, consisting of both decomposition and polymerization.

Frey and Smith (16), working at 575°C. with a flow system, showed the high-temperature reaction of ethylene to be homogeneous in silica vessels, and identified methane, ethane, hydrogen, and higher olefins in the products. They also decomposed propylene under similar conditions, yielding butene and higher hydrocarbons together with large amounts of methane and ethylene.

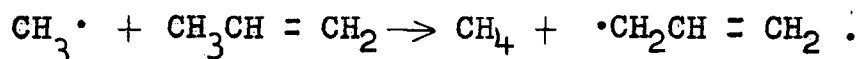
Isobutylene, heated in a flow system, was shown by Hurd

and Spence (17) to be much more stable than isobutane under similar conditions, a behaviour attributed by these workers to the greater strength of the C-C single bond in isobutylene to the corresponding bond in the saturated compound. At temperatures above 600°C. they found the isobutylene pyrolysis to be homogeneous and independent of concentration since the reaction rate was unchanged by increase of the surface-to-volume ratio of the reaction tube or by dilution with nitrogen or hydrogen. Similar conclusions were reached by Hurd and Meinert (18) from experiments with propylene in a pyrex flow system at temperatures above 525°C. The propylene decomposition was, however, slightly slower in the presence of nitrogen, which appeared to lessen the formation of liquid products by diluting the primary reaction products, hindering their polymerization.

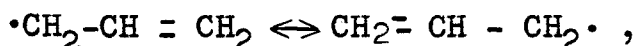
Rice has proposed a free-radical chain mechanism for olefin decompositions (10). Here, a number of complications arose, which were not encountered in devising the mechanisms of paraffin decompositions; (a) The double bond exerts a strong influence on the reactivity of the adjacent H atoms: the α -H atoms are rendered inactive, whereas the β -H atoms are activated. Rice has therefore assumed that in a reaction involving the abstraction of a hydrogen atom from an olefin molecule, the attack of a free radical will be almost exclusively at the β -H atoms. (b) A free radical is able to react with an unsaturated hydrocarbon not only by abstracting H atoms, but also by adding to one of the doubly-bound carbon

atoms. In proposing a chain mechanism for the process, Rice has neglected such addition reactions, assuming them to be of importance only at lower temperatures.

For an unsaturated radical Rice has assumed the following type of behaviour. Consider, as an example, the proposed reaction between propylene and a methyl radical:



The methyl radical abstracts a β -H atom to yield methane and an allyl radical. The latter, because of a resonance effect,



is considered much more stable than an ordinary free radical; hence, the decomposition:



seems unlikely. This conclusion is substantiated by the fact that allene has not been detected among the products of olefinic decompositions. Since the reaction of allyl radicals with surrounding olefin molecules regenerates allyl radicals, these are assumed to disappear only by collision with one another. The diallyl so formed is presumed to decompose, yielding the observed oily products. The presence of unsaturated radicals also introduces the possibility of isomerization of the olefins.

On the basis of these assumptions Rice has postulated a fundamental difference between the decomposition mechanisms of the lower and higher members of the olefin series. The decompositions of propylene and the butylenes are presumed to

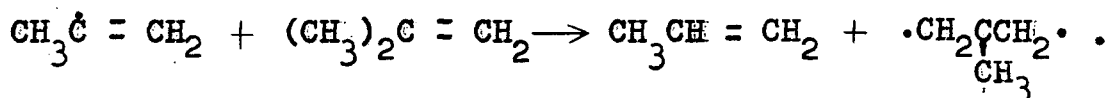
involve no chain cycle other than initiation: initial rupture of a β C-C bond is followed by radical abstraction of H atoms from olefin molecules, producing allyl-type radicals which disappear by combination with one another. For higher olefins, a chain mechanism is proposed, yielding paraffin hydrocarbons and conjugated diolefins. Thus Rice has assumed that, because of their unsaturated nature, olefins decompose differently than do most other organic compounds.

Egloff and Wilson (19), in considering the mechanisms for the thermal reactions of gaseous hydrocarbons, regarded ethylene as the basic material, since above a certain temperature the reaction products of any hydrocarbon are essentially those of ethylene at that temperature. They reasoned that the thermal reactions of higher hydrocarbons must be studied below 750°C . in order that they be characterized by differences due to the nature and stability of the particular molecules concerned. Since, at the initial temperatures of reaction, olefins were found to polymerize to nonaromatic substances, it was concluded that points of unsaturation are conducive to polymerization.

The pyrolysis of ethylene, propene, and the three butenes was studied by Tropsch, Parrish, and Egloff (20) in a flow system, at temperatures (1100 to 1400°C .) considerably higher than those used in previous investigations. They observed that, as the experimental conditions were gradually made more severe, the volume contraction resulting from polymerization gradually

became masked by expansion due to decomposition, until only a volume increase remained. By a consideration of the activation energies of the two competing processes, they inferred that decomposition does not precede polymerization under severe conditions, but that polymerization is the primary step, the polymer so formed being unstable under the experimental conditions, and decomposing to the observed gaseous products.

Rice and Haynes (21) pyrolyzed isobutylene in a high-temperature flow system designed to eliminate the formation of oily and tarry material. Propylene, methane, hydrogen, ethylene, ethane, acetylene, allene, and methyl acetylene were found. On the basis of their results these investigators suggested a free-radical mechanism involving rather short chains due to the formation of appreciable amounts of propylene by some non-chain reaction such as the following:



They also suggested that the methyl acetylene is formed from allene by a radical chain mechanism. Isobutylene was also pyrolyzed at high temperatures by Szwarc (22), who found the reaction to be homogeneous and first-order, and proposed a chain mechanism to explain the low activation energy found. In similar experiments with propylene, the same author (23) demonstrated the homogeneity and first-order character of the decomposition and proposed a unimolecular mechanism in which the rate determining step involves the breaking of the C-C

bond, followed by a sequence of rapid reactions between the radicals so created.

Rice and Wall (24), decomposing isobutylene with short contact times at 851 to 900°C. at pressures between 50 and 200 mm. and obtained identical products by carrying out the reaction both in a quartz tube and in a stainless steel tube.

The first use of a static system, such as that used in the present investigation, was made by Ingold and Stubbs (25) in studying the thermal decomposition of propylene. Operating over a pressure range of 50 to 500 mm. and a temperature range of 570 to 650°C. they showed the decomposition to be a homogeneous first-order reaction with an activation energy of 57.1 kcal. per mole, the decomposition products being mainly methane, ethylene, hydrogen, a condensable intermediate which subsequently decomposed, and carbon. They concluded that over this temperature range propylene decomposes mainly by a molecular rearrangement reaction, the inhibiting action of propylene itself preventing the propagation of chains. It was suggested that at higher temperatures, such as those used by Szwarc (23), it is possible that a radical mechanism, with or without the propagation of chains, may predominate due to the instability of the allyl radical.

The picture of lower olefin pyrolysis thus appears to be none too clear at the present time. A great variety of experimental conditions have been employed by different workers so that correlation proves somewhat difficult. The reactions

appear to be homogeneous and first-order. At low temperatures polymerization predominates, accompanied by a volume contraction; as the temperature is raised a point is reached where there is no observable pressure change, indicating that the two competing processes of polymerization and decomposition are offsetting one another; at higher temperatures decomposition predominates. Both free-radical chain mechanisms and molecular rearrangement mechanisms have been proposed to account for the observed reaction products. It is possible that different mechanisms may operate under different conditions of temperature and pressure.

Decomposition of the Pentenes

As was the case for the lower olefins, the pyrolysis of the pentenes has been studied mainly by flow methods.

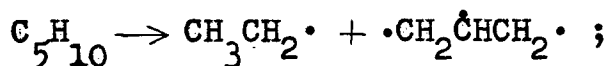
Norris and Reuter (26) heated α pentene-2 under a variety of conditions in a flow system at 600°C. Rough analyses gave evidence for the formation of methane, butene, butadiene, propylene, ethylene, and higher straight-chain hydrocarbons, but for no branched-chain products. A comparison of the thermal behaviour of certain pentanes and pentenes was made by Norris and Thomson (27). The decompositions were performed at or near the cracking temperatures of the hydrocarbons, thus yielding the products first formed. For both pentanes and pentenes a certain temperature was noted at which the hydrocarbon pyrolysis began. For a pentene an additional significant temperature was observed above which the rate of expansion

either remained constant or decreased as the temperature was raised. Such reversal temperatures, which occurred, for the three pentenes studied, 53 to 65°C. higher than the temperatures at which the hydrocarbons began to decompose, were attributed to simultaneous pyrolysis and polymerization.

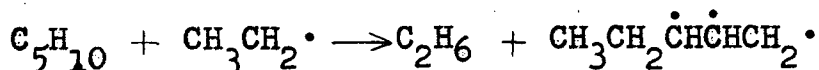
Hurd and Goldsby (28), in the pyrolysis of pentene-1 and pentene-2 at 550 to 600°C. in a flow system, established that isomeric unsaturated hydrocarbons were important reaction products, one-third to two-fifths of the total products consisting of isomeric pentylenes.

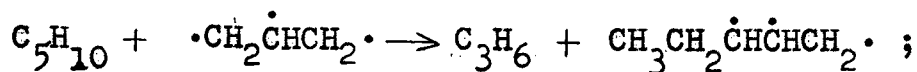
Both static and flow methods were used by Pease and Morton (29) in a study of the pyrolysis of pentene-2. They showed that the reaction was homogeneous and monomolecular at temperatures between 500 and 600°C. Since the pressure-time curves rose perfectly regularly from the start to something short of 100% pressure increase, they concluded that polymerization is not an important primary reaction.

Chain mechanisms were proposed by Rice (10) for the decomposition of higher olefins. The decomposition mechanism suggested for pentene-1 was the following: initiation occurs by splitting of the β C-C bond:

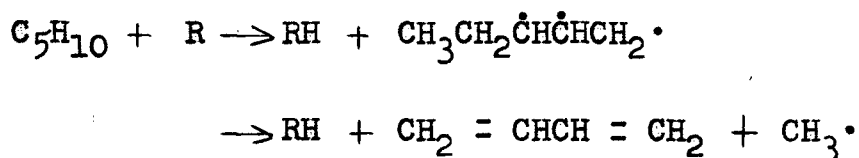


this is followed by reaction of the radicals formed with pentene molecules:





and a chain reaction takes place:



where $\text{R} = \text{CH}_3\cdot$

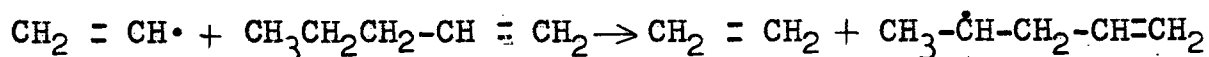
This scheme predicts the formation of equal proportions of methane and butadiene, which should therefore constitute the main decomposition products.

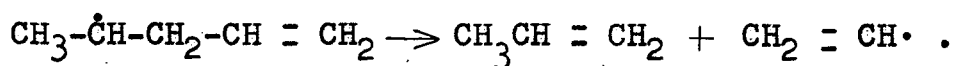
Both pentene-1 and pentene-2 were studied by Hurd, Goodyear, and Goldsby (30) in a flow system at temperatures between 500 and 600°C. Pentene-2 was found to be the more stable. Analyses were made of the entire gaseous reaction products, showing the chief products from both to be methane, butene-1, propylene, ethane, and ethylene, together with small amounts of butene-2, butadiene, and hydrogen, and, in the case of pentene-1, some propane. Isomerization of pentene-1 to pentene-2 and the reverse, at temperatures above 580°C. was established by precise distillation. The non-formation of isopropylethylene from pentene-2 was taken as evidence against an allylic type of intramolecular wandering of the methyl radical. This is also assumed to exclude intramolecular wandering of the H radical as the mechanism for the observed conversion.

Mikhailov and Arbuzov (31), in pyrolyzing pentene-1 and

pentene-2 in a flow system in the temperature range 500 to 700° C., found that the use of steam as a diluent tended to prevent polymerization.

Gorin, Oblad, and Schmuck (32) investigated the pentene decompositions under conditions designed to promote maximum survival of the diolefin products. A flow system was employed with nitrogen as a diluent. At 800°C. the main reaction of pentene-1 was found to be a splitting to ethylene, propylene, butylene, and butadiene. Pentene-2 yielded mainly butadiene, with smaller amounts of ethylene and propylene. In the pyrolysis of mixtures of n-pentane and pentene-2, no selective cracking of the olefin was observed. On the basis of these observations, Gorin proposed a modified Rice mechanism for the decomposition of the pentenes. Rice's free-radical chain mechanism for olefin decomposition involved the fundamental assumption that the chain sequence reaction, wherein an alkyl radical reacts with an olefin, takes place exclusively by removal of a β -H atom. This predicts that pentene-1 should decompose exclusively to methane and butadiene in the primary process. Since Gorin's analyses showed that only 30% of the pentene-1 decomposes in this way, and that the majority of the reaction involves splitting to light olefins, he suggested that the free radicals do not react exclusively with the β -hydrogens at high temperatures but also with the γ - and δ -hydrogens. The chain sequence predicted is:





Two further points of evidence indicate short chains: (a) relatively large amounts of ethane were formed; by assuming the primary reaction to be, exclusively, a splitting of the β C-C bond to yield an allyl and an ethyl radical, each of which subsequently reacts with pentene to produce ethane, a maximum value of 7 was calculated for the chain length; (b) ethylene was formed in considerably greater amounts than was propylene. Gorin explains this as follows: abstraction of a δ -H from pentene-1 yields a radical which must decompose to ethylene and an allyl radical. The relatively stable allyl radical will tend to dimerize or to combine with other radicals rather than perpetuate the chain by combining with the pentene-1 to give propylene. Butenes are assumed to result from the chain-stopping recombination of a methyl and an allyl radical. The experimental results for pentene-2 were found in better agreement with the Rice predictions, butadiene forming the principal reaction product.

The pyrolysis of pentene-2 and trimethylethylene by flow methods at 778 to 850°C. and high pressures in the presence of steam was carried out by Hepp and Frey (33). These investigators also found butadiene to be the principal reaction product from pentene-2, with lesser amounts of pentadiene, ethane, butene, ethylene, and propylene. In the case of trimethylethylene, formation of the allyl radical in the primary process seemed unlikely, indicating the operation of

some mechanism other than that proposed by Gorin for the butene formation. The authors suggest addition of a hydrogen atom to one of the doubly-bound C atoms, with the formation of a high-energy radical, decomposing to an olefin and a smaller radical. This proposal was substantiated by the detection of relatively large amounts of hydrogen from the trimethylethylene and pentene-2 decompositions. For pentene-1 however such H atom addition would lead only to C_2 and C_3 hydrocarbons.

Recently, a comparative study of the thermal decompositions of several olefins in a static system was made by Molera and Stubbs (34). The hydrocarbons studied were butene-1, pentene-1, hexene-1, heptene-1, butene-2, isobutene, 2-methylbutene-1, and 3-methylbutene-1. Analyses were made in some cases. The decompositions were shown to be of the first order, and the activation energies were determined. A reaction mechanism was proposed for the isobutene decomposition. In the case of pentene-1, the initial part of the pressure increase-time curve was found to be a straight line passing through the origin, with a decrease in rate as the reaction came to an end. The activation energy, measured over the temperature range 430 to 530°C., was found to be 53.1 kcal. per mole for 100 mm. pentene pressure, and 54.6 kcal. per mole for 300 mm. pressure. Addition of nitric oxide produced no appreciable effect on the reaction rate; added propylene and ethylene both caused a slight decrease in the rate. No analyses were made for the reaction products from pentene-1.

From this summary it is seen that, although several investigations have been made on the pyrolysis of pentenes, with the exception of the experiments of Pease and Morton (29) and those of Molera and Stubbs (34), these experiments have been done in flow systems under conditions of temperature and pressure different from those used in the present work. The pentene decompositions have been found homogeneous and first-order. At temperatures of about 800°C., the reaction products from pentene-1 are mainly light olefins with a lesser amount of butadiene, while pentene-2 yields mainly butadiene. High temperatures seem to favour diolefinic products. At lower temperatures (500 to 600°C.) the chief products of both are methane, butene-1, propylene, ethane, and ethylene. Isomerization takes place above 580°C. At low temperatures polymerization predominates. Various reaction mechanisms have been proposed.

Basis of the Present Investigation

Olefinic hydrocarbons exhibit, on pyrolysis, certain interesting peculiarities not found in the case of saturated organic compounds. Furthermore, the pyrolysis of a normal saturated paraffin yields an olefin and a lower paraffin. Therefore, for a full interpretation of a paraffin decomposition, a knowledge of the decomposition kinetics of the olefinic part of the product would be required. Secondary decomposition of the products has been shown to lead to a sigmoid type of pressure increase-time curve which, for analysis, entails a

knowledge of all the products and their relative stabilities (35). It would be necessary to know, for example, if the ethylene and propylene, which are found in the reaction products of most paraffins, are produced directly from the paraffins, or by the secondary decomposition of a higher olefin. Accordingly, olefin decompositions deserve study not only on their own merits, but also because of their potential use in further elucidating the mechanisms of paraffin decompositions.

Pentene-1 was selected for investigation in the present study as it is a typical "higher olefin" of the type believed to be formed in the pyrolysis of the higher paraffins. The object of the work was to obtain additional information on the thermal stability of this compound and also on the mechanisms involved in its pyrolysis.

EXPERIMENTAL

The thermal decomposition of pentene-1 was studied in the gas phase. The decomposition was carried out in a closed quartz reaction vessel, heated externally by a furnace, and the extent of the reaction was followed by observation of pressure changes, using a mercury capillary manometer. The experimental conditions were varied by changing the pressure and temperature of the gas, by adding inert gases, inhibitors, and a free-radical-producing substance to the reaction system, and by altering the surface-to-volume ratio of the reaction vessel.

Reagents

The pentene-1 used in this investigation was obtained from Phillips Petroleum Company, Special Products Division, Bartlesville, Oklahoma. Since this material was specified as "Research Grade," it was not subjected to further purification.

Propylene, also "Research Grade," was obtained from the same source. The gas was condensed in a liquid nitrogen trap and pumped before admission to a storage bulb in the system.

"Reagent Grade" argon was obtained from The Matheson Company Incorporated, E. Rutherford, N. J.

Nitrogen was obtained from the Canadian Liquid Air Company and was specified as "Commercial Grade."

Nitric oxide was prepared by the action of a sulfuric acid solution of ferrous sulfate on sodium nitrite (36). The gas was freed from carbon dioxide and higher oxides of nitrogen by

passage through 6 normal sodium hydroxide and a tube containing sodium hydroxide pellets. It was dried by passage through phosphorus pentoxide.

Lead tetraethyl was obtained from the Imperial Oil Company in the form of an approximately 10% solution in a hydrocarbon solvent, containing ethylene dichloride, ethylene dibromide, and a dye. Owing to the extreme toxicity of lead tetraethyl no attempt was made to obtain this compound in a pure form.

Monochlorotrifluoromethane was obtained from the Canadian Ice Machine Company.

Description of the Apparatus

The apparatus used in this investigation was an all-glass static system, as shown in Fig. 1. This consisted essentially of an externally heated quartz reaction vessel, A, connected to an evacuating system, N, a mercury manometer, B, for pressure measurement, storage vessels, C, D, E, F, G, and H, for reactants, and a sampling system, K. The quartz reaction vessel had a volume of approximately 200 ml. and an outside diameter of 55 mm. It was connected to the evacuating system and mercury manometer by quartz tubing and a ground-glass joint, J_1 . The Picein wax used for the seal did not develop any leaks during several months of continuous heating. The pressure in the system was measured by a closed U-tube mercury manometer, B, connected to the reaction vessel by means of capillary tubing. Pressure readings were made with reference to a mirror scale graduated in millimeters.

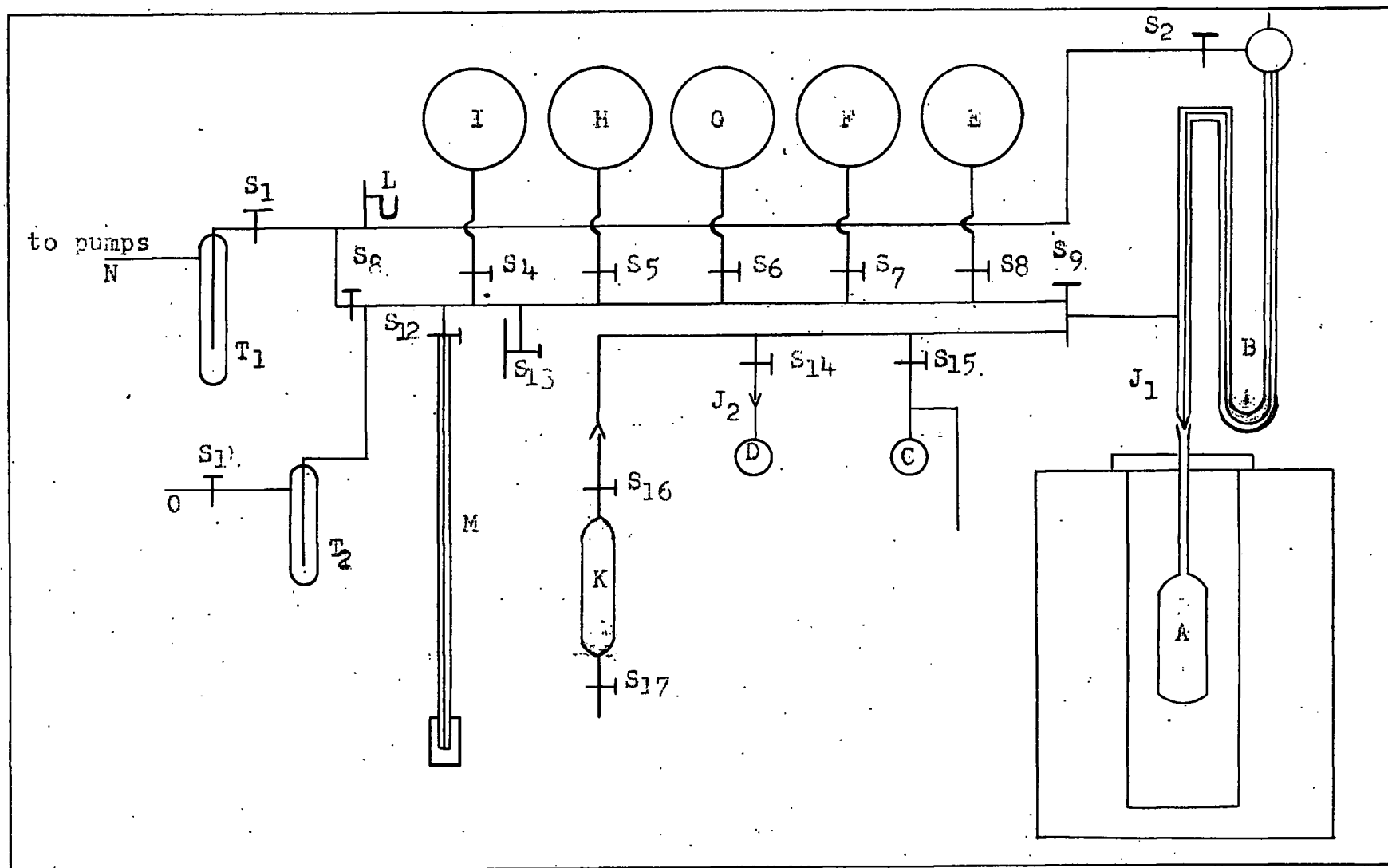


Fig. 1. Diagram of apparatus.

The system was evacuated by a mercury diffusion pump backed by a rotary oil pump. A trap, T_1 , cooled in dry ice-acetone, was situated between the mercury pump and the rest of the system in order to prevent mercury vapour from diffusing to the two galleries and the reaction vessel and also to prevent reaction vapours from reaching the pumping system. Through the upper and lower galleries, which could be evacuated separately or simultaneously, the reaction vessel was evacuated. A discharge tube, L, attached to the system, and capable of connection with all parts of the system, was used to indicate the attainment of a "black vacuum."

Pentene-1, which is a liquid at room temperature and pressure, was stored in a small bulb, C, attached to the lower gallery. The bulb was filled through a small-bore side-arm by suction from a vacuum in the system above. Before use, the pentene was thoroughly frozen in liquid nitrogen and pumped to remove traces of air. It was volatilized by warming the bulb in a beaker of warm water. The lead tetraethyl solution was stored in a small bulb, D, connected to the lower gallery by a ground-glass joint, J_2 . The gaseous materials, propylene, argon, nitrogen, nitric oxide, and freon, were stored in 2-liter glass bulbs, E, F, G, H, and I, attached to the upper gallery. These were filled in the following ways. To admit propylene, the cylinder containing the liquid under pressure was connected to the apparatus at O with pressure tubing. With taps S_{10} and S_{11} open, the upper gallery, connecting

tubes, and trap T_2 were evacuated. Trap T_2 was cooled in liquid nitrogen. With taps S_8 and S_{10} closed, the reducing valve on the cylinder was opened, and sufficient propylene gas was allowed to enter and condense in trap T_2 . After thorough pumping of the condensed propylene, trap T_2 was warmed, and the propylene was vaporized into the evacuated storage globe.

The other gases used were admitted in a different manner. The cylinder (or, in the case of nitric oxide, the generator) containing the gas was attached to the system through the 2-way stopcock S_{13} by pressure tubing. A strong stream of gas^{was} allowed to flush out the connecting tubing, and the upper gallery and storage bulb were evacuated. The 2-way stopcock was then reversed, and the gas allowed to enter until the pressure, as registered by an open mercury manometer, M , attached to the upper gallery, was approximately one atmosphere.

To prevent condensation of the lead tetraethyl or of the reaction products, the lower gallery and capillary connections were wound with Chromel resistance wire and could be heated electrically.

The stopcocks which were not subjected to heating were sealed with Apiezon M grease which was found to provide an excellent vacuum seal. As this grease is not effective at high temperatures, heated stopcocks were sealed with Dow Corning "Silicone High Vacuum" stopcock grease which maintains its consistency up to 200°C ., although does not give such an efficient seal as the Apiezon grease.

The reaction vessel was heated in an electric furnace constructed by Patrick (37). The furnace, built from a cylindrical quartz core, three inches in diameter, was heated by alternating current in three sections of Chromel resistance wire winding. It was insulated with several inches of powdered asbestos, and the top opening was sealed with a mixture of powdered asbestos and alundum cement.

The temperature of the reaction vessel was measured by two Chromel-Alumel thermocouples placed in contact with the wall of the vessel, at top and bottom respectively. These were connected to the potentiometer circuit through a double-throw switch, to permit rapid consecutive reading. The thermocouples were calibrated by use of the melting points of pure tin, lead, zinc, and aluminum, and the transition temperature of potassium sulphate, which covered the range of temperature used in this investigation.

The temperature of the furnace was adjusted to give a constant reading over the length of the reaction vessel by means of three variable resistances, each connected in series to one of the three furnace windings. These three sections were connected in parallel to the power supply.

The temperature was controlled automatically by an electronic thermoregulator operating a relay. Closing of the relay shorted out a controlling resistance in the power supply, so increasing the current to the furnace. A diagram of the furnace circuit is shown in Fig. 3.

The thermoregulator, of the type developed by Coates (38), was constructed by Coope (39). The circuit diagram is shown in Fig. 2. Operation of the instrument is based on the reversal of phase of the out-of-balance e.m.f. of an a-c. bridge which occurs on passing from one side of balance to the other. The circuit is composed of four main parts: an a-c. bridge, a circuit for amplifying the bridge output, a circuit for converting the bridge output to variable d-c. voltage, and a relay.

The a-c. bridge consists of a centre-tapped transformer, T_1 , a resistance thermometer, R_1 , and a standard variable resistance, R_2 , which can be adjusted to balance the bridge at any desired temperature. The bridge output, e_{g1} , is amplified by V_1 and applied to the grid of V_2 as the much larger alternating voltage e_{g2} . An alternating voltage, e_{a2} , is applied to the anode of V_2 which will therefore pass current only during the half cycles in which e_{a2} is positive. Hence the magnitude of the anode current, i_2 , depends on both the magnitude and the phase of the a-c. grid voltage, e_{g2} . The anode current generates a potential difference across R_3 which is smoothed by C_1 , R_4 , and C_2 , and applied to the grid of the output triode, V_3 as the d-c. voltage, e_{g3} . The anode current of V_3 controls the furnace through the relay.

In the apparatus used, T_1 was a Type 167-D 110 to 6 v. centre-tapped transformer. The anode supply to V_2 was provided by the 110 v. a-c. mains. V_1 was a 6SJ7 pentode, V_2 a

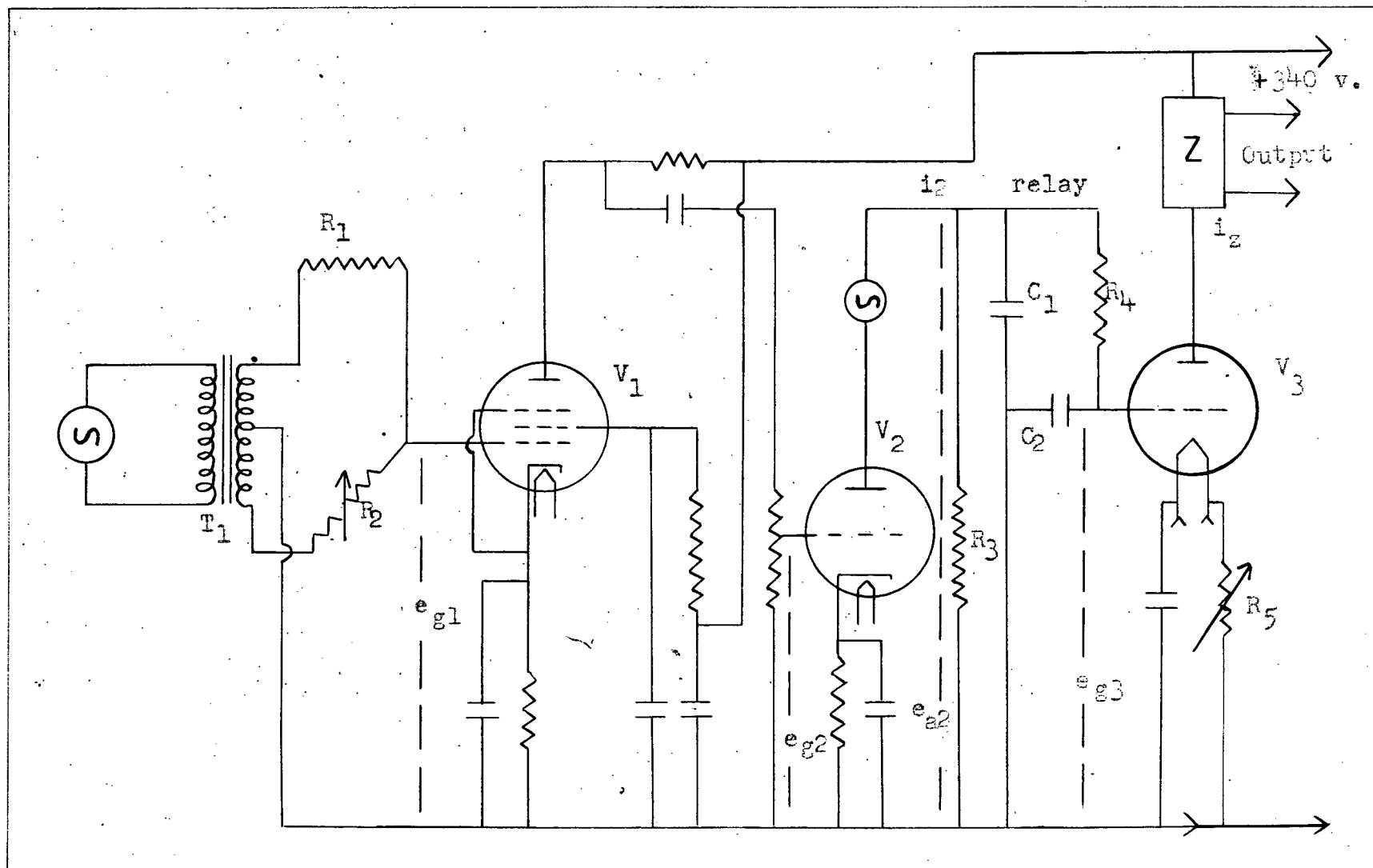


Fig. 2. Circuit diagram of thermoregulator.

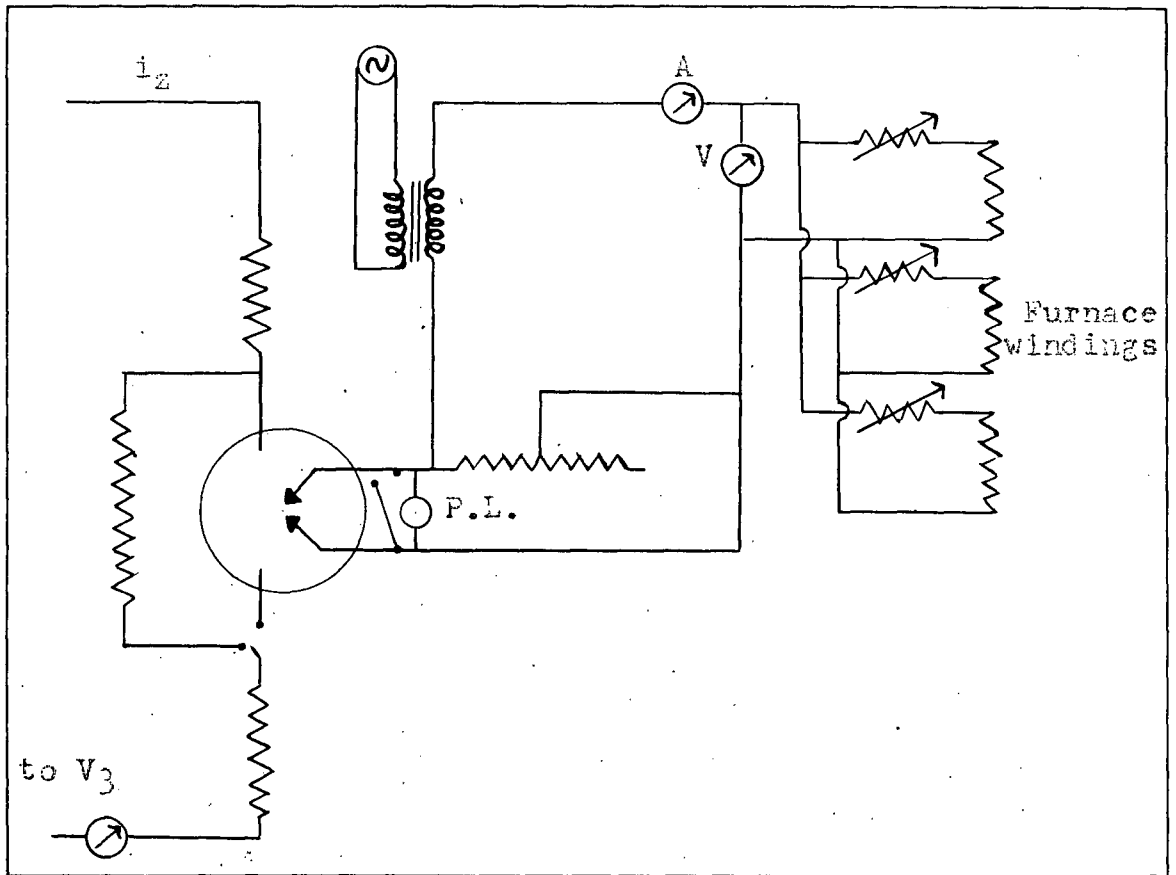


Fig. 3. Relay and output circuits controlling furnace temperature.

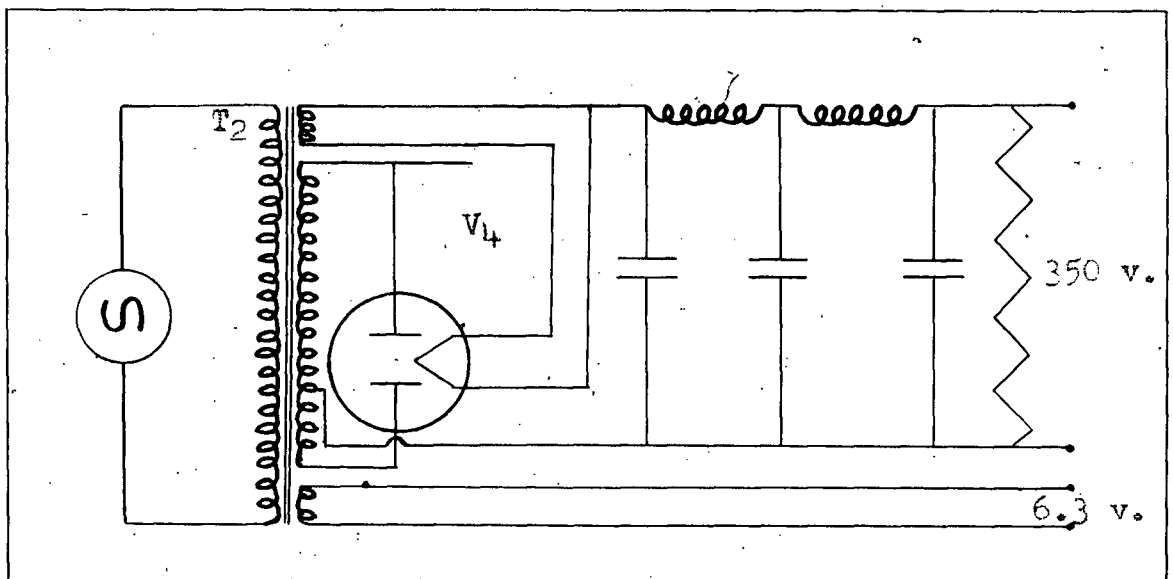


Fig. 4. Power supply for thermoregulator.

6SF5 triode, and V_3 a 6B4G power output triode. The 350 v. d-c. anode supply to V_1 and V_3 was provided by a full-wave rectifier and smoothing circuit shown in Fig. 4. In the powerpack, T_2 was a Thordardson T-13R13 transformer, and V_4 a type 80 full-wave rectifier. The variable resistance R_2 in the a-c. bridge was a standard 0.1 to 1000 ohm decade dial resistance box. The Type M molybdenum resistance thermometer used by Coope was found inadequate for the temperature range used in the present investigation. A platinum resistance thermometer was constructed from 11 ft. of 0.05 in. platinum wire of 30 ohms resistance. The wire was tightly coiled and wound on a thin mica strip. The ends were silver-soldered to thick copper lead wires, which were fastened to an alundum rod and mounted inside the furnace.

The relay circuit consisted of a Sunvic Type 602 vacuum relay with suitable series and shunting resistances.

The instrument was able to control the furnace temperature to within $\pm 0.5^\circ\text{C}$. at the temperature of this investigation.

Description of a Typical Experimental Run

The furnace was first adjusted to the desired temperature. Since several hours were required to heat the furnace from room temperature and to allow for the temperature distribution along the length of the furnace to reach equilibrium, it was maintained continuously at temperatures in the required range. Before an experimental run the variable resistance in the thermoregulator was adjusted to the appropriate temperature.

With the amplifier set at zero gain, the negative grid bias of V_3 was checked so the relay was at the trip point when the bridge was balanced. This relay trip point, about 16 ma., was indicated by a pilot light in the relay output circuit. With the gain set at low sensitivity the furnace was allowed to warm up; the gain was then adjusted for maximum sensitivity, and the furnace temperature was allowed to reach equilibrium. The three rheostats controlling the temperature distribution required separate adjustment for each temperature.

The mercury diffusion pump was used to evacuate the system to a "black vacuum." The pentene was cooled in a bath of liquid nitrogen and thoroughly pumped to remove traces of air. With taps S_3 and S_9 closed, and tap S_{15} open, the bulb containing the pentene was immersed in a beaker of warm water, from 50 to 100°C. depending on the initial pressure required, and a few seconds were allowed for some of the pentene to vaporize. Tap S_9 was then opened cautiously and the pressure in the reaction vessel, as indicated by the manometer, was allowed to increase sufficiently. Taps S_9 and S_{15} were then closed. At the completion of the filling, the timer was started, and the course of the reaction was followed by pressure-time measurements made at regular intervals. Constant tapping of the manometer was found necessary in order to prevent the mercury from sticking in the capillary tubing. At the conclusion of a reaction, taps S_3 and S_9 were opened to the pumps, and the system was thoroughly evacuated.

In an experiment involving a gaseous material, both the upper and lower galleries were first evacuated. Tap S_8 was closed, the upper gallery was opened to the reaction vessel, and a sufficient pressure of the desired gas was allowed to enter. After reversing of tap S_9 , the pentene was volatilized and admitted to the reaction vessel as described previously.

General Form of the Pressure-time Curves

Plots of pressure change vs. time for the decomposition of 150 mm. of pentene-1 at three different temperatures are shown in Fig. 5. At high temperatures the initial portion of the curve is a straight line passing through the origin, followed by a gradual decrease in rate as the reaction comes to an end. If, in such an experimental run, the initial pressure increase was too rapid to observe the exact initial pressure, this value was obtained by extrapolation of the straight line to zero time. Estimation of the initial rate from the slope of this straight line portion of the curve thus presented no difficulty. At lower temperatures there is at first a slight decrease of pressure, followed by a short period during which Δp is inappreciable. The curve then rises to a maximum, and subsequently decreases as the reaction comes to an end. The rates for comparison purposes were therefore taken as the maximum slopes of such curves, the initial rates obviously being useless as criteria for comparison.

Reproducibility of the rate curves was not found difficult to attain. To ensure the reproducibility of runs used in the

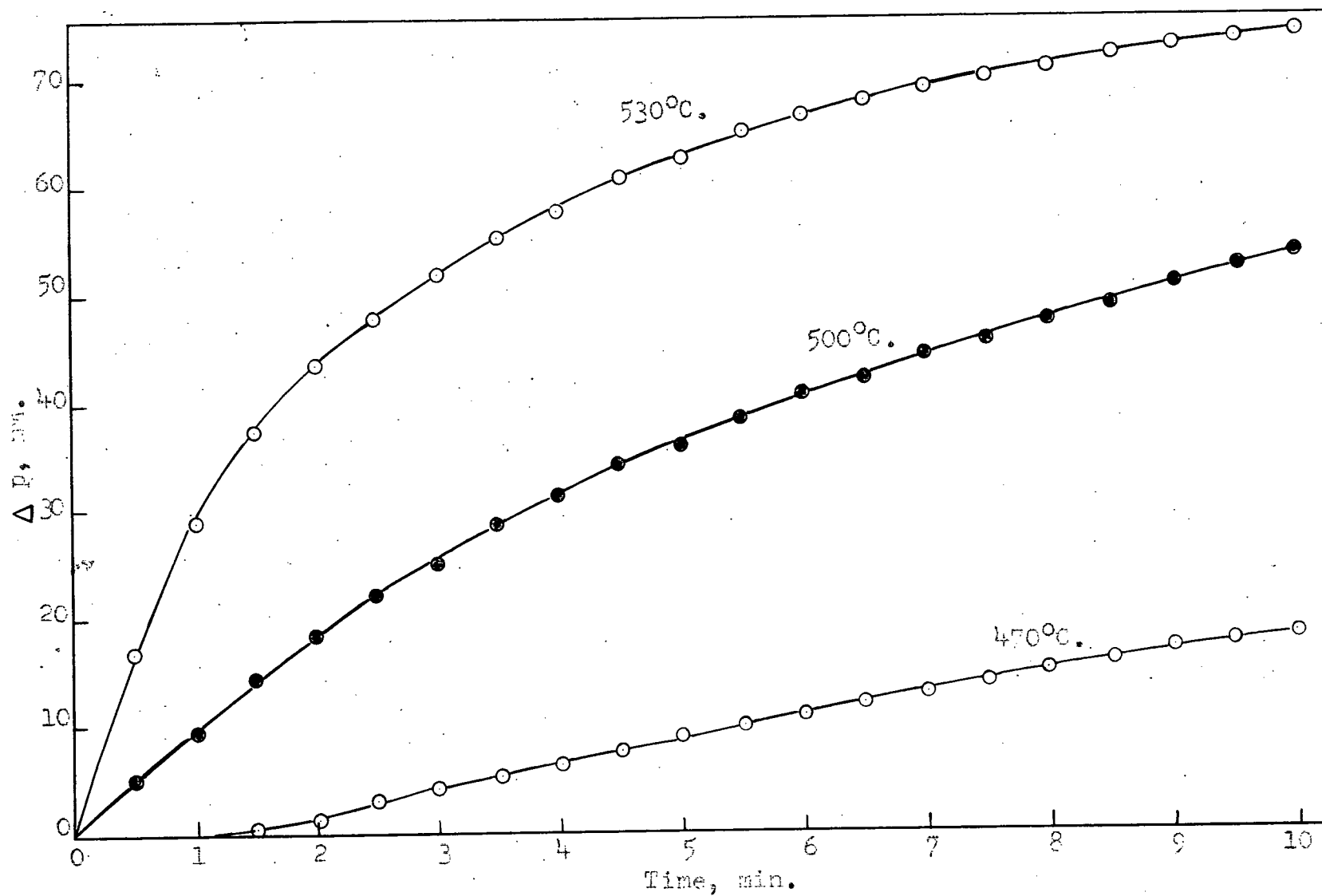


Fig. 5. Δp -time curves for decomposition of 150 mm. pentone-1.

calculations, each was made in duplicate or triplicate.

Dependence of the Rate on the Initial Pentene Pressure

The dependence of the rate of pressure change on the initial pentene pressure was investigated over a range of initial pressures from 60 to 247 mm. In Table I are recorded the results for experiments conducted at 500°C. and various initial pentene pressures.

TABLE I

Dependence of reaction rate on initial pentene pressure at 500°C.

Initial pentene pressure, mm.	Reaction rate, mm./min.
60	3.80
100	6.03
111	7.64
152	9.32
200	11.3
246	14.5

The Δp -time curves for these runs are shown in Fig. 6. The order was determined from the plot of $\log dP/dt$ vs. $\log P_0$, shown in Fig. 7. Integration of the equation:

$$dP/dt = k P_0^n,$$

yields:

$$\frac{d \log dP/dt}{d \log P_0} = n,$$

hence the slope of the curve gives the order of the reaction. The slope of the best line through these points is unity: it

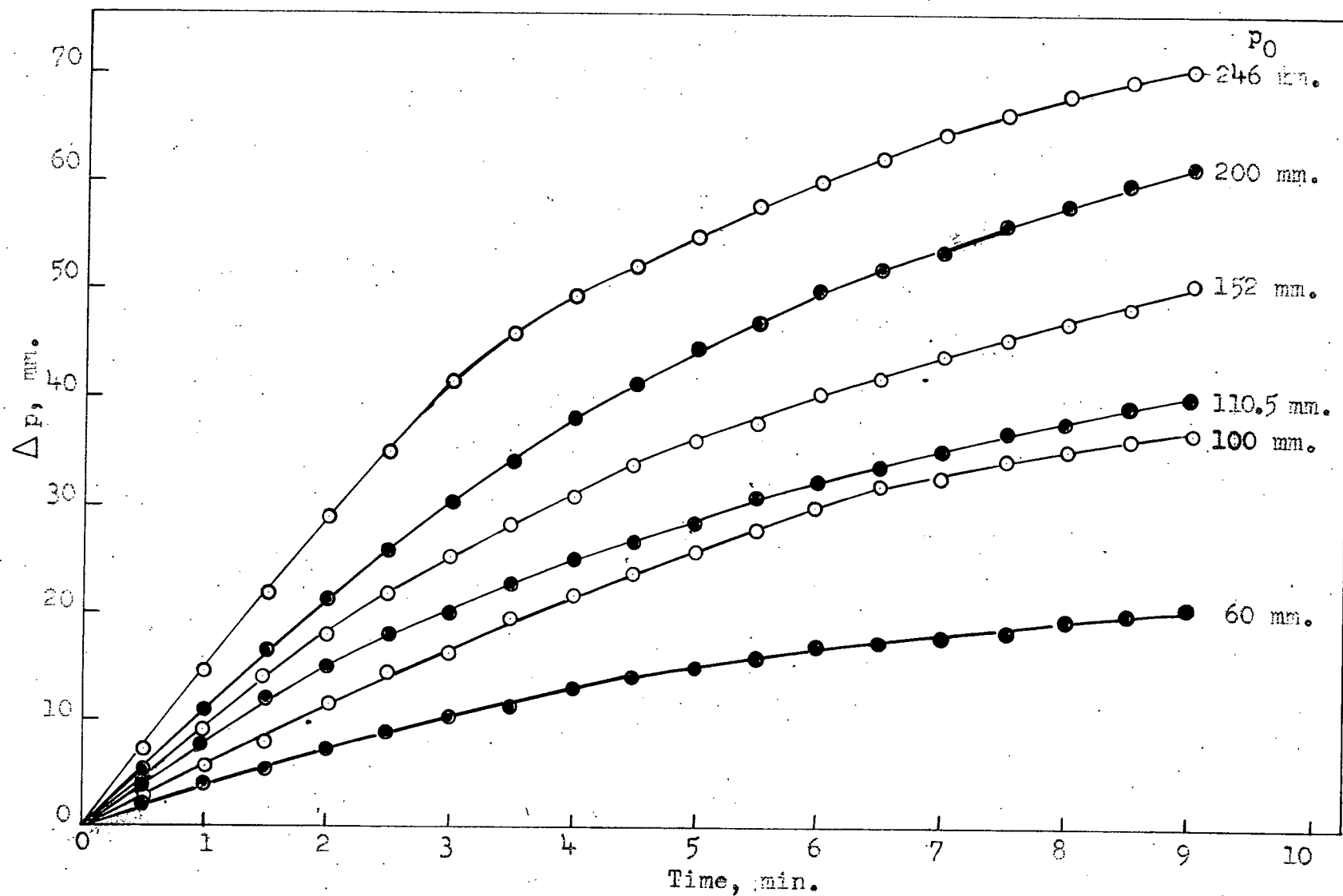


Fig. 6. Variation of rate with initial pentene pressure, at 500°C.

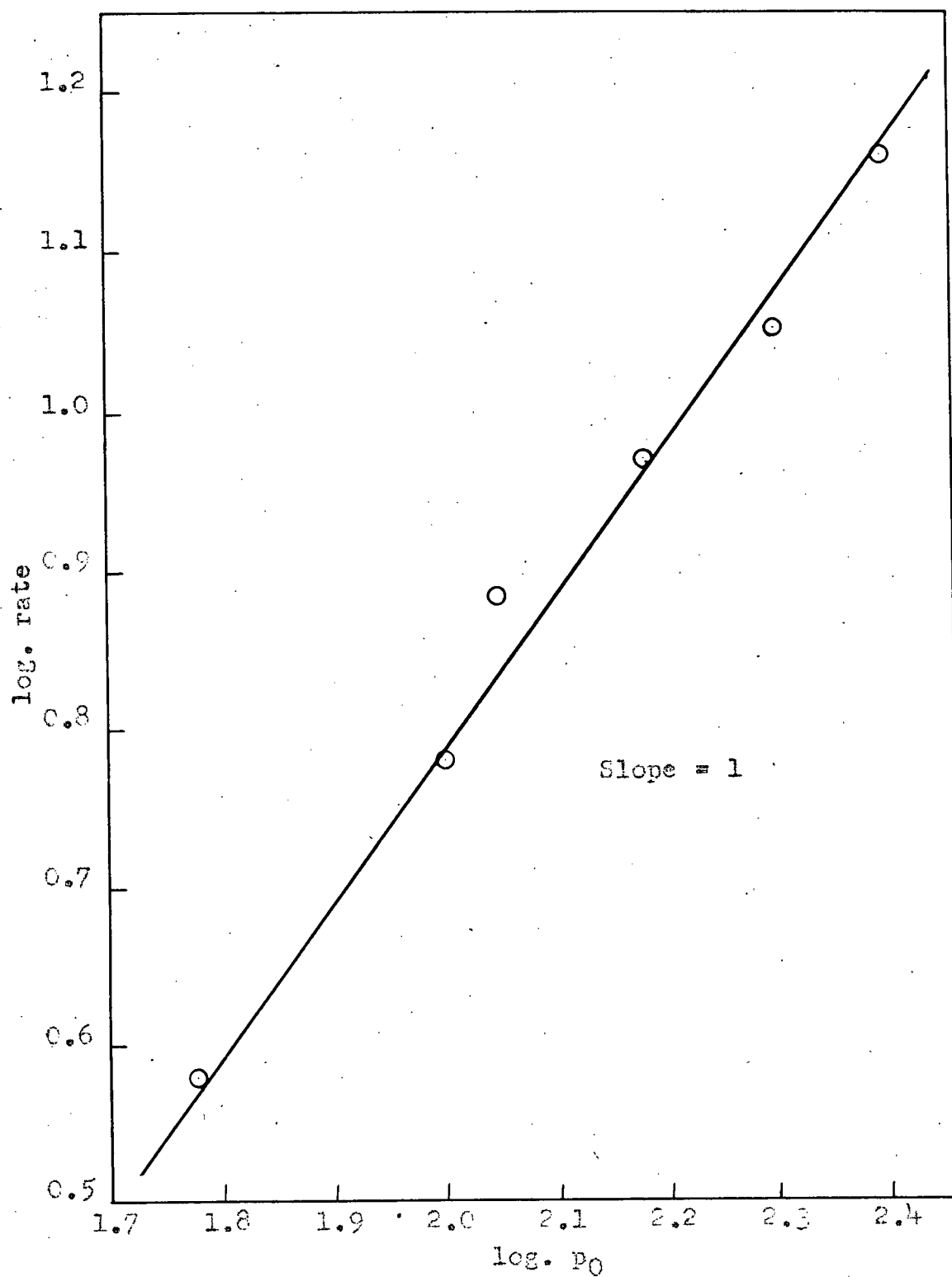


Fig. 7. Variation of rate with initial pentene pressure, at 500°C.

is therefore concluded that the reaction is first-order with respect to the pentene pressure.

Rate constants were calculated from the first-order equation:

$$dP/dt = k P_0$$

and are given in Table II. They were found approximately constant over the range of pressures investigated.

TABLE II

Reaction rates and rate constants for various initial pentene pressures, at 500°C.

Initial pressure, mm.	Rate, mm./min.	Rate constant, min. ⁻¹ x 10 ²
60	3.80	6.34
100	6.03	6.03
111	7.64	6.88
152	9.32	6.13
200	11.3	5.65
246	14.5	5.90

Effect of Increased Surface-to-Volume Ratio in Reaction Vessel

A qualitative estimation of the degree of heterogeneity of a gaseous reaction can often be determined by varying the surface-to-volume ratio in the reaction vessel.

The quartz reaction vessel was packed with short pieces of pyrex tubing. As no quartz tubing was available, the results of such surface increase can be of a qualitative nature only. The ends of the pieces of tubing were fire-polished in order

to avoid possible catalysis by "active centers" at sharp edges. A 10-fold increase in the surface-to-volume ratio was obtained in this way. In Fig. 8 are shown the Δp -time curves for the decomposition of 110 mm. of pentene-1 at 500°C. in both packed and unpacked reaction vessels.

Clearly the effect of increased surface is very small. A slight decrease in the initial rate was shown, indicating the possibility of a small amount of chain termination on the surface. In addition, a slight lowering of the final pressure attained may have been due to adsorption of the products. From the results it may be concluded that the reaction is essentially homogeneous.

Effect of Addition of Inert Gases

In homogeneous gas-phase reactions involving activation of the reactant molecules by bimolecular collisions, it has often been found possible, by decreasing the partial pressure of the reactant gas, to maintain the normal reaction rate by the addition of some inert gas.

Accordingly, experiments were carried out in the presence of both argon and nitrogen. Fig. 9 shows the rate curves for the decomposition of 100 mm. of pentene both alone and in the presence of 100 mm. of argon. A curve for the decomposition of 200 mm. of pentene at 530°C. is included for comparison. Fig. 10 shows a similar set of curves in which nitrogen is substituted for argon.

In both cases, the presence of the inert gas does not

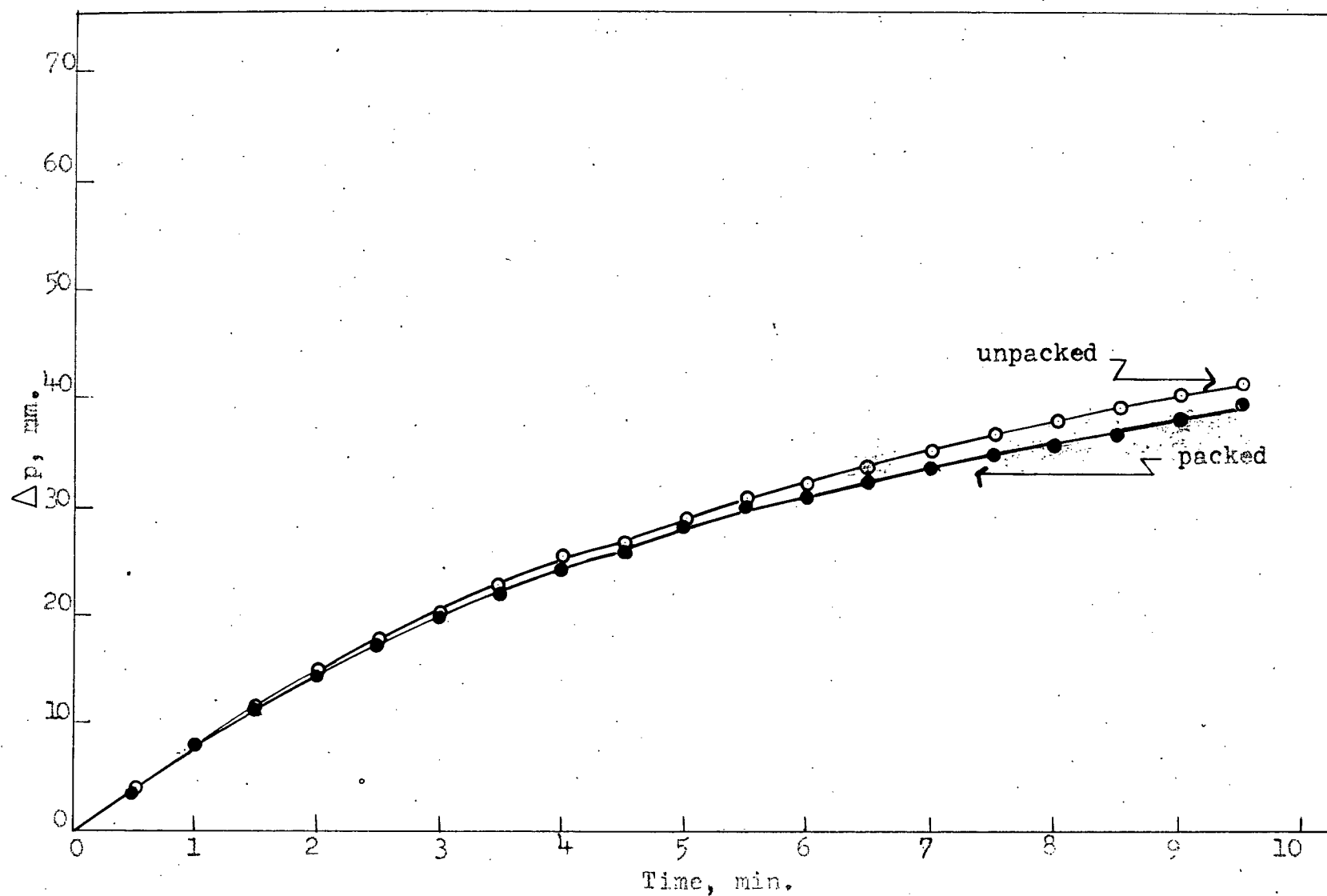


Fig. 8. Δp -time curves for decomposition of 110 mm. of pentene-1 at 500°C. in packed and unpacked reaction vessels.

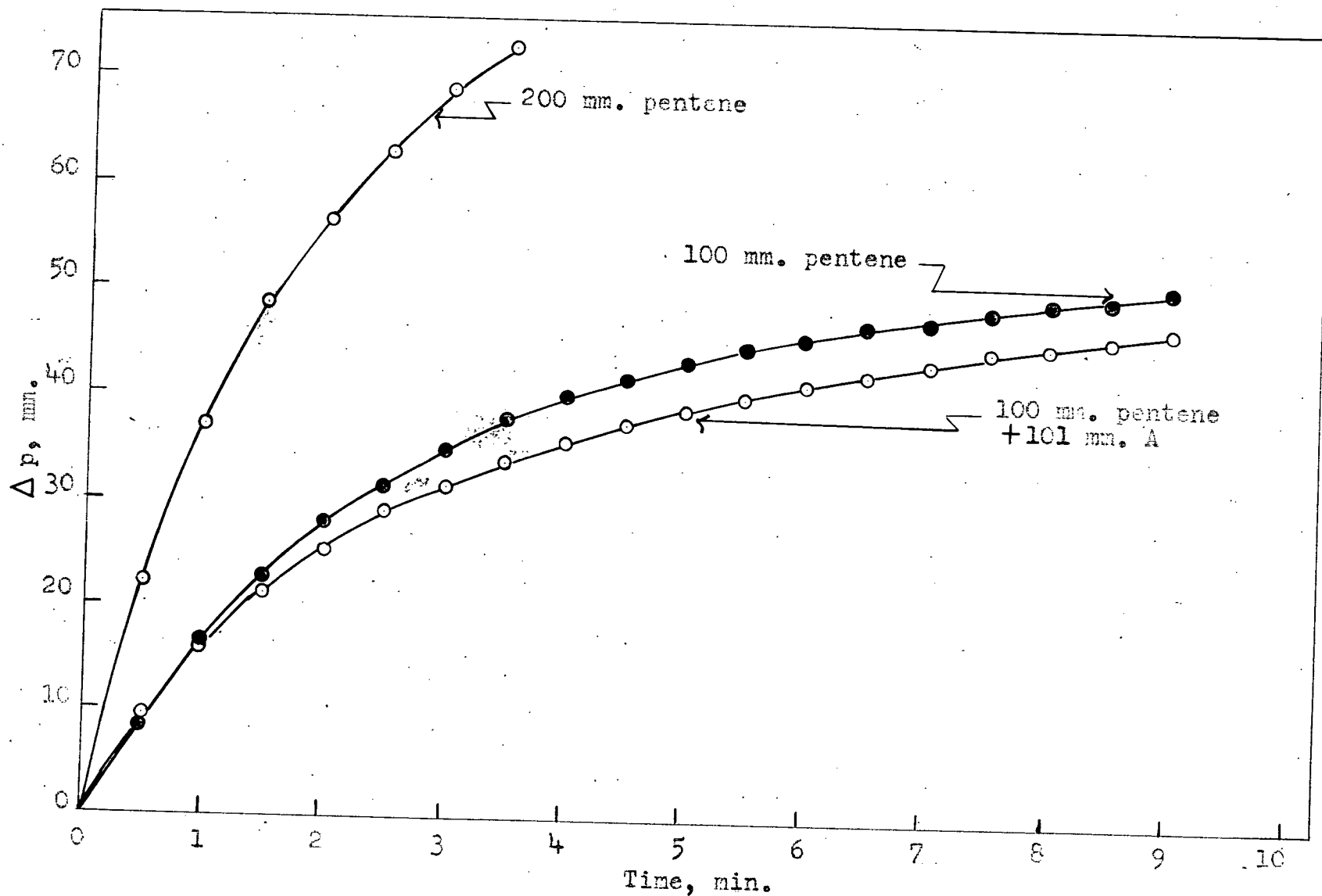


Fig. 9. Effect of A on rate, at 530°C.

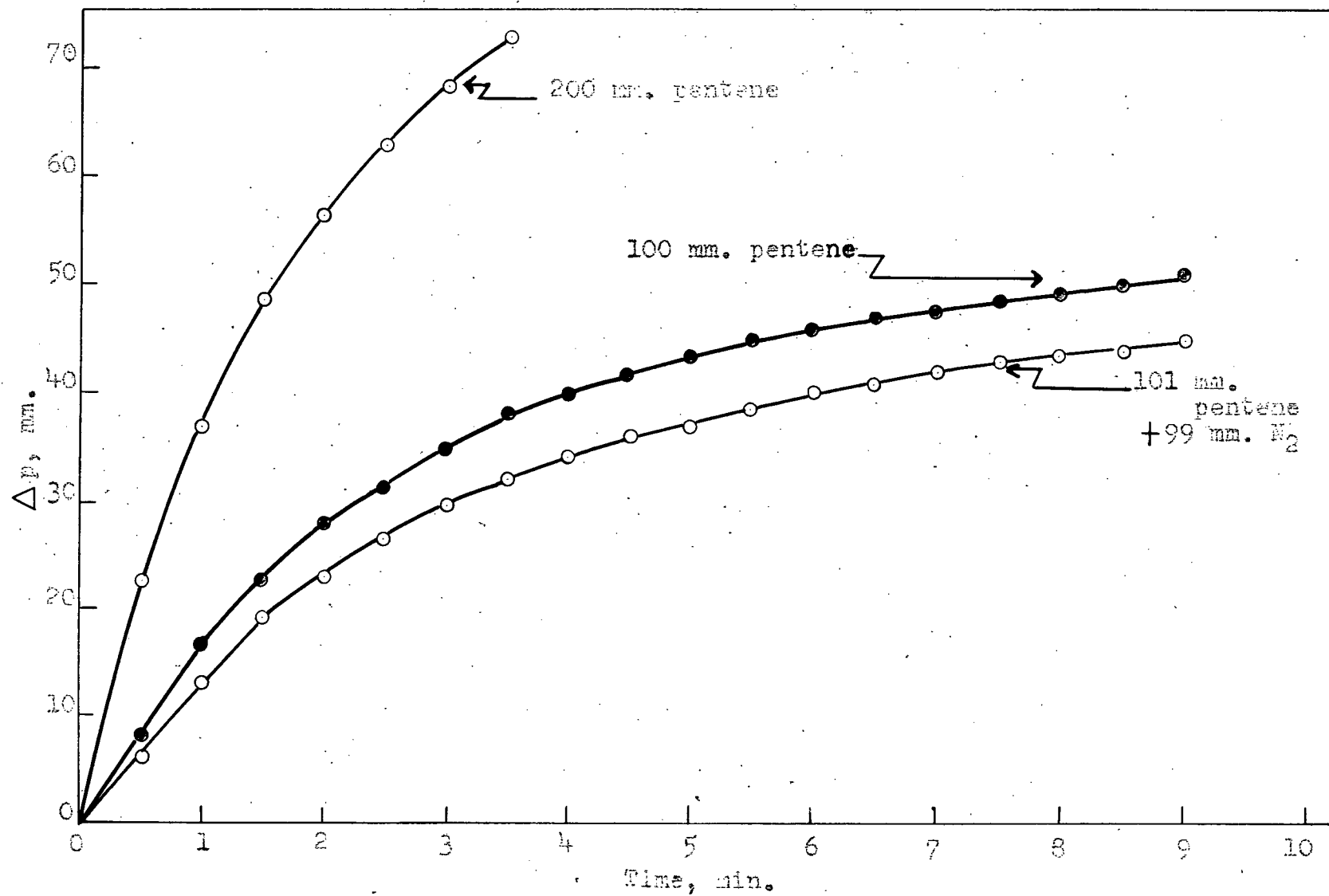


Fig. 10. Effect of N_2 on rate, at $530^\circ C$.

serve to maintain the high-pressure reaction rate. In fact, rates for the diluted reactions of 100 mm. of pentene are somewhat lower than the normal value for 100 mm. of pentene alone. This observation leads to the conclusion that the reaction is not a simple collisional process, but rather that it involves the intervention of some type of free-radical chain process. The observed decrease in rate could then be attributable to chain termination by radical recombination in the gas phase due to three-body collisions with inert gas molecules. Since surface effects were found to be negligible, any radical recombinations must, indeed, take place in the gas phase rather than at the surface of the reaction vessel.

Effect of Addition of Nitric Oxide

A method frequently employed to test for the presence of free-radical chains in a gas reaction is to add small amounts of some substance capable of inhibiting any such chains by reaction with the free radicals. Nitric oxide has often been found an effective substance for this purpose.

Experiments were done at 516°C. with 120 mm. of pentene. Consecutive runs were made with 1, 5, 11, and 50 mm. of nitric oxide. A second set of observations was made with 54 mm. of pentene and 1, 6, 10, and 13 mm. of nitric oxide respectively. Δ p-time curves for these runs are plotted in Fig. 11.

It is observed that nitric oxide has no appreciable effect on the reaction rates. This result may be interpreted in several ways: (a) that radical-chain processes are absent in

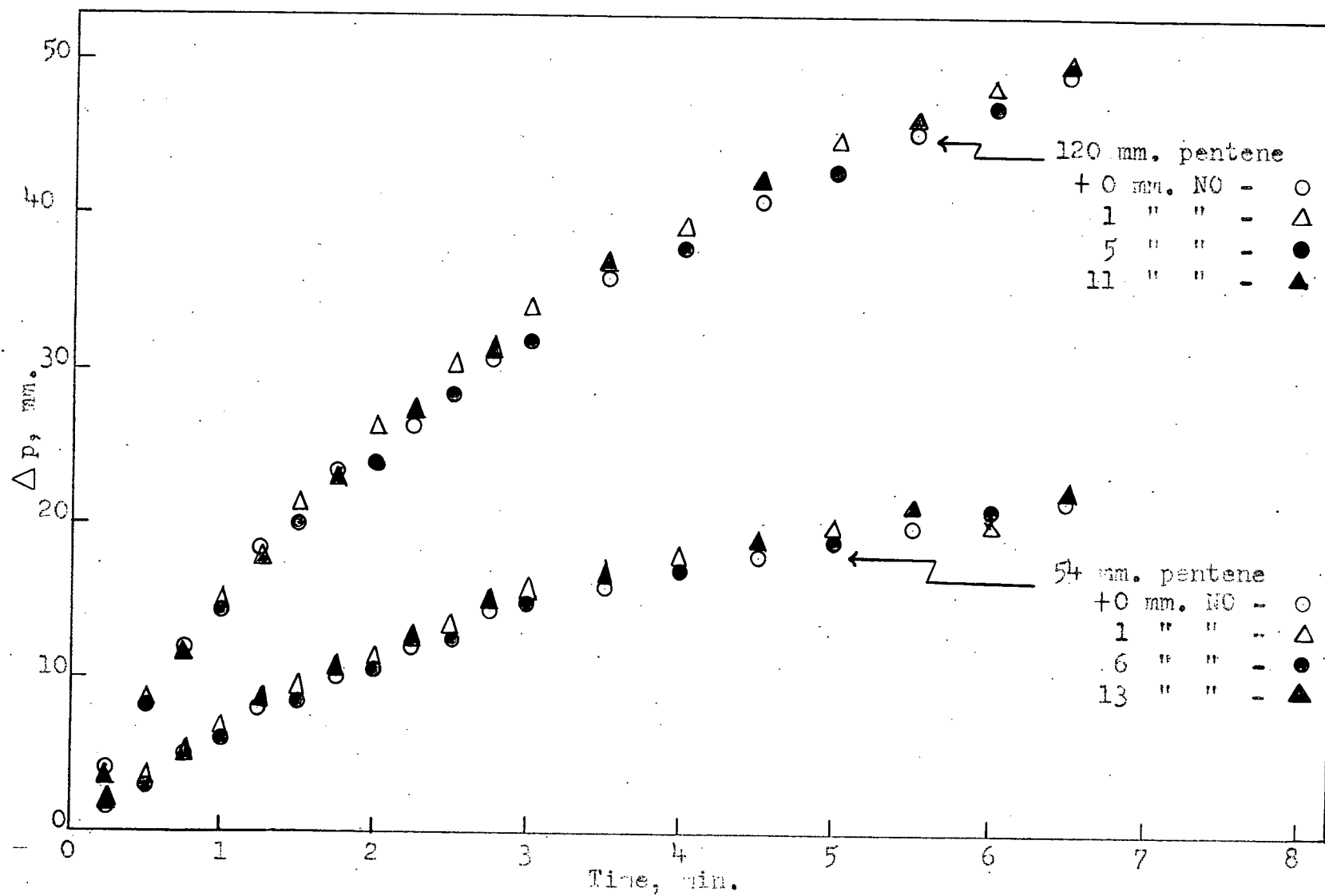


Fig. 11. Effect of NO on rate at 516°C.

this reaction; (b) that any inhibitory action of nitric oxide is masked by a catalytic effect; that is, that nitric oxide can start chains as well as stopping them; or (c) that the presence of some other chain inhibitor, presumably a reaction product, is more efficient in combining with the free radicals than is nitric oxide. In the latter case, any chain steps in the normal reaction would be mostly those of chain termination.

Effect of Addition of Propylene

Another substance which has frequently been used as an inhibitor of free-radical chains is propylene. Since propylene was found by previous investigators to constitute one of the decomposition products of pentene-1 (32, 34), it was of interest to determine if the presence of further amounts of this substance would inhibit the reaction rate.

Fig. 12 shows Δp -time curves for an experiment conducted at 516°C. with an initial pentene pressure of 110 mm., and for successive runs in the presence of 4, 6, and 24 mm. of propylene respectively. In Fig. 13 reaction rates are plotted as functions of the amount of propylene added. The results for three different initial pentene pressures are recorded in Table III.

Propylene was found to cause a decrease in the observed reaction rates. Quite considerable amounts of propylene were necessary to cause appreciable inhibition. In each case, the first few millimeters added produced no change in the reaction rate. As the partial pressure of the propylene was increased, the rate gradually decreased to approximately 80% of its

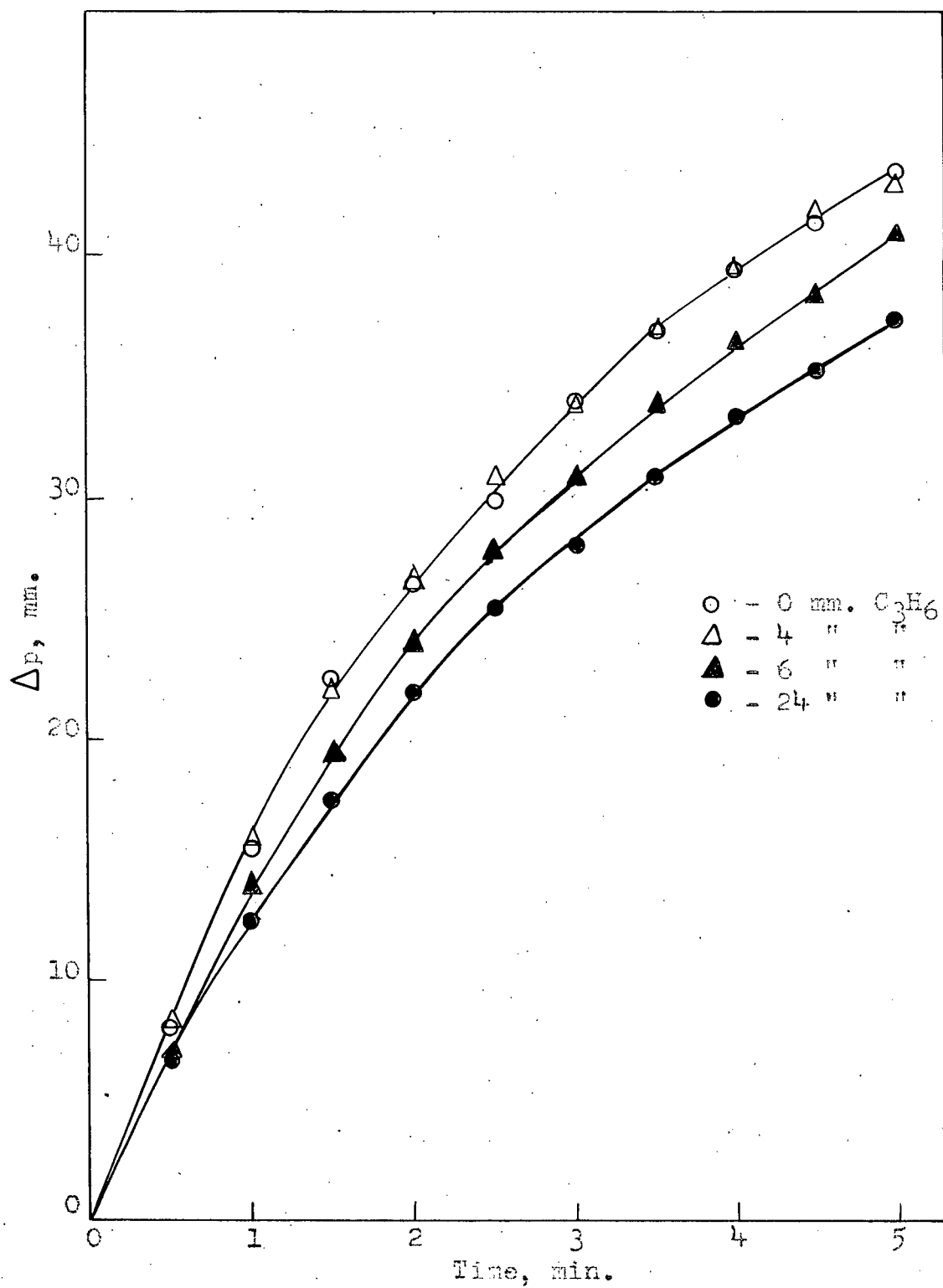


Fig. 12. Effect of propylene on rate of decomposition of 110 mm. pentene at $516^\circ C$.

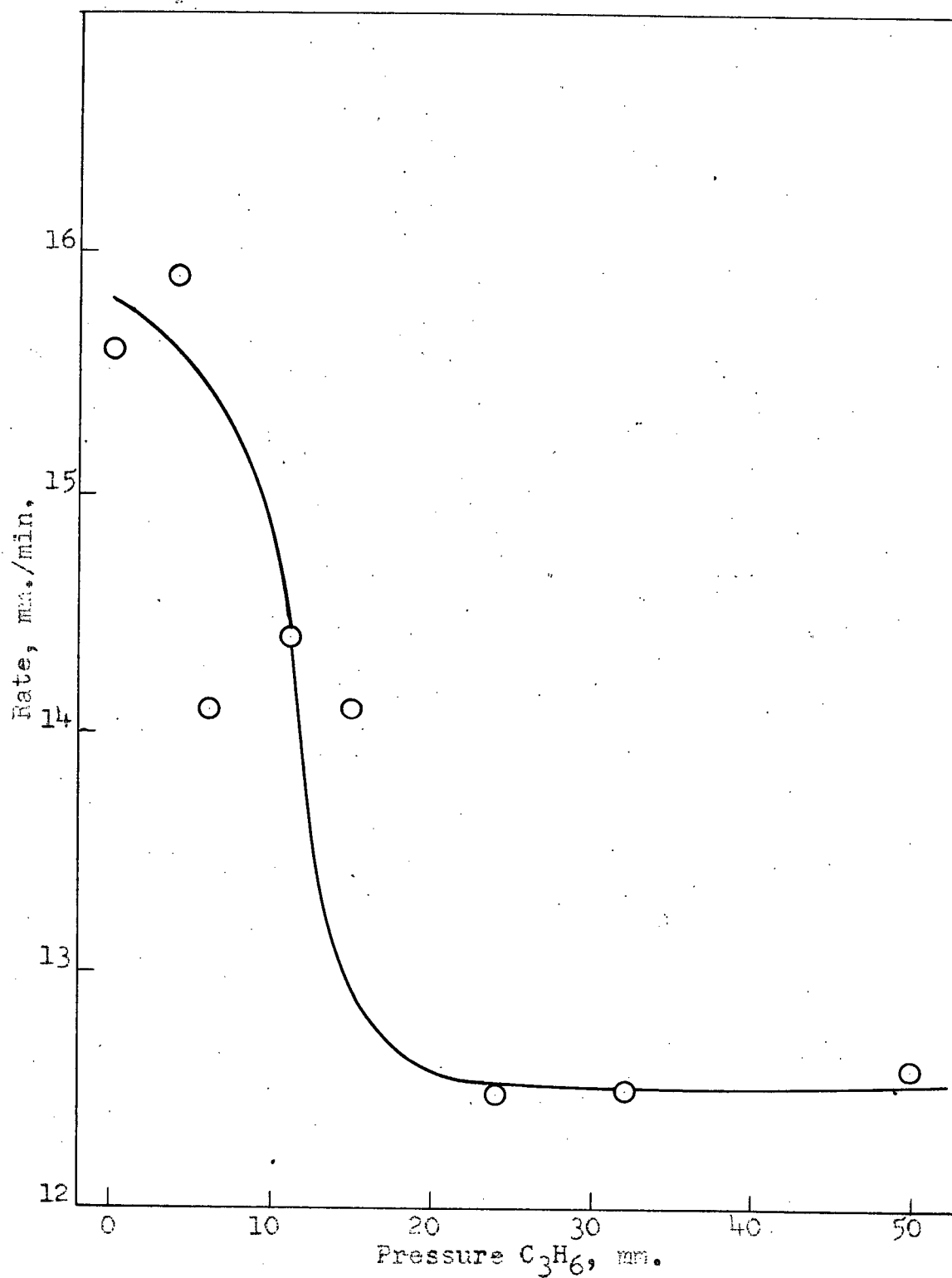


Fig. 13. Propylene inhibition of 110 mm. pentene, at $516^\circ C$.

initial value. As is shown by the long, flat minimum of the inhibition curves, further additions of propylene were without effect. The greater the initial pentene pressure, the greater was the amount of propylene required to produce maximum inhibition.

TABLE III

Rates of pentene-1 decomposition maximally inhibited by propylene, at 516°C.

Pentene pressure, mm.	Normal rate, mm./min.	Propylene pressure for maximum inhibition, mm.	Rate of maximally inhibited reaction, mm./min.
54	5.83	10	5.90
110	14.9	20	12.5
200	23.4	40	18.7

Since propylene alone, at this temperature, polymerises at a negligible rate (26), its effect on the pentene decomposition would seem to represent a true inhibition rather than an illusory effect due to a pressure decrease superimposed on the normal increase.

If the propylene is effective in suppressing all the chains, the residual reaction may represent a process of simple molecular rearrangement to products. However, it is possible that the maximally inhibited reaction is still a modified chain reaction. Such observations suggest the participation of free-radical chains, repressible by propylene, in the normal decomposition. The function of propylene is presumably

to terminate radical chains by combining with the chain carriers to form stable molecules or less active chain carriers.

Effect of Addition of Inert Gases on Rate of Maximally-Inhibited Decomposition

Since the decrease in the normal reaction rate due to dilution with inert gases could possibly be due to suppression of a chain reaction by three-body collisions in the gas phase, it was of interest to investigate the effect of such dilution on the maximally inhibited reaction. Figs. 14 and 15 show rate curves for the decomposition, at 516°C. , of 100 mm. of pentene, inhibited by 20 mm. of propylene, in the presence of 100 mm. of argon, and 100 mm. of nitrogen, respectively. The curves for the undiluted inhibited reactions are included for comparison. Neither argon nor nitrogen causes a decrease in the rate of the inhibited reaction. Rather, there is, in each case, a slight increase, possibly due to an increase in the collision rate of a non-chain part of the reaction.

Effect of Addition of Lead Tetraethyl

A further means of detecting the presence of free-radical chains is to add small amounts of an initiator, at temperature conditions under which the reactant gas is normally stable. The initiator must be a substance known to decompose into free radicals at the appropriate temperature. Metal alkyls are useful for this purpose.

In an attempt to initiate the decomposition of pentene-1 at low temperatures, lead tetraethyl was selected as a sensitizer, since this substance is known to decompose readily at

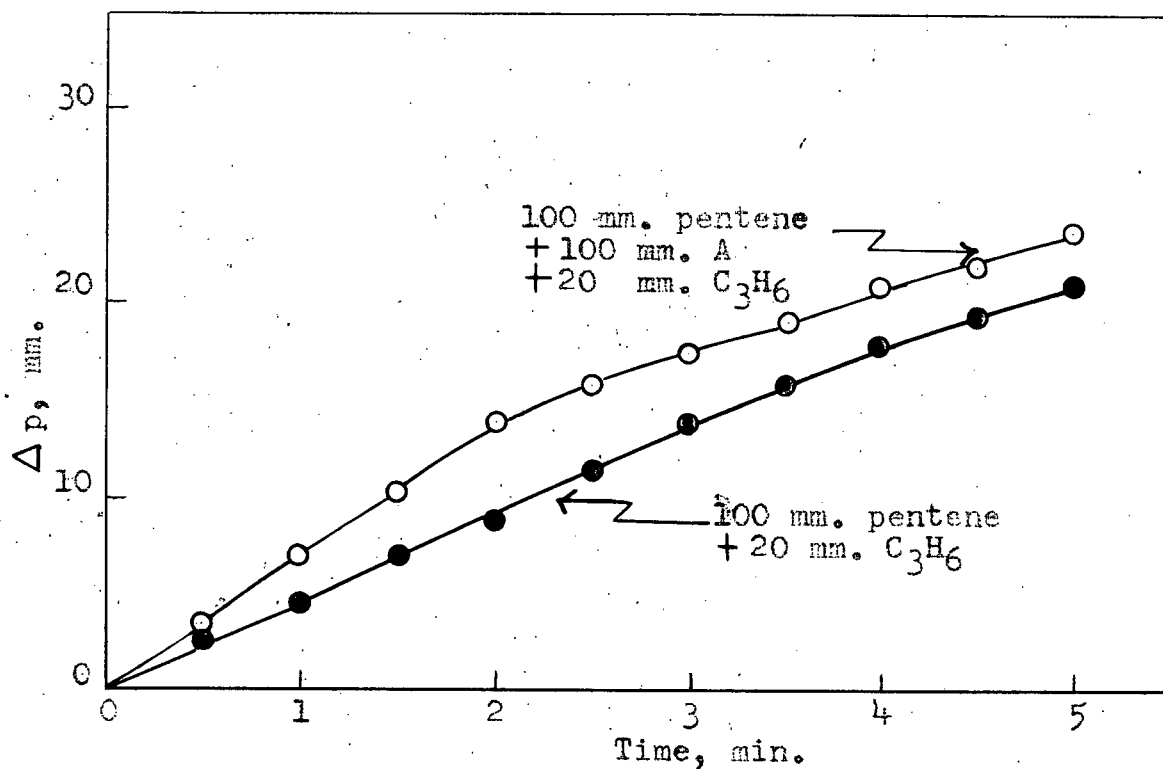


Fig. 14. Effect of A on maximally inhibited reaction.

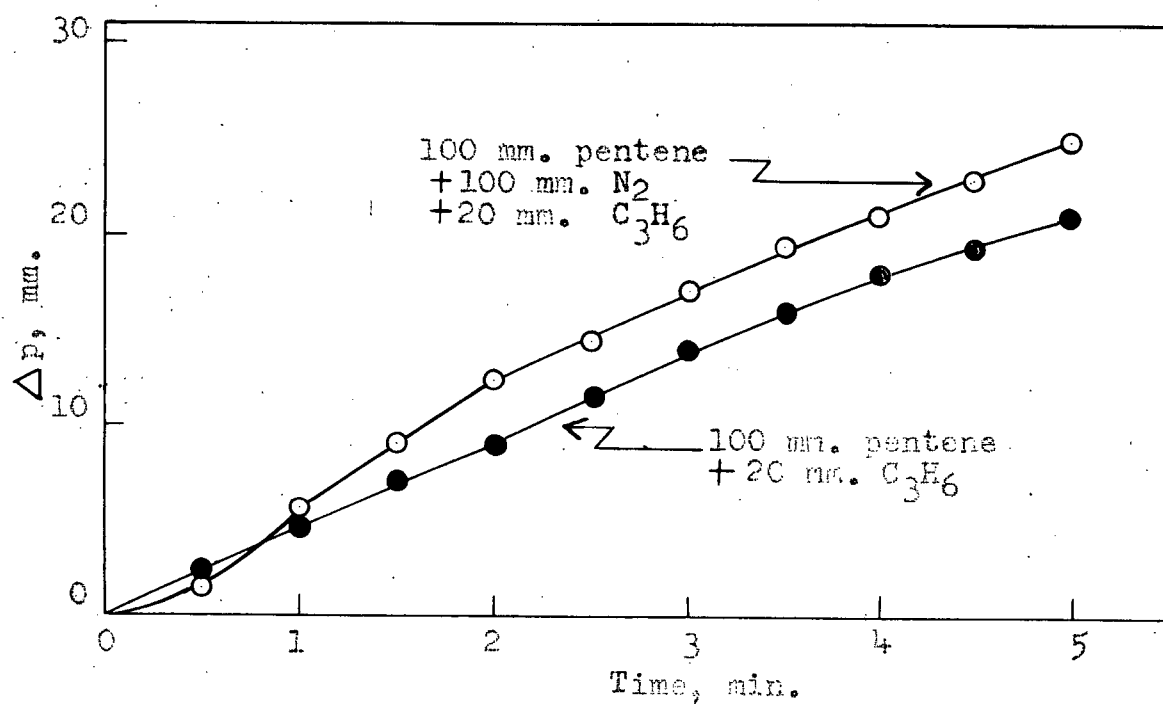


Fig. 15. Effect of N_2 on maximally inhibited reaction.

350°C., yielding ethyl radicals (42). Pure lead tetraethyl was unobtainable: the mixture used was a solution of $\text{Pb}(\text{C}_2\text{H}_5)_4$ in ethylene dibromide and ethylene dichloride. Results from sensitization experiments can therefore be of a qualitative nature only.

Experiments carried out at 350°C. led to a decrease in pressure, indicating that, at this low temperature, free ethyl radicals induce polymerization rather than decomposition of the pentene.

Similar runs were made at temperatures at which pentene-1 normally decomposes at a measurable rate. Fig. 16 shows Δp -time plots for the decomposition of 110 mm. of pentene, in the presence of 15 mm. of $\text{Pb}(\text{C}_2\text{H}_5)_4$, at temperatures of 470, 500, and 530°C. Curves for the normal decompositions are shown for comparison.

At each temperature, an increase in rate is exhibited in the presence of $\text{Pb}(\text{C}_2\text{H}_5)_4$. Free ethyl radicals thus appear to catalyze the reaction. This behaviour suggests that free radicals can cause decomposition of pentene-1 to a small degree. However, since the exact nature of the $\text{Pb}(\text{C}_2\text{H}_5)_4$ mixture used was unknown, no very definite conclusions can be drawn.

Dependence of the Rate of Decomposition on Temperature

The activation energy of a reaction may be determined from a study of the temperature dependence of the reaction rate. The dependence of the rate of decomposition on temperature was investigated at various initial pressures of pentene

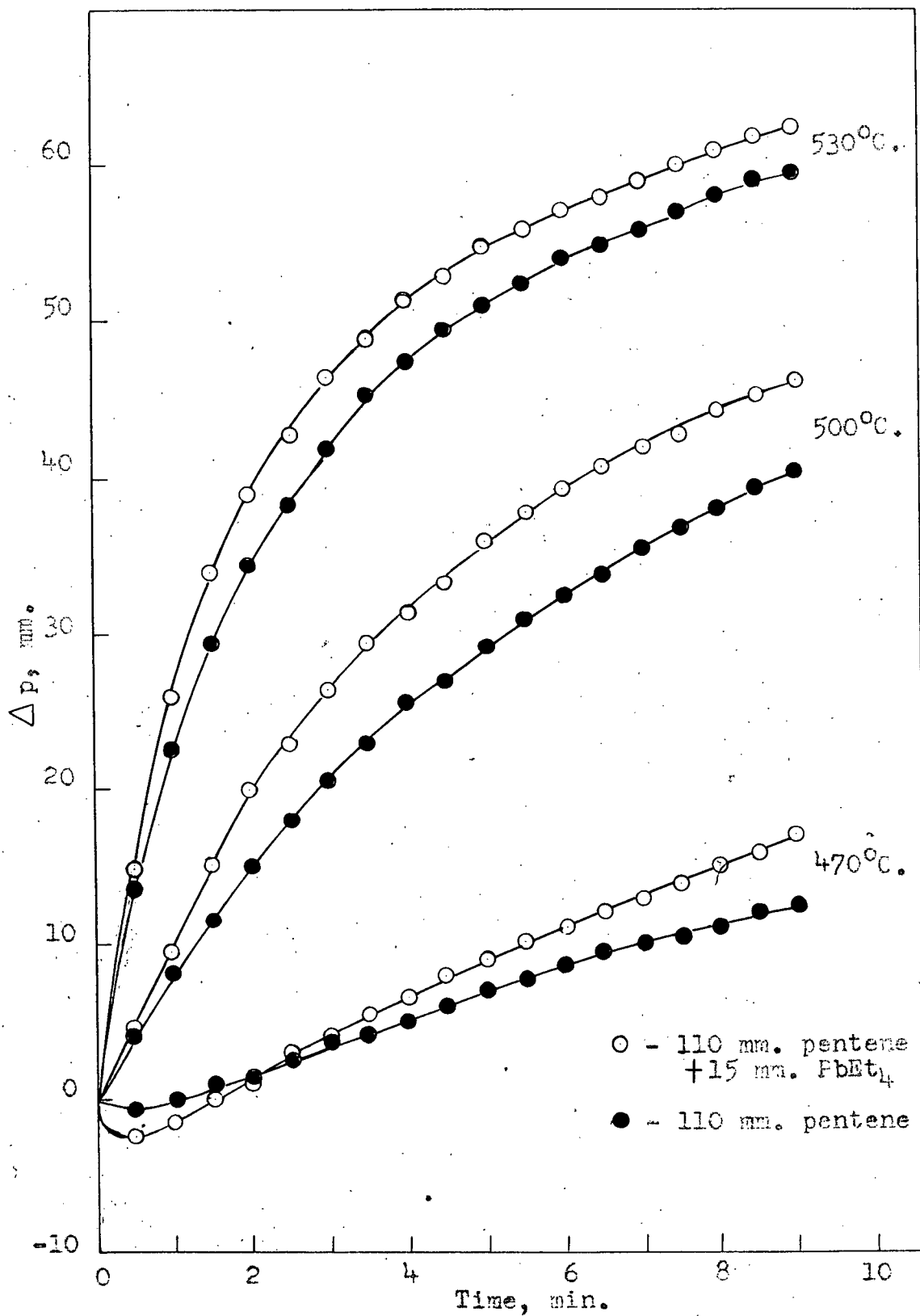


Fig. 16. Effect of PbEt_4 on rate of decomposition of 110 mm. pentene.

in the temperature range between 470 and 530°C. Table IV contains the results for the experiments involved. Two or three runs were made at each temperature for each initial pentene pressure, and the rates listed are averages of the initial rates, as calculated from the maximum slopes of the Δp -time curves.

TABLE IV

Temperature dependence of the reaction rates and reaction rate constants at various initial pentene pressures

Initial pressure, mm.	Temp., °C.	$1/T \times 10^3$	dP/dT , mm./min.	Rate constant, $\text{sec.}^{-1} \times 10^4$	Log ($k \times 10^4$)
60	530	1.247	11.5	32.0	1.505
	516	1.268	6.62	18.4	1.265
	500	1.293	3.80	10.6	1.025
	486	1.318	2.04	5.66	0.753
	470	1.348	0.910	2.53	0.403
110	530	1.247	25.4	38.5	1.585
	516	1.268	14.8	22.4	1.350
	500	1.293	7.64	11.6	1.064
	486	1.318	4.04	6.11	0.786
	470	1.348	1.82	2.76	0.441
150	530	1.247	30.9	34.4	1.547
	516	1.268	18.3	20.4	1.310
	500	1.293	9.32	10.4	1.017
	486	1.318	5.00	5.55	0.744
	470	1.348	2.18	2.42	0.384
200	530	1.247	40.0	33.4	1.524
	516	1.268	23.4	19.5	1.290
	500	1.293	11.3	9.41	0.974
	486	1.318	5.98	4.98	0.697
	470	1.348	2.76	2.30	0.362
247	530	1.247	52.7	34.6	1.551
	516	1.268	29.0	19.6	1.292
	500	1.293	14.5	9.78	0.990
	486	1.318	7.85	5.30	0.724
	470	1.348	3.63	2.45	0.389

A plot of $\log k$ versus $1/T$ for an initial pentene pressure of 150 mm. is shown in Fig. 17. The linearity of the curve shows that the Arrhenius Equation is valid over this range of temperatures; that is,

$$k = A e^{-E/RT}$$

Since integration of this equation yields the expression:

$$\ln k = \ln A - E/RT,$$

therefore the slope of the $\ln k$ vs. $1/T$ graph is equal to $-E/RT$. The activation energies for each initial pentene pressure were calculated from the slopes of the respective Arrhenius plots; the results are listed in Table V.

TABLE V

Activation energies for normal decomposition of pentene-1

Pentene pressure, mm.	Slope	Activation energy, kcal./mole
60	10.95	50.2
110	11.23	51.5
150	11.47	52.6
200	11.61	53.2
247	11.60	53.2

From the rate constant at 500°C . the frequency factor, A , was calculated to be approximately $10^{11} \text{ sec.}^{-1}$. This value is in agreement with those normally found for such first-order decomposition reactions.

In the activation energy values listed in Table V, there

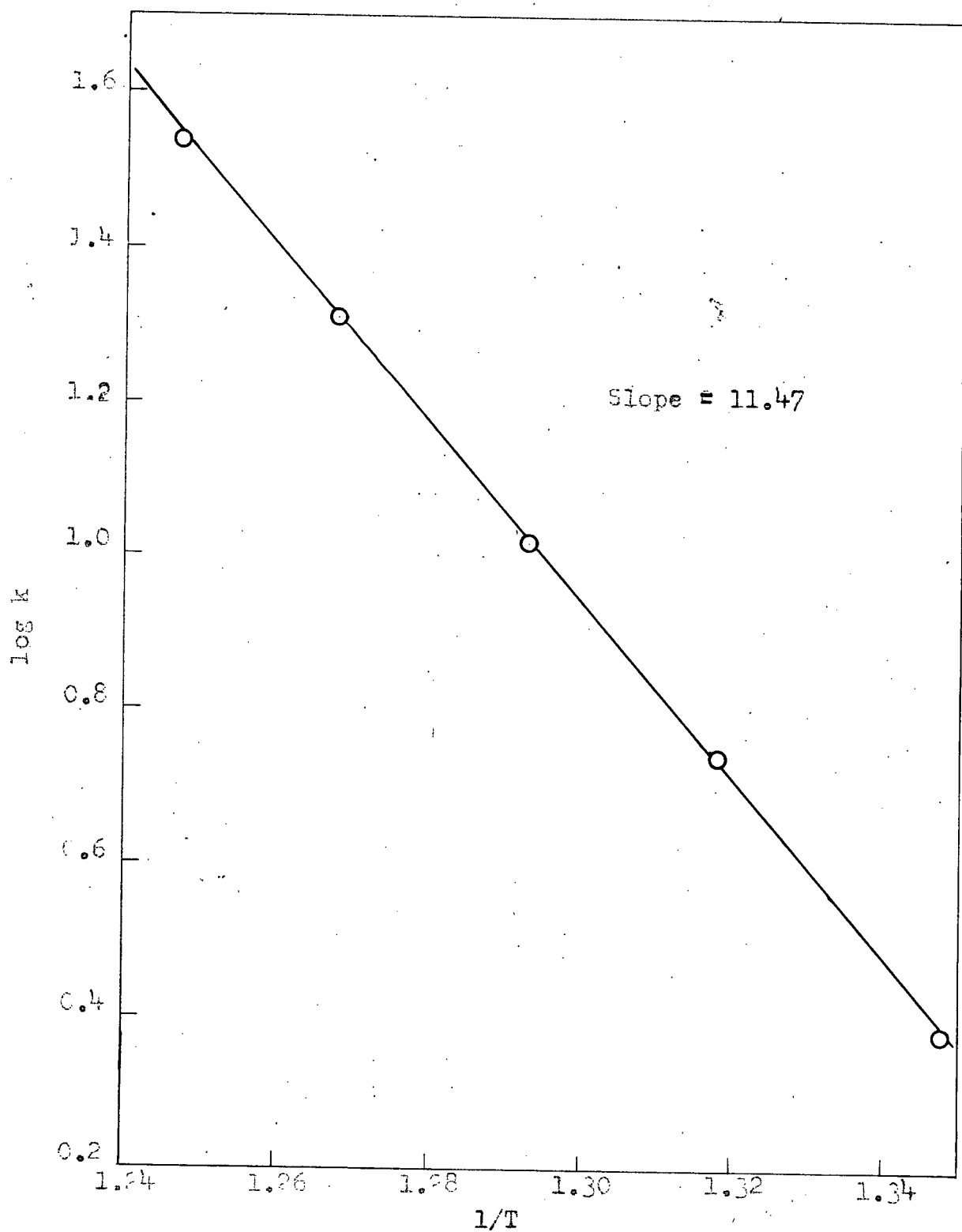


Fig. 17. Dependence of rate of decomposition of 150 mm. pentene on temperature.

is evident a slight increase corresponding to increase in initial pentene pressure. In Fig. 18 the plot of activation energy as a function of pentene pressure yields a curve that is almost linear. It was of interest to investigate this variation of activation energies. A possible explanation of the observed trend in the values is the following: a higher activation energy at higher pressures may be due to a process of collisional deactivation of activated molecules. When a pentene molecule enters into a collision, it gains a certain amount of energy, which it subsequently distributes among its various internal degrees of freedom. Further favourable collisions transfer more energy, and when the amount of energy necessary for decomposition has been localized to a specific bond, this bond will break. Now it is possible that, during this internal redistribution of energy, a higher pressure, and a correspondingly higher collision rate, may cause a greater proportion of unfavourable collisions, leading to deactivation. Thus, in order for an activated molecule, at high pressures, to possess sufficient energy for decomposition it must gain, in favourable collisions, larger amounts of energy than it would require at lower pressures. The corresponding increase in the height of the potential barrier for the decomposition reaction would be evidenced in a somewhat greater value of the activation energy.

Effect of Addition of Inert Gases on Activation Energy

Assumption of the above mechanism leads to the prediction

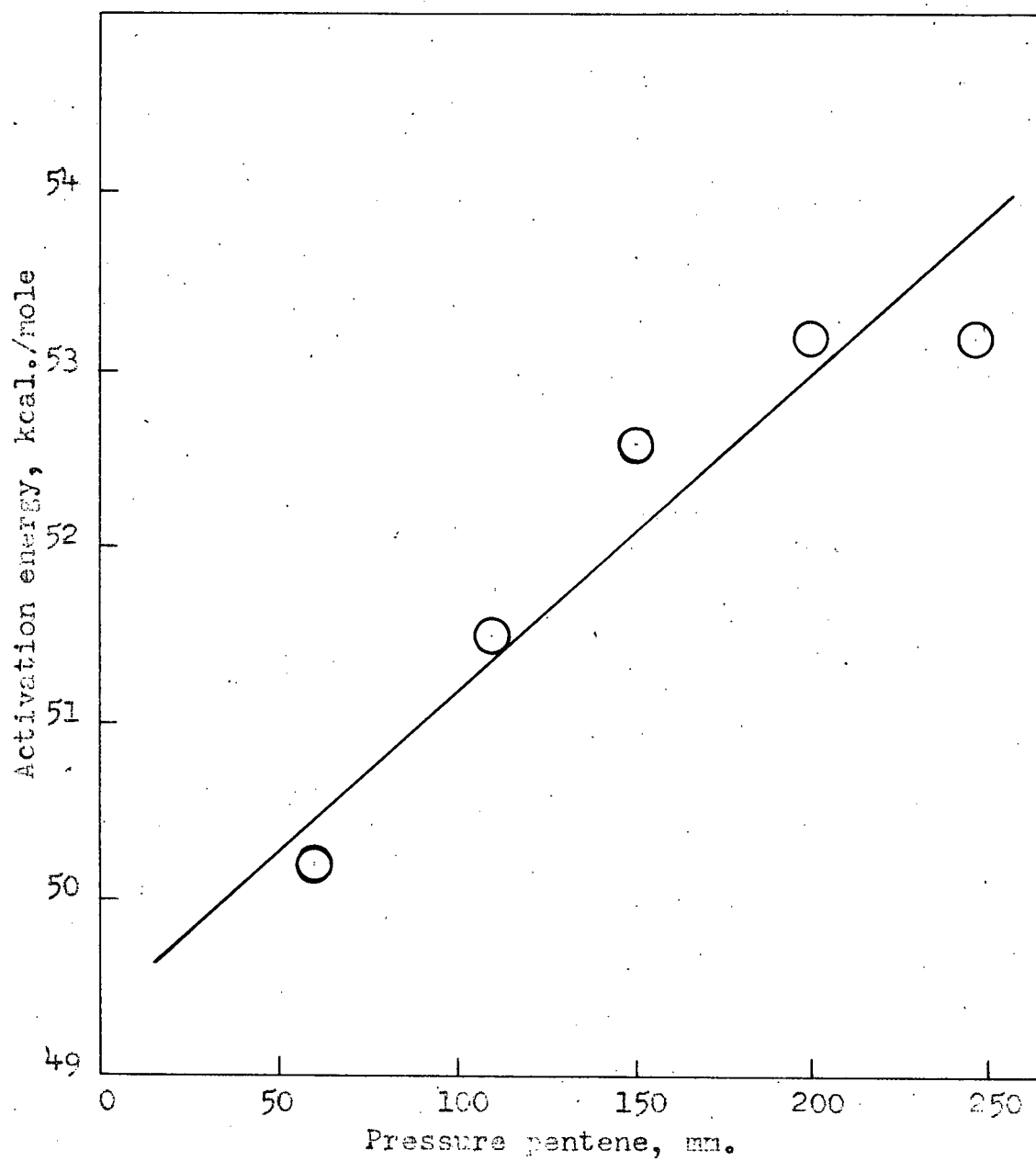


Fig. 18. Dependence of activation energy of normal reaction on initial pentene pressure.

that the presence of an inert gas will produce the same type of collisional effect. This prediction involves the further assumption that all molecules, regardless of complexity, are equally capable of transferring energy. In an effort to test the validity of this idea, experiments were done in which the partial pressure of pentene was decreased, the total pressure being maintained by the addition of inert gases. In Table VI are listed the results for two sets of runs in which 100 mm. of pentene was decomposed in the presence of 100 mm. of argon and 100 mm. of nitrogen respectively. Results for 100 and 200 mm. of pentene alone are included for comparison. These runs were made in the temperature range of 470 to 530°C.

TABLE VI

Activation energies for decomposition of pentene-1 in the presence of inert gases

Total pressure, mm.	Pentene pressure, mm.	Argon pressure, mm.	Nitrogen pressure, mm.	Activation energy, kcal./mole
200	100	100	0	50.6
200	100	0	100	51.0
100	100	0	0	51.2
200	200	0	0	53.2

Clearly, increase of pressure due to the presence of either Argon or nitrogen does not produce any significant increase in the activation energy.

Effect of Addition of Freon on Activation Energy

Since the molecular weight of nitrogen, 28, and the atomic weight of argon, 40, are both less than the molecular weight of pentene, 70, and, furthermore, the number of degrees of freedom for both these molecules is considerably less than for pentene, it was hoped to obtain more satisfactory results with the use of a heavier and more complex molecule, which would still be inert at the temperatures required. Fluorocarbons are known to be both extremely stable to heat and chemically inert. As no pure fluorocarbons were available, a freon, monochlorotrifluoromethane, was used, with the hope that it would prove sufficiently inert for the purpose. 100 mm. of the freon gas showed no significant pressure increase when subjected, for over an hour, to the temperatures used in the pentene decomposition.

Experiments were therefore done with 100 mm. of pentene in the presence of 100 mm. of freon. The reaction showed a considerable increase in rate, amounting to approximately a 57% increase above the normal value. The activation energy was found to be 53.5 kcal. However, samples of the reaction mixtures, taken after ten minutes, gave positive tests for halogen with alkali and alcoholic silver nitrate. Since the freon gas alone, when tested similarly, did not give positive test for halogen, it was concluded that some methyl chloride, methyl fluoride, or other alkyl halide had been formed in the reaction, and hence that the freon used was not inert at these temperatures

in the presence of pentene.

Effect of Addition of Propylene on Activation Energy

Since propylene has been found to inhibit the pentene decomposition, presumably by a chain terminating mechanism, the residual reaction may be regarded as a process of molecular rearrangement. It was of interest to investigate the activation energy of this residual reaction in order to determine whether there still existed a variation of activation energy with pressure.

The activation energies for the maximally inhibited decompositions were investigated at three different initial pressures over the temperature range from 470 to 530°C. The results are shown in Table VII.

TABLE VII

Activation energies of maximally inhibited decomposition

Total pressure, mm.	Pentene pressure, mm.	Propylene pressure, mm.	Activation energy, kcal./mole
64	54	10	49.5
134	110	24	50.7
250	200	50	52.0

The values for the activation energy of the residual reaction are very close to those of the total reaction, being approximately 1 kcal. lower. In Fig. 19 is shown a plot of activation energy as a function of initial pentene pressure. Again, an increase in pressure corresponds to an increase in activation

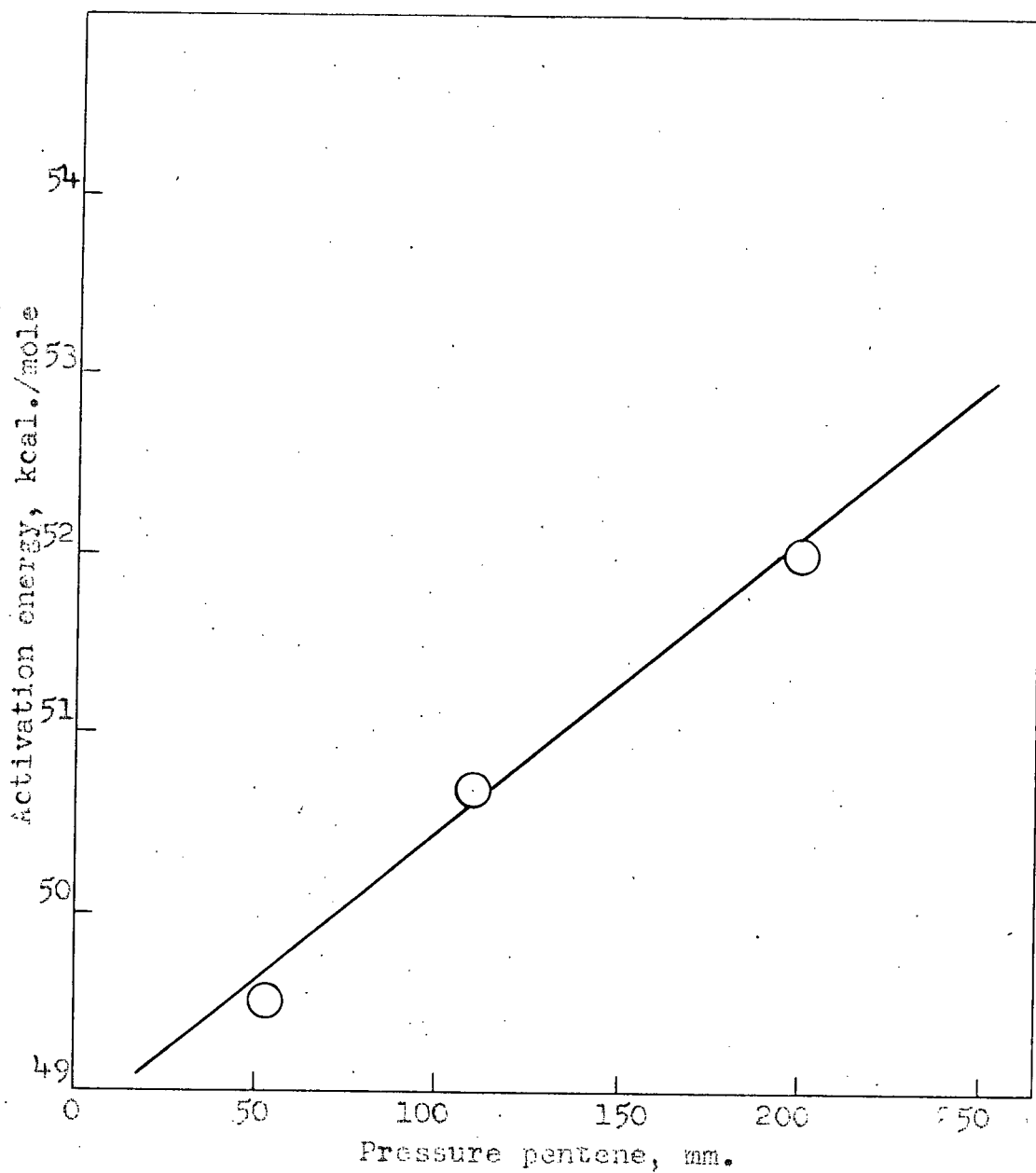


Fig. 19. Dependence of activation energy of kinetically inhibited reaction on initial pentene pressure.

energy. Hence this effect is not peculiar to the uninhibited part of the reaction alone.

The close similarity between the activation energy values for the inhibited reaction and for the total reaction indicates that the two processes are able to proceed with almost equal ease.

Effect of Addition of Inert Gases on Activation Energy of Maximally-Inhibited Reaction

Since the maximally inhibited decomposition was found to exhibit an increase in activation energy with increased initial pressure of hydrocarbon, the ability of inert gases to maintain the high activation energy value of the residual reaction was investigated. Two sets of experiments were done over the range of temperatures from 470 to 530°C. with pentene inhibited with propylene, and in the presence of argon and of nitrogen respectively. Results obtained are shown in Table VIII. Values for the inhibited decomposition of 200 mm. of pentene-1, in the absence of inert gas, are shown for comparison.

TABLE VIII

Activation energies of maximally inhibited decomposition diluted with inert gases

Total pressure, mm.	Pentene pressure, mm.	Propylene pressure, mm.	Argon pressure, mm.	Nitrogen pressure, mm.	Activation energy, Kcal./mole
220	100	20	100	0	50.2
220	100	20	0	100	50.5
250	100	50	0	0	52.0

As was found in the case of the uninhibited decomposition, neither argon nor nitrogen is effective in increasing the value of the activation energy of the residual reaction.

Effect of Addition of Nitric Oxide on Activation Energy

Although nitric oxide was found ineffective in inhibiting the pentene decomposition, it was thought possible that its presence might affect the value of the activation energy. Accordingly the temperature dependence of the decomposition of pentene in the presence of nitric oxide was investigated at three different initial pressures. Results for these experiments are given in Table IX.

TABLE IX

Activation energy of decomposition in presence of nitric oxide

Total pressure, mm.	Pentene pressure, mm.	Nitric oxide pressure, mm.	Activation energy, kcal./mole
60	50	10	50.4
230	200	30	53.4

Clearly, the addition of nitric oxide has no appreciable effect on the value of the activation energy. The increase with increased pressure is again observed.

Summary of the Experimental Results

The main results obtained in this investigation may be summarized as follows:

- (1) Pentene-1 decomposes at a measurable rate at temperatures

above 470°C . The pressure-time curves at this temperature show an initial decrease, followed by a rapid increase as the rate builds up to its maximum value. At somewhat higher temperatures there is only an increase in pressure, indicating that at the high temperatures polymerization is not an important primary process.

(2) The reaction rate is of the first order with respect to the initial pentene pressure. At 500°C . the reaction rate constant is approximately 9.061 min.^{-1} .

(3) Increase of the surface-to-volume ratio causes no appreciable alteration in the rate of the reaction. The reaction is therefore essentially homogeneous.

(4) Addition of argon and of nitrogen causes a slight decrease in the rate of the reaction, the effect being more pronounced in the case of nitrogen. This phenomenon suggests that the reaction is not a simple collisional activation process; rather, the operation of a free-radical chain mechanism is indicated, wherein the inert gas molecules are able to function as third bodies, favouring radical recombination.

(5) Nitric oxide has no effect on the rate of the reaction. This behaviour suggests three possibilities:

- (a) the absence of free radicals;
- (b) a catalytic effect of nitric oxide, equal and opposite to its inhibitory action;
- (c) the presence of some reaction product, such as

propylene, which is able to combine with radicals more effectively than is nitric oxide. This latter alternative suggests extremely short reaction chains, the majority of the free-radical reactions involved being chain terminating steps.

(6) Added propylene causes a 20% reduction in the rate of the reaction. Beyond a certain amount, further addition of propylene does not affect the rate. This phenomenon suggests the operation of a free-radical chain mechanism, repressible by propylene. The residual reaction may or may not involve chains.

(7) The presence of inert gases in the maximally inhibited reaction causes a slight increase in the rate. This behaviour suggests that the residual reaction, in the presence of propylene, does not involve free-radical chains.

(8) The presence of lead tetraethyl, at low temperatures, induces polymerization of pentene-1. At temperatures at which the normal decomposition proceeds at a measurable rate, small amounts of lead tetraethyl accelerate the decomposition. It would appear probable therefore that both the low-temperature polymerization and the high-temperature decomposition are processes involving free radicals.

(9) The dependence of the rate of the reaction upon temperature is in accordance with the Arrhenius Equation. The activation energy for the normal reaction is approximately 52 kcal.

per mole. The frequency factor, at 500°C., is approximately 10^{11} sec^{-1} .

(10) Increase in the initial pentene pressure is accompanied by an increase in activation energy, amounting to between 1 and 2 kcal. per mole for a pressure increase of 100 mm.

(11) The energy of activation is unaffected by the addition of nitrogen or argon to the reaction system.

(12) The presence of CF_3Cl considerably increased both the rate of pressure change and the activation energy for the process. Positive evidence for the presence of an alkyl halide in the reaction mixture indicates that the freon is not inert in the presence of pentene-1 at the temperatures employed.

(13) Addition of propylene produces no appreciable change in the values of the activation energy. The maximally inhibited reaction exhibits an increase of activation energy with increase of pressure. The mechanism causing the pressure-dependence of the activation energy would therefore appear to be also operative in the residual reaction, and not a property of the repressible portion of a chain mechanism.

(14) Addition of inert gases to the maximally inhibited reaction produces no appreciable effect on the activation energy.

(15) Addition of nitric oxide produces no appreciable effect on the activation energy.

DISCUSSION

Nature of the Primary Activation Process

The first question which arises in predicting the mechanism of a thermal decomposition reaction concerns the fundamental nature of the primary activation process. The primary act in the decomposition of any organic molecule may be either an internal rearrangement to stable products or a bond rupture producing free radicals, which subsequently cause further decomposition by a chain mechanism. In any particular instance, one of these mechanisms may be operative to the virtual exclusion of the other, or the two processes may occur simultaneously in potential competition.

In order to decide upon the relative effectiveness of these two types of mechanism in the thermal decomposition of pentene-1, it will be necessary to consider the experimental evidence which has been accumulated both for and against the presence of radical chains. The evidence in favour of the participation of a free-radical chain mechanism may be summarized as follows:

- (a) the presence of inert gases in the reaction mixture causes a decrease in the reaction rate;
- (b) added propylene inhibits the reaction, reducing the rate to approximately 80% of its original value;
- (c) added free radicals accelerate the reaction.

However, further experimental results do not appear to support

these observations:

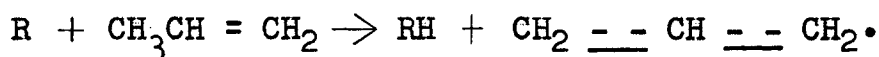
- (d) nitric oxide is incapable of causing inhibition of the reaction;
- (e) the reaction rate is not sensitive to a change in the surface-to-volume ratio in the reaction vessel.

These points will be considered in turn.

For a homogeneous decomposition reaction, dependent upon collisional activation for causing direct molecular rearrangements, the presence of inert gases would be expected to accelerate the rate of decomposition. That is, if the partial pressure of reactant molecules were decreased, inert gas molecules should maintain, by collisions, the high-pressure energy distribution among the molecules, so tending to prevent a falling off in rate. If, however, a chain mechanism is operative, an inert gas may affect the rate in one of two possible ways: (a) if chains are terminated heterogeneously, the inert gas, by impeding diffusion of radicals to the surface of the reaction vessel, may be expected to accelerate the reaction; (b) if radicals recombine homogeneously, an inert gas should retard the reaction by favouring recombination of radicals at ternary collisions. Now, since the surface has been shown to play no significant part in the decomposition of pentene-1, obviously recombination of any radicals that may be present must be a homogeneous process. It has been shown that both argon and nitrogen, even when present in large proportions,

fail to cause any acceleration; rather, they have been observed to exert a definite retardation on the reaction rate. Thus it may be inferred that the decomposition of pentene-1 involves a free-radical mechanism, in which reaction chains are terminated homogeneously, partially, at least, by ternary collisions.

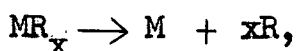
The effect of propylene will next be considered. In acting as an inhibitor, a propylene molecule is believed to function, essentially, as a third body for removing radicals: the propylene molecule replaces a chain carrier by a more stable allyl-type radical, less efficient for continuing the chain process:



Other unsaturated molecules may be expected to act similarly; for example, it has been shown that isobutene inhibits the decomposition of pentane (40). In the pentene-1 decomposition, the presence of a large amount of unsaturated material, due both to the pentene itself and to its decomposition products, may be expected to cause appreciable inhibition in the course of the normal reaction. Thus it might be expected that a large proportion of any free-radical chains which may be initiated in the primary process will be terminated in this way. If repression of the radical chains is incomplete in the normal reaction, the addition of increasing amounts of propylene should supplement such inhibition to the point of complete chain termination. Such was indeed found to be the case. Propylene inhibition reduced the rate to about 80% of its

normal value. Molera and Stubbs have also reported some inhibition of the pentene-1 decomposition by propylene (34).

The third positive criterion for the presence of free-radical chains is the observed catalysis of the decomposition by lead tetraethyl. There seems to be little doubt that a metal alkyl, such as lead tetraethyl, decomposes with the formation of free radicals:



where M is the metal and R the alkyl radical (41). Such metal alkyls have frequently been used as sensitizers. Catalysis of an organic decomposition by the presence of small amounts of such substances is regarded as evidence for a free-radical mechanism: the added radicals are believed to attack reactant molecules and accelerate their decomposition. The observed catalysis of the pentene-1 decomposition, then, by small amounts of lead tetraethyl, indicates that free radicals are able to cause decomposition of the pentene. Such indications do not, however, prove conclusively that chains are effective in the normal decomposition.

On what would appear to be the negative side of the argument for the action of free radicals in the pentene decomposition, are the results from experiments on nitric oxide inhibition and from experiments on surface effects. It is possible, however, to interpret the results of these experiments in such a way that the observed results are not necessarily contradictory, and a chain process may still provide a plausible

explanation of the reaction mechanism.

Nitric oxide produced no alteration in the decomposition rate. Molera and Stubbs report the same result (34). Assuming the effect of all inhibitors of chain reactions to be essentially the same; that is, to reduce the concentration of chain radicals, it would seem contradictory that propylene should be capable of causing appreciable inhibition, whereas nitric oxide is completely ineffective. In order to provide an argument in favour of a chain mechanism, it must be shown that the observed lack of inhibition does not constitute proof of a non-chain reaction: one of the following assumptions must be made: (a) that nitric oxide can start chains as well as stop them in pentene; (b) that the radicals present in the pentene decomposition combine with nitric oxide too slowly for appreciable inhibition; or, (c) that the inhibitory effect due to the necessarily high concentration of olefins present in the reaction mixture will swamp out any effect of nitric oxide. The first of these assumptions was adopted by Rice and Polly in order to account for similarly unusual inhibition results for the decomposition of acetaldehyde (42). They proposed the following scheme by which nitric oxide can both start and stop chains:





Decomposition was assumed to occur with chain termination either by steps (V) and (VI), corresponding to a low activation energy for step (IV), or by steps (VII) and (VIII), with a high activation energy for step (IV). It is possible to assume a scheme of this type for the pentene-1 decomposition: nitric oxide may react with a pentene molecule, yielding HNO plus a radical, R_2 , which decomposes, producing R_1 , a smaller radical able to initiate the chain step (IV). According to this scheme, nitric oxide also functions as an inhibitor by combining with R_1 and R_2 . It is possible, on this basis, to predict no net effect of nitric oxide on the observed reaction rate.

Assumption (b), that the reaction between nitric oxide and the radicals present is too slow to produce appreciable inhibition, hardly seems a probable explanation: it is very likely that, if radicals are present at all, both methyl and ethyl radicals would be among these, and in most other organic decomposition reactions involving these radicals, nitric oxide has been found to exhibit very marked inhibitory effects (1).

A consideration of the unsaturated nature of the decomposing pentene molecule and of the probable unsaturated nature

of its decomposition products, suggests that (c) is the most reasonable assumption, more especially in the light of the experimentally observed inhibition by propylene. Unsaturation, present in large concentration, must far surpass nitric oxide in their ability to terminate chains. Any inhibitory effects of nitric oxide are completely masked. The results of other investigators bear out this conclusion. Eltenton, from mass spectrometric investigations, concluded that propylene reacts more easily than does nitric oxide with methyl radicals(43); at high temperatures he detected both methyl and allyl radicals in the decomposition of propylene. Observations made by Steacie and Folkins on the nitric oxide inhibition of paraffin decompositions demonstrate that the inhibition falls off as the reactions proceed, the rates approaching their normal values (44). These investigators have attributed their findings to the building up with time of olefin concentration in the products, the ensuing inhibition by products swamping out the effect of nitric oxide.

Assumption (c) appears more convincing than (a). It is rather improbable that the opposed accelerating and retarding actions of nitric oxide should exactly counterbalance each other, yielding no net effect.

The second argument which seems to suggest a non-chain process is the homogeneity of the reaction. If long chains are assumed, a large increase in the surface-to-volume ratio would be expected to facilitate heterogeneous radical

recombinations. However, if the chains are short, relatively more homogeneous chain-breaking processes will occur while a given number of hydrocarbon molecules decompose; hence, any competing chain-breaking process due to inhibition on the surface will be less important. There are indications that the chains are short. In the first place, quite considerable amounts of propylene are required in order to bring about appreciable inhibition: this fact suggests a large number of relatively short chains rather than a few long ones, since the amount of inhibitor used to stop chains must logically depend on the number of such chains present. Further, if it is assumed that the maximally inhibited reaction represents a state of affairs in which all chains are cut down to their primary process, the average chain length may be calculated from the ratio of the normal to the inhibited rate. A low value of about 1.25 is obtained. This means either: (a) that radicals from every 4 primarily decomposing molecules cause the decomposition of 1 more; or, (b) that only one in 100, say, of the primary processes yields radicals, but that each of these causes the decomposition of about 25 molecules. In comparison with the extremely long chains found in many organic decomposition reactions, even the second possibility does not lead to an extremely large value for the absolute chain length. Short chains were also postulated by Gorin on the basis of his analytical results for the pentene-1 decomposition in a flow system (32).

A consideration of the foregoing results therefore appears to point to a mechanism involving a split of pentene molecules to free radicals, which subsequently initiate short chains, terminated both by ternary collisions in the gas-phase and by combination with unsaturated molecules. The long, flat minima of the inhibition curves show that a definite fraction of the reaction is exempt from inhibition. Presumably this residual reaction consists of an intramolecular rearrangement process of low activation energy. Although lack of further inhibition does not preclude the possibility that the maximally inhibited reaction is itself a modified chain reaction, the fact that inert gases exert an accelerating rather than a retarding effect on the rate of the inhibited process, would suggest the absence of chains. The fact that the activation energy values for the normal and the inhibited reactions are very close probably renders the two competing mechanisms of about equal importance in the overall reaction process, and explains why they are able to operate simultaneously.

According to the simple collision theory, the rate constant may be calculated from the collision number, z , and the observed energy of activation for the reaction by use of the equation:

$$k = z e^{-E/RT} .$$

The k obtained will be the rate constant expected from simple collisional activation in two squared terms. Rate constants have been calculated in this way for both the normal and the

maximally inhibited decomposition of 200 mm. of pentene-1 at 500°C. The value of z , the number of molecules colliding /cc. /sec., was calculated from the equation:

$$z = 2n^2\sigma^2 \left[\frac{\pi RT}{M} \right]^{\frac{1}{2}},$$

where n represents the number of molecules in a unit volume, σ the molecular diameter (5×10^{-8} cm.), R the gas constant/mole, T the absolute temperature, and M the molecular weight of pentene. This yields a value for z of 1.7×10^{27} molecules colliding /cc./sec. In Table X the calculated values of k are compared with those obtained experimentally. Now, although the activation energy for the inhibited reaction is somewhat lower than that for the normal reaction, it is seen from Table X that the observed rate constant is still greater than would be expected from simple collisional activation in two squared terms. Hence the internal rearrangement process must be one in which many degrees of freedom contribute to the activation.

TABLE X

Calculated and observed rate constants for normal and inhibited reactions

	k from $z e^{-E/RT}$, sec. ⁻¹	k from actual rate, sec. ⁻¹
Normal reaction	5.2×10^{-8}	9.4×10^{-4}
Maximally inhibited reaction	1.4×10^{-7}	1.9×10^{-4}

A consideration of the bond strengths involved imposes certain restrictions on the proposed chain mechanism. According to Stevenson's results (45), based on electron impact data, we may assign a bond energy value of approximately 77 kcal. to the weakest bond in the pentene molecule; that is, to the C-C bond in the β position with respect to the doubly-bound carbon atom. The activation energy of the overall reaction is thus considerably lower than the energy necessary to disrupt the weakest link in the molecule. If, then, a chain process is important, only exceptional molecules, too rare to affect the mean activation energy, can give radicals. This suggests relatively few chains. In order that the chain process be important in relation to the competing intramolecular mode of decomposition, the chains must be of appreciable lengths.

Now, it has been observed that the activation energy for the inhibited reaction is somewhat lower than that for the overall process. It follows that inhibition must increase with temperature. Therefore the average chain length must increase with temperature, suggesting that the chain reaction is more important at higher temperatures, when more thermal energy is available.

Thus it would appear that the decomposition of pentene-1 is a complex process, involving a free-radical chain mechanism, inhibitable both by reaction products and by added propylene, together with an intramolecular rearrangement process of low activation energy, a large number of internal degrees of

freedom contributing to the activation process. At high temperatures the contribution of the chain mechanism to the overall reaction becomes more important. The absolute chain length increases with temperature: probably very short chains predominate at lower temperatures, most of the chain steps being those of termination, whereas at higher temperatures the chains are longer-lived. Chain termination takes place homogeneously both by ternary collisions, with pentene molecules acting as third bodies, and by addition of radicals to unsaturated molecules.

Without detailed analyses of the reaction products, no conclusions can be drawn as to the exact mechanism of the decomposition. It is to be hoped that future mass spectrometric analyses will be able to elucidate more completely the complex kinetics of the thermal decomposition of pentene-1.

Dependence of Activation Energy on Initial Pentene Pressure

It was found that the value of the activation energy exhibited a small increase with an increase in the initial pentene pressure. Such a phenomenon in the pentene-1 decomposition has also been reported by Molera and Stubbs (36). These authors, however, do not comment upon their findings. Such a trend of activation energies contrasts sharply with the behaviour of normal paraffin hydrocarbons, which exhibit a large decrease of activation energy with increasing pressure.

The increase of activation energy with pressure found for the normal reaction of pentene-1 has been shown to apply also

to the maximally inhibited reaction. Thus it would appear that the explanation for this behaviour must lie in the activation mechanism of the molecular rearrangement process. A possible explanation for the phenomenon has been suggested in the experimental section of this thesis (p. 34). This suggestion involves a mechanism of collisional deactivation: activated molecules, whose energy of activation is distributed in several squared terms and so is not mobilized for the rupture of specific bonds, are deactivated by collisions with normal molecules at high pressures. That is, the relative probability of unfavourable to favourable collisions must be assumed to be greater at higher pressures. Due to this siphoning of energy by unfavourable collisions, there will follow an increase in the energy that a pentene molecule must gain by favourable collisions in order to reach the top of the potential energy barrier. Such an effect would be manifested in a higher value of the activation energy at higher pressures.

Experiments performed with high pressures maintained by the presence of foreign gases have failed to provide any supporting evidence for this hypothesis. Their presence exerts no appreciable effect on the observed values of the activation energy for either the normal or the inhibited reaction. It may be, however, that argon and nitrogen are not molecules of sufficient complexity for the purpose. It is hoped that in future work it may be possible to find a molecule comparable in complexity to the pentene itself, yet still inert at the

temperatures of the pentene decomposition. Such a molecule, possessed of several more degrees of freedom, might be expected to exert a collisional effect similar to that shown by pentene. Thus no definite conclusions can be drawn as to the validity of the proposed collisional deactivation process. In the light of the results obtained with nitrogen and argon, it would appear more probable that the phenomenon arises from some inherent property of the mode of decomposition of the pentene molecule itself. Since the inhibited part of the mechanism is believed to proceed with a slightly greater activation energy than the residual reaction, it might be speculated that higher pressures favour a chain mechanism; that is, that as the pentene pressure is increased, the contribution of a chain mechanism to the composite reaction becomes of increasing importance. Were this the case, it should follow that reactions with increasing pentene pressure should demand increasing percentages of propylene for inhibition. The present observations on propylene inhibition, however, are not sufficiently detailed to form the basis of a decision of this sort. Presumably only a small extra amount of propylene would be required to lead to such a small change in the activation energy.

It must be realized, however, that due to the poor method available for activation energy determination, a variation of two or three kcal. need not necessarily be of significance. A small error in the reaction rate would lead to a large error

in the slope of the Arrhenius plot, and a consequently large error in the value of the activation energy. If such small errors in the observed rate were consistent, there could result a consistent but erroneous trend in the calculated activation energies. For this reason not too much significance should be attached to the present results of the dependence of activation energy on pentene pressure. A small, consistent contribution from some secondary reaction could conceivably lead to the phenomenon observed. Investigations made over a far greater pressure range would be necessary before any definite conclusions could be made as to the genuine existence of an increase of activation energy with increasing pressure.

REFERENCES

- (1) Steacie, E.W.R. Atomic and Free Radical Reactions.
Reinhold Publishing Corporation, New York. 1946.
- (2) Echols, L.S. and Pease, R.N. J.Am.Chem.Soc. 58:1317.
1936.
- (3) Sickman, D.V. and Rice, O.K. J.Chem.Phys. 4:608. 1936.
- (4) Frey, F.E. Ind.Eng.Chem. 26:198. 1934.
- (5) Hinshelwood, C.N. The Kinetics of Chemical Change.
Clarendon Press, Oxford. 1949.
- (6) Staveley, L.A.K. Proc.Roy.Soc.(London), A162:557. 1937.
- (7) Hobbs, J.E. and Hinshelwood, C.N. Proc.Roy.Soc.(London),
A167:447. 1938.
- (8) Wall, L.A. and Moore, W.J. J.Am.Chem.Soc. 73:2840. 1951.
- (9) Stubbs, F.J. and Hinshelwood, C.N. Proc.Roy.Soc.(London),
A200:458. 1950.
- (10) Rice, F.O. and Rice, K.K. The Aliphatic Free Radicals.
Johns Hopkins Press, Baltimore. 1935.
- (11) Rice, F.O. and Herzfeld, K.F. J.Am.Chem.Soc. 56:284.
1934.
- (12) Kossiakoff, A. and Rice, F.O. J.Am.Chem.Soc. 65:590.
1943.
- (13) Williams-Gardner, A. Fuel, 4:430. 1925. (C.A. 20:280.
1926.)
- (14) Noyes, A.A. Mass.Inst.Tech.Quarterly, 1:278. 1888.
(Hurd, C.D. and Spence, L.U. J.Am.Chem.Soc. 51:3561.
1929.)
- (15) Ipatiev, V. Ber. 36:2008. 1903. (Hurd, C.D. and Spence,
L.U. J.Am.Chem.Soc. 51:3561. 1929.)
- (16) Frey, F.E. and Smith, D.F. Ind.Eng.Chem. 20:948. 1928.
- (17) Hurd, C.D. and Spence, L.U. J.Am.Chem.Soc. 51:3561. 1929.
- (18) Hurd, C.D. and Meinert, R.N. J.Am.Chem.Soc. 52:4978.
1930.

- (19) Egloff, G. and Wilson, E. Ind.Eng.Chem. 27:917. 1935.
- (20) Tropsch, H., Parrish, C.I. and Egloff, G. Ind.Eng.Chem. 28:581. 1936.
- (21) Rice, F.O. and Haynes, W.S. J.Am.Chem.Soc. 70:964. 1948.
- (22) Szwarc, M. J.Chem.Phys. 17:292. 1949.
- (23) Szwarc, M. J.Chem.Phys. 17:284. 1949.
- (24) Rice, F.O. and Wall, L.A. J.Am.Chem.Soc. 72:3967. 1950.
- (25) Ingold, K.U. and Stubbs, F.J. J.Chem.Soc. 382:1749. 1951.
- (26) Norris, J.F. and Reuter, R. J.Am.Chem.Soc. 49:2624. 1927.
- (27) Norris, J.F. and Thomson, G. J.Am.Chem.Soc. 53:3108. 1931.
- (28) Hurd, C.D. and Goldsby, A.R. Ph.D. Thesis. Northwestern University. 1932. (Hurd, C.D. J.Ind.Eng.Chem. 26:50. 1934.)
- (29) Pease, R.N. and Morton, J.M. J.Am.Chem.Soc. 55:3190. 1933.
- (30) Hurd, C.D., Goodyear, G.H. and Goldsby, A.R. J.Am.Chem.Soc. 58:235. 1936.
- (31) Mikhailov, B.M. and Arbuzov, Yu.A. Compt.rend.acad.sci. U.R.S.S. 3:433. 1936. (C.A. 30:4472. 1936)
- (32) Gorin, E., Oblad, A.G. and Schmuck, R.F. Ind.Eng.Chem. 38:1187. 1946.
- (33) Hepp, H.J. and Frey, F.E. Ind.Eng.Chem. 41:827. 1949.
- (34) Molera, J.J. and Stubbs, F.J. J.Chem.Soc. : 381. 1952.
- (35) Stubbs, F.J. and Hinshelwood, C.N. Proc.Roy.Soc.(London) A200:458. 1950.
- (36) Blanchard, A.A. In Inorganic Syntheses, ed. by W.C. Fernelius. McGraw-Hill, New York. 1936.
- (37) Patrick, W.N. M.A. Thesis. University of British Columbia. 1952.
- (38) Coates, G.E. J.Sci.Instr. 21:86. 1944.

- (39) Coope, J.A.R. M.Sc. Thesis. University of British Columbia. 1952.
- (40) Eltenton, G.C. J.Chem.Phys. 10:403. 1942.
- (41) Rice, F.O., Johnston, W.R. and Evering, B.L. J.Am.Chem. Soc. 54:3529. 1932.
- (42) Rice, F.O. and Polly, O.L. J.Chem.Phys. 6:273. 1938.
- (43) Eltenton, G.C. J.Chem.Phys. 10:465. 1942.
- (44) Steacie, E.W.R. and Folkins, H.O. Can.J.Res. B17:105. 1938.
- (45) Stevenson, D.P. J.Chem.Phys. 10:291. 1942.