PREFACE

This investigation was undertaken in order to elucidate mechanisms of pyrolysis of organic compounds.

The uninhibited decomposition of ethane was studied, and it was concluded on the basis of experimental and theoretical considerations that the initiating step in the reaction is the second-order splitting of ethane into two methyl radicals.

The pyrolysis of ethane was next inhibited by nitric oxide, and the resultant reaction was studied theoretically and experimentally. It was concluded that the residual reaction after inhibition is a free radical process, and a mechanism is proposed.

The pyrolysis of propylene was investigated in view of the importance of the substance as an inhibitor. The reaction was interpreted in terms of a free radical mechanism which accounts for the observed products and characteristics of the reaction. It was also shown that allyl radicals abstract deuterium from deuterated methane.

The inhibited decompositions of other compounds were considered in terms of free radical mechanisms and the scheme for inhibition mechanisms was generalized. This was extended to cover the decompositions of alkyl halides, and it was demonstrated that lack of inhibition is not necessarily

an indication of a unimolecular reaction.

The above work was done under the direction of Professor Laidler, whose scientific judgement has been the mainstay of the investigation. For this and the many valuable discussions during the preparation of the thesis the author wishes to express his appreciation.

I would also like to thank my wife for her help and encouragement.

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ABSTRACT

Uninhibited Decomposition of Ethane

The uninhibited ethane decomposition has been studied from 823°K to 903°K with the object of deciding between the Rice-Herzfeld and Küchler-Theile mechanisms. The reaction was found to be accurately of the first order at the higher pressures and lower temperatures employed, and to have an activation energy of 73.1 kcal. under these conditions. The rate was decreased slightly by an increase in surface area, and the order was then slightly greater than unity. At lower pressures and higher temperatures the order of the reaction was 3/2. Evidence is adduced in support of the conclusion that the initiating reaction is a second-order split of C_2H_6 into $2CH_3$, as proposed by Küchler and Theile, and that the terminating step is $C_2H_5 + C_2H_5$ at the higher pressures and $H + C_2H_5$ at the lower ones. The mechanism is shown to give a satisfactory interpretation of the time-course of the reaction, of the effects of adding ethylene and hydrogen, and of the effect of increasing the surface area. Calculated rates, using the rate constants for the elementary steps, are in good agreement with experiment.

Decomposition of Ethane Inhibited by Nitric Oxide

The pressure-time curve for the decomposition of ethane when fully inhibited by nitric oxide is initially sinusoidal. The initial rates are proportional to the first power of the pressure at higher pressures, and to the 3/2 power at lower pressures; the rates at the inflection point are proportional to the pressure to a power which is slightly greater than unity. The activation energy corresponding to the initial rates in the first-order region was found to be 77.5 kcal $mole^{-1}$, and the frequency factor 3.12×10^{15}. The reaction was slightly inhibited by increasing the surface: volume ratio, and the induction period disappeared on addition of ethane. The facts are shown to be consistent with a mechanism in which initiation occurs by the reaction $NO + C_2H_6 \rightarrow C_2H_5 + HNO$, which is estimated to have an activation energy of 52 kcal. At the beginning of the reaction and at lower pressures termination is considered to occur by $H + HNO \rightarrow H_2 + NO$; as ethylene accumulates the ratio $[C_2H_5]/[H]$ increases and the termination step becomes $C_2H_5 + HNO \rightarrow C_2H_6 + NO$. The mechanism is shown to account for the fact that propylene and other inhibitors give rise to the same limiting rate.

Decomposition of Propylene

The main products of the propylene decomposition, studied between 580°C to 640°C, were found to be ethylene, methane and hydrogen, in the approximate ratio 2:2:1. Smaller amounts of ethane, propane, butenes, benzene, toluene and diallyl were found, but no allene was detected. The order of the reaction was 3/2, and the activation energy 56.7 kcal mole^{-1}. A mechanism is proposed, involving an initial split into C_3H_5 + H and including abstractions by both CH_3 and H; the main chain-terminating step is H + C_3H_5. The mechanism is shown to predict the rates of formation of the individual reaction products, and to account satisfactorily for the observed activation energy. Hydrogen atom abstractions by the allyl radical were demonstrated. It is shown that the facts are consistent with the suggestion that in the propylene-inhibited paraffin decompositions there is H abstraction by C_3H_5 and chain termination by reaction between C_3H_6 and an alkyl radical. This proposal explains why NO and propylene give rise to the same rates for the fully inhibited reactions, and why smaller amounts of NO are required to produce a given degree of inhibition.

General Theory of Inhibition.

Free radical mechanisms for other inhibited reactions have been proposed. It is possible by the application of

these mechanisms to explain first, three halves, or second order reactions when inhibited by nitric oxide. It is also shown that application of the above mechanisms to the decomposition of alkyl halides leads to the conclusion that lack of inhibition is not necessarily an indication of the absence of free radical processes.

GENERAL INTRODUCTION

The pyrolytic reactions of gases have not been explained satisfactorily in most cases. The question of competing unimolecular and free radical reactions has introduced serious complications into the theoretical interpretation of experimental data. The problem hinges on the much disputed question of inhibition: is the inhibited reaction a unimolecular split into products?

The suggestion that this is the case was put forward over 20 years ago, and has been maintained against some very serious objections. Among the objections one can list the fact that the products of the inhibited and uninhibited reactions are in most cases identical; the degree of isotopic mixing is the same for a given degree of reaction whether an inhibitor is present or not; and last but not least is the fact that induction periods are observed in some of the inhibited reactions.

The free radical mechanisms put forward by Rice and Herzfeld, and generalized by Goldfinger, Letort and Niclause, can be made to account for the uninhibited reaction rates and products in terms of free-radical processes.

However, if unimolecular reactions are in competition with the free radical process one has to assume that about the

same percentage of all hydrocarbon pyrolyses would have to occur by one or more molecular mechanisms leading to identical products as those of the free radical reaction.

The inhibition of reactions by propylene has brought to light even more strenuous objections. Propylene itself is decomposing under the experimental conditions and is producing free radicals. All of the radicals thus produced have now been shown to be capable of abstracting hydrogen and starting chains. It is inconceivable in the light of present knowledge that propylene would act as a radical trap and remove all free radicals from a reaction.

In view of this it is proposed in the present thesis that inhibited pyrolyses are free radical reactions involving other types of chains. Our hypothesis, when suitably applied, can explain all the available data and suggest many interesting experiments which will support or modify our conclusions.

Part I

THE UNINHIBITED DECOMPOSITION OF ETHANE

INTRODUCTION

The kinetics of the thermal decomposition of ethane are of special interest and importance, since the mechanism of the reaction is a simple but typical example of the decomposition of the various paraffins. During the past thirty years much information has accumulated concerning the reaction, and about the various elementary processes that are believed to occur. The present investigation of the uninhibited reaction was carried out with a view to coming to some conclusion regarding the mechanism that is involved. First the previous work on this problem will be reviewed.

Review of Previous Work

The first kinetic investigation of the problem was that of Pease (1), which indicated that the reaction is quite well represented by the equation

$$C_2H_6 = C_2H_4 + H_2.$$

Pease also concluded from his experiments that the reaction was first order and homogeneous.

In 1931 Marek and McClure (2) reinvestigated the reaction and obtained results which were later recalculated by Paul and Marek (3) to give an activation energy for the reaction. They reported the rate constant as:

$$k = 1.1 \times 10^{16} e^{-77000/RT} \text{ sec}^{-1}.$$

However, the study was carried out in a flow system, and the results are therefore somewhat suspect.

In 1935 Sachsse (4) investigated the reaction in a static system. He obtained the rate constant

$$k = 1.3 \times 10^{14} e^{-69800/RT} \text{ sec}^{-1}$$

where k is the rate constant extrapolated to infinite pressure. This extrapolation seems to be of little significance in view of the present knowledge that the reaction is not a simple unimolecular one. A feature of his work was the use of the increase in pressure as a measure of the rate of reaction. Sachsse also found that other products were obtained in addition to hydrogen and ethylene. This was confirmed by Storch and Kassel (5) who found that methane was produced at a rate which could be represented by:

$$\frac{d[CH_4]}{dt} = k_1[C_2H_6] + k_2[C_2H_6][C_2H_4]$$

They attempted to explain the course of the reaction by a non-chain mechanism which is now unacceptable.

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Küchler and Theile (6) in 1939 described a thorough study of ethane decomposition. The rate constant reported was

$$k = 5.2 \times 10^{15} e^{-76400/RT} \text{ sec}^{-1}.$$

Their work was mainly concerned with the study of the influence of foreign gases on the reaction. The results indicate that the presence of inert gases brings about a definite increase in the rate of reaction. This result is worth noting, in view of its implications concerning the mechanism of the reaction.

Steacie and Shane (7) investigated the thermal decomposition of ethane, hoping to determine an accurate activation energy for the reaction. They used a 15-liter vessel in order to minimize surface effects. The following rate constant was obtained:

$$k = 1.0 \times 10^{14} e^{-69700/RT} \text{ sec}^{-1}.$$

In the same paper, they compare the results of the previous investigations and arrive at 72 $\pm$ 2kcal mole^{-1} as the best activation energy obtainable from all of the available data.

While the over-all reaction rates were being investigated by the above workers, evidence was gathering that indicated that the reaction was complex and involved free radicals. Dintses and Frost (8, 9, 10) in a series of papers showed that the reaction was not a simple molecular process,

and concluded that chain processes were operating. Moreover they found that the reaction was inhibited by its own products. The expression which best described the course of an individual run was given as

$$k = \frac{1}{t}\left(\log \frac{1}{1-x} - Bx \right)$$

where x is the fraction reacted, t is time and B is a constant. They obtained no direct evidence of radicals.

The presence of radicals in the reaction system was first reported in 1933 by Rice and Dooley (11). Using the Paneth (12) technique they found an activation energy of 79.5 ± 3 kcal $mole^{-1}$ for the assumed reaction

1. $$C_2H_6 \rightarrow 2CH_3$$

This unfortunately was not supported by analytical evidence.

Elteton (13, 14) detected methyl and ethyl radicals in decomposing ethane, using the mass spectrometer. His findings at various pressures, up to 100 mm., suggest that reaction 1 is second-order. Owing to experimental difficulties however, this is not a firm conclusion.

Further evidence of free radicals came from the work of Lossing et al. (15) who detected methyl and traces of ethyl radicals in the pyrolysis of ethane.

The first chain mechanism to explain the observed phenomena was suggested by Rice and Herzfeld (16) in 1934.

The reaction was considered to be initiated by the unimolecular and first-order dissociation of ethane:

1. $$C_2H_6 \rightarrow 2CH_3.$$

This was followed by an abstraction of a hydrogen atom from an ethane molecule by a methyl radical:

2. $$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5.$$

The ethyl radical thus produced was assumed to decompose unimolecularly and initiate the chain:

3. $$C_2H_5 \rightarrow C_2H_4 + H$$

4. $$H + C_2H_6 \rightarrow H_2 + C_2H_5$$

Termination was taken to be:

5. $$H + C_2H_5 \rightarrow C_2H_6 \text{ or } C_2H_4 + H_2.$$

By equating all rates of radical production to zero under steady-state conditions the following rate was obtained:

$$v = \left(\frac{k_1 k_3 k_4}{k_5} \right)^{1/2} [C_2H_6]. \qquad [1]$$

This predicts the correct order of the reaction, and a suitable assignment of activation energies of the individual reactions led to a correct prediction of the over-all activation energy.

Recent measurements of the rates of the elementary processes, however, predict the over-all activation energy as given by the Rice-Herzfeld mechanism to be 65.6 kcal mole^{-1}. This is too low to be acceptable. It also appears from detailed calculation that under most of the experimental conditions the important terminating step will be:

6. $C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$ or $C_2H_4 + C_2H_6$

rather than reaction (5). If this chain-ending step is accepted, the Rice-Herzfeld scheme predicts a half-order reaction.

As an alternative mechanism Küchler and Theile (6) suggested that the correct order will again be predicted if reaction (1) occurs in the low-pressure region of a unimolecular process and is therefore of the second-order as represented by the equation:

1a. $C_2H_6 + X \rightarrow 2CH_3 + X.$

The steady-state treatment of their mechanism gives

$$v = k_3 \left(\frac{2k_{1a}}{k_6} \right)^{1/2} [C_2H_6] \qquad [2]$$

when X is taken as ethane.

As already mentioned, there is some evidence that the initiating reaction is second-order. The problem with the Küchler and Theile mechanism has been the lack of positive

evidence in its favor (18, 19). It will be shown later in the discussion how this problem can be resolved.

It will be clear from the foregoing discussion that there still remains a question as to the correct mechanism for the uninhibited decomposition of ethane. There is general agreement that the chain propagating reactions are:

3. $$C_2H_5 \rightarrow C_2H_4 + H$$

and

4. $$H + C_2H_6 \rightarrow H_2 + C_2H_5.$$

but disagreement exists with regard to the initiation and termination steps. The two rival mechanisms, those of Rice and Herzfeld and of Küchler and Theile, lead to somewhat different kinetic consequences, and the theoretical and experimental work to be described was designed with the object of coming to a decision between the two mechanisms.

EXPERIMENTAL

Apparatus

The investigation was carried out in an all-glass apparatus shown schematically in Figure 1; a photograph is shown as Plate 1. A high capacity vacuum pump (P_1) was employed to back the silicone oil diffusion pump (P_2) connected to a common manifold, with a tap-off to each vessel. Two similar two liter bulbs (V_1 and V_2) were used for gas storage.

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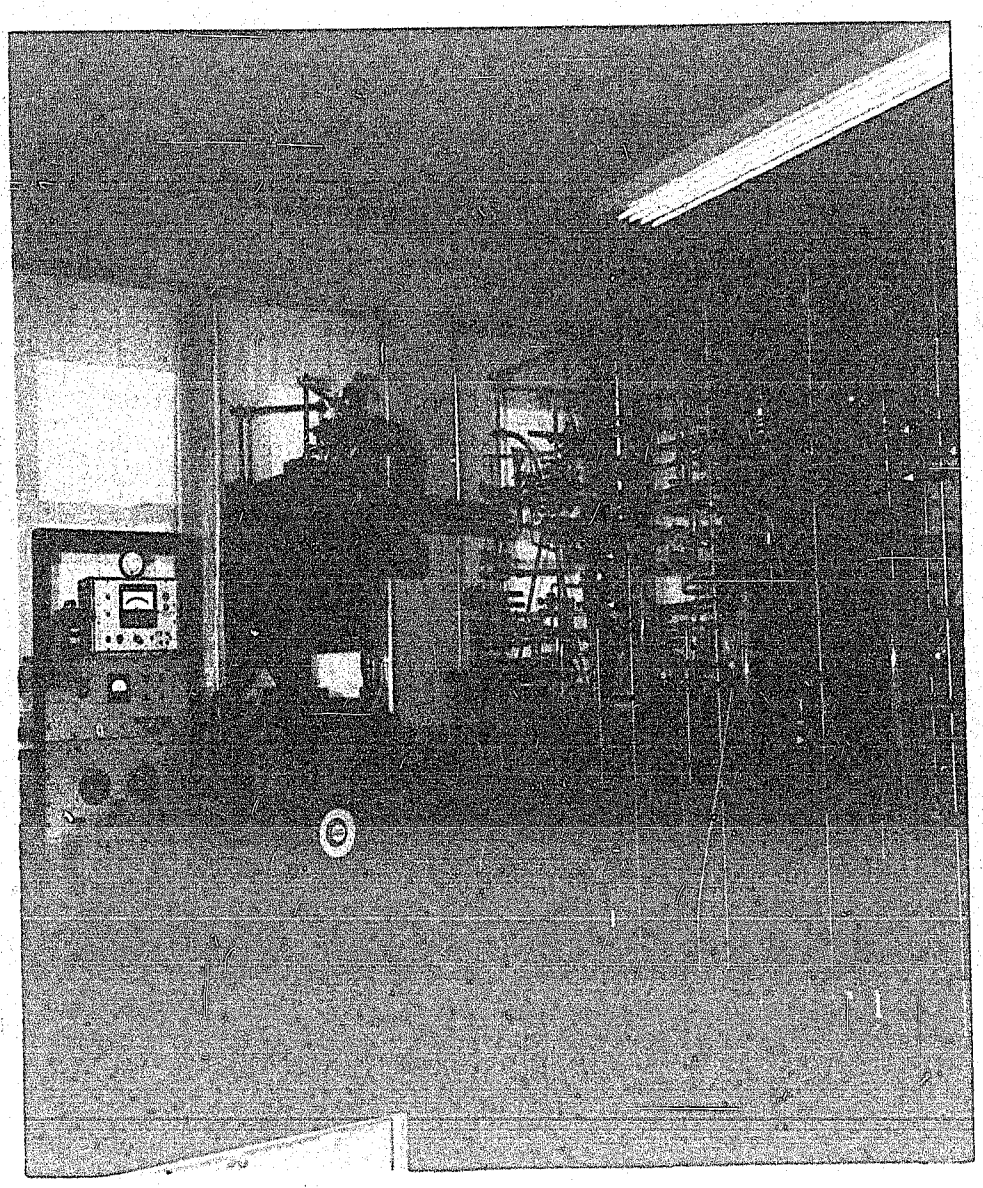


Plate 1 Over-All View of Apparatus.

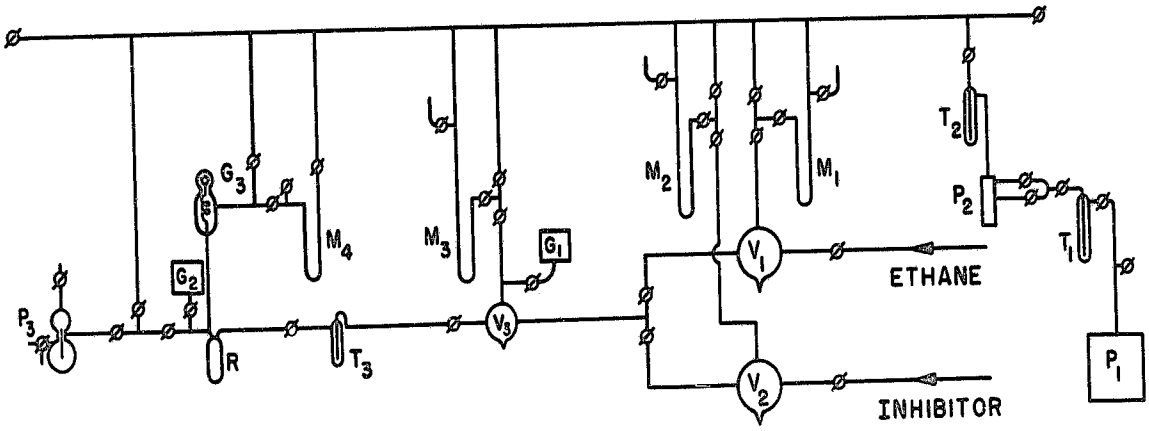


Figure 1 Schematic diagram of apparatus.

Each bulb was connected to a mercury manometer (M_1 and M_2) and had a nipple for freezing out the gases for purification. The storage bulbs were in turn connected to a one liter mixing bulb (V_3). This had a manometer (M_3) and a freezing nipple, and was used for preparing mixtures of ethane and inhibitor. From the mixing bulb the gases were led to the reaction vessel (R). The vessel was made of quartz and kept in the furnace.

The furnace consisted of a four-inch copper round (B), one foot long, with a hole bored into it to accommodate the reaction vessel. Two windings of nichrome wire around the furnace block were used for temperature control. The block and windings were encased in an asbestos box filled with powdered asbestos. The whole assembly was on a jack and could be raised to enclose the reaction vessel, or lowered in order to change the vessel. The temperature of the furnace was controlled to slightly below the desired temperature by manual adjustment of a Variac on one winding, and then brought up to the desired set point and controlled by means of a thermocouple-activated off-on controller (C) operating the second winding. The surges due to the off-on control could be minimized by adjusting the voltage on the second winding. The sensing thermocouple of the controller was placed in a hole in the copper block of the furnace. The temperature of the reaction was measured

by a second calibrated thermocouple placed in a well in the reaction vessel. This was read on a "Minimite" (M) self compensating potentiometer and was never noticed to vary during a run. A check with a more accurate potentiometer showed that the temperature variation was never more than $0.2^{o}C$.

Above the reaction vessel was a quartz spiral (G_3) with a mirror on its axial prong (Fig. 2 and Plate 2). The spiral was immersed in silicone oil in order to dampen spurious oscillations, and the pressure above the oil could be adjusted and measured on a mercury manometer (M_4). A beam of light from a 500-watt projection lamp (L) was focussed on the mirror of the spiral and reflected into a Beckman Photopen Recorder (R) where a record of the course of the reaction was obtained. The spiral gauge could always be made to record "on-scale" by adjustment of the pressure above the spiral. When low pressures were read, as during pumping down after a reaction, a calibrated Autovac Pirani gauge (G_2) was used. The sensing head of the Pirani gauge was joined to the tubing leading to the spiral gauge from the reaction vessel.

The reaction vessel and gauge could be pumped out without disturbing the mixing bulb, by means of another lead from the connection to the spiral gauge. This lead was also connected to a Toepler pump (P_3) for sampling. All the tubing above the reaction vessel to the nearest stopcocks consisted

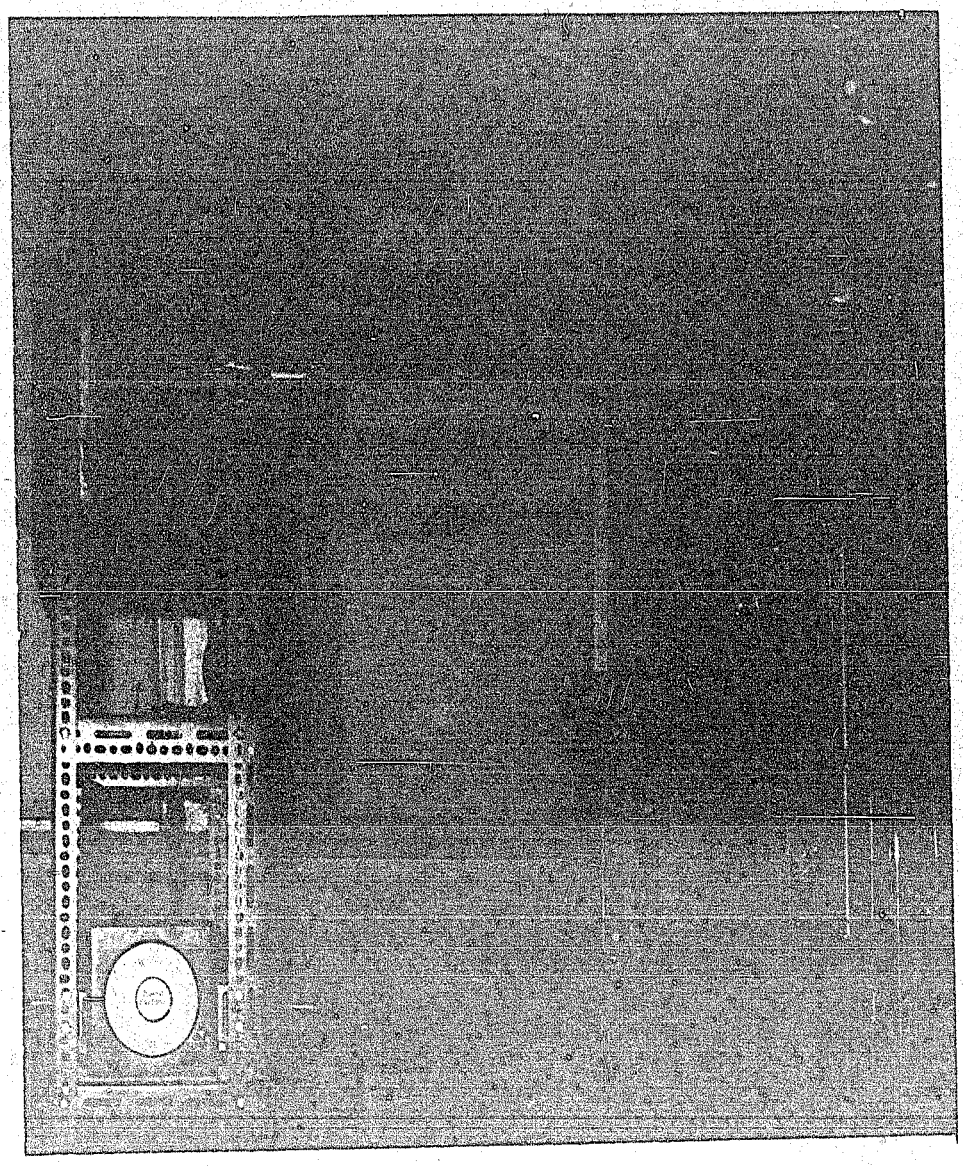
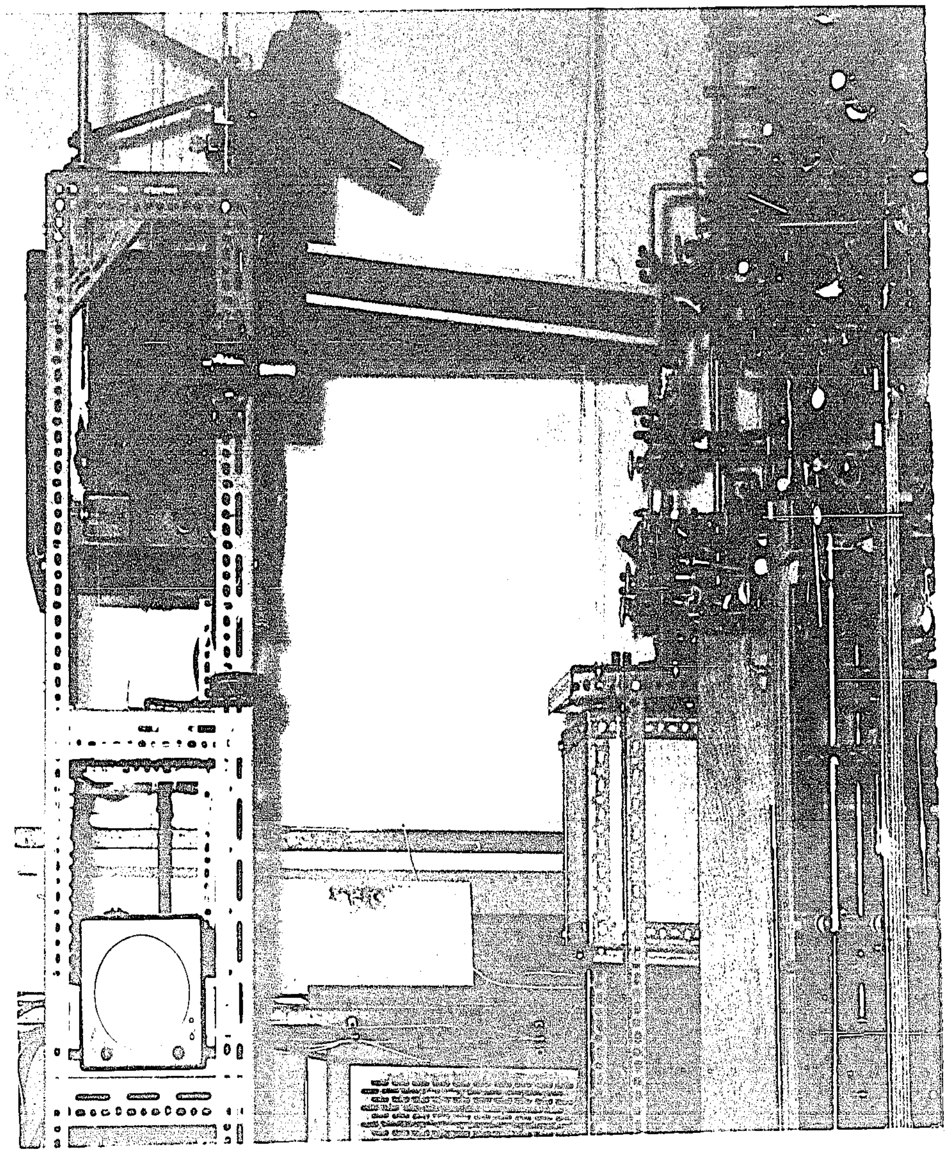


Plate 2 Detail of Photopen Recorder and Spiral Gauge.



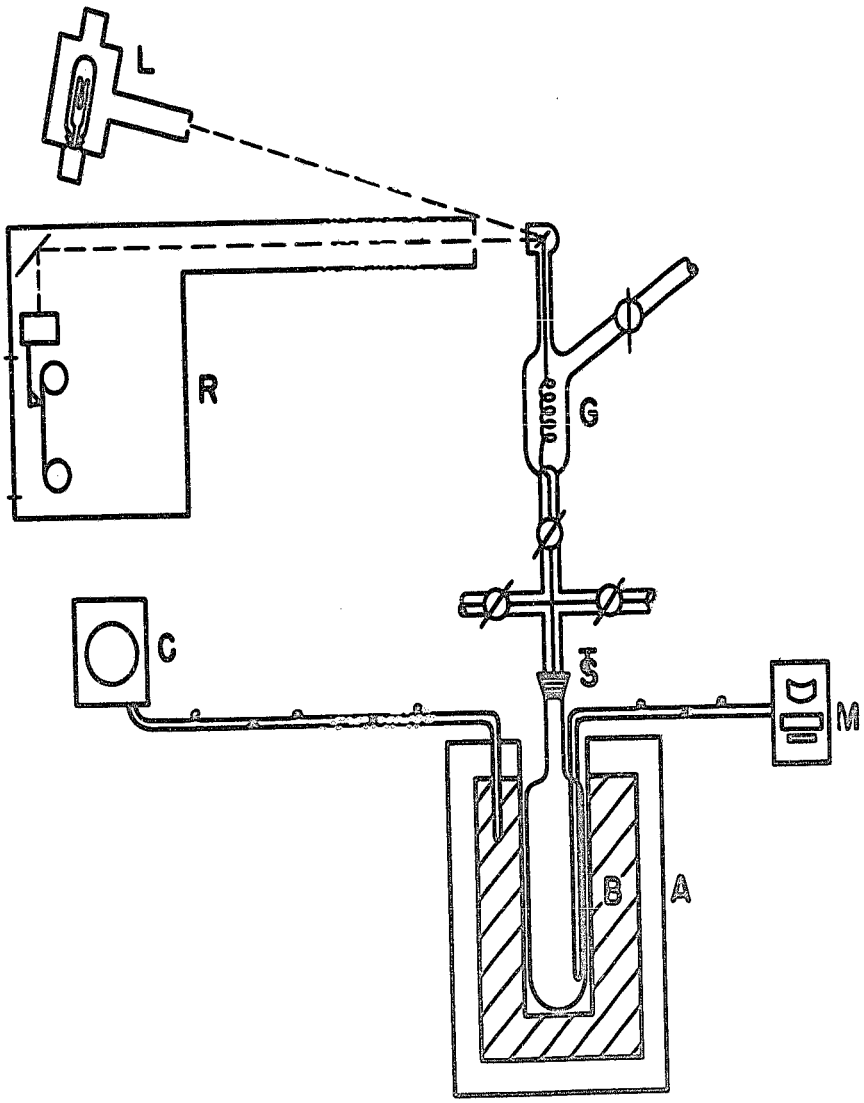


Figure 2 Arrangement of quartz spiral gauge, lamp and photopen recorder.

of 1 mm capillary tubing, to minimize dead space. The dead space was estimated to be 4 cc, which is very small in comparison with the 250 cc volume of the reaction vessel.

The apparatus was checked for leaks and all the instruments and volumes were calibrated. During the course of the investigation two reaction vessels were used. Both were 15 cm long by 4.6 cm in diameter. One was packed with quartz tubing to give a 25.5 times larger surface-to-volume ratio than the unpacked vessel.

Method

In operation, the reaction vessel was pumped out to 10μ and isolated from the pumps by a stopcock. Gas was then let in from the mixing bulb. The photopen immediately locked on the reflected beam of light, and followed it. After a suitable length of time the reaction mixture was pumped out and a fresh sample introduced at a lower initial pressure. The reagents used were Matheson Research Grade gases, purified by redistillation and deaeration.

The measured rates were readily reproducible, and pumping down to 1μ was not found to be of any advantage.

The rates of reaction were obtained by measuring the initial slopes of the ΔP vs time curves obtained by the Photopen Recorder. Most runs were duplicated during the course of investigation, and points from various runs are plotted without

distinction in the figures shown later. A readable slope was obtainable at all times by varying the speed of the chart, by a suitable selection of gear ratios in the drive mechanism.

Results

The pyrolysis of ethane was investigated in the temperature range between 550°C to 630°C. The photopen recorder automatically recorded ΔP vs time as shown on Fig. 3. Initial rates were obtained from this by drawing slopes at the origin or by using the Gerber Derivimeter. Usually the reaction was only allowed to proceed long enough to permit an accurate determination of the initial slope. More than two hundred runs were made in each vessel under varying conditions of temperature and pressure.

The results of a series of such runs, at pressures above 50 mm., and at temperatures from 550°C to 630°C, are plotted in Fig. 4 for both the packed and the unpacked vessel. From this the order of the reaction was determined for both vessels. The reaction proved to be first order under these conditions for the unpacked vessel and the corresponding rate constants are given in Table 1. In the case of the packed vessel the order was somewhat greater than one, and the best estimate gave an order of 1.15. The rate constants were not obtained in view of this non-integral order, but for the purpose of comparison the rates at 100 mm. are given

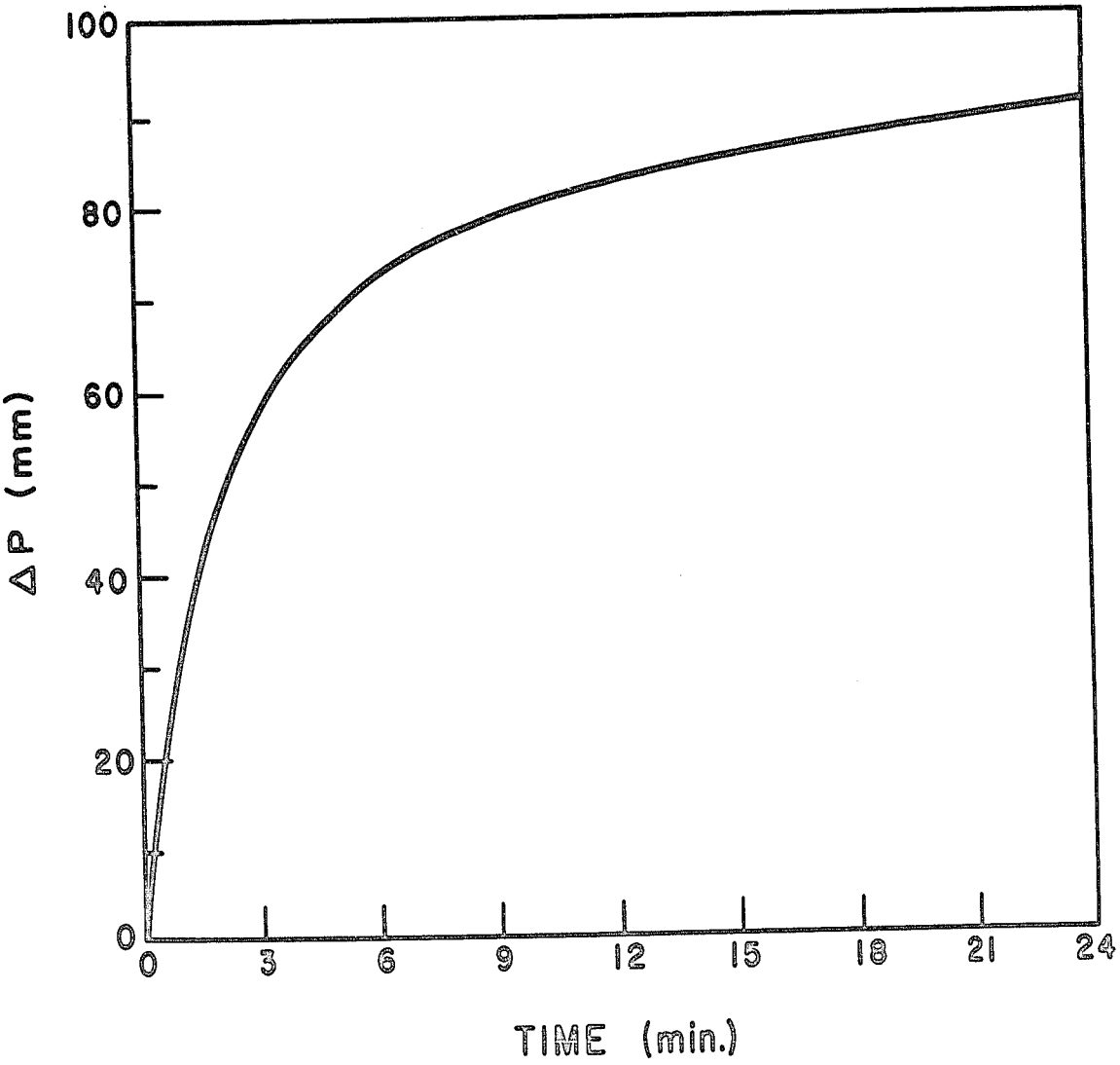


Figure 3 Pressure-time record at 640°C and an initial pressure of 271 mm., for the uninhibited reaction.

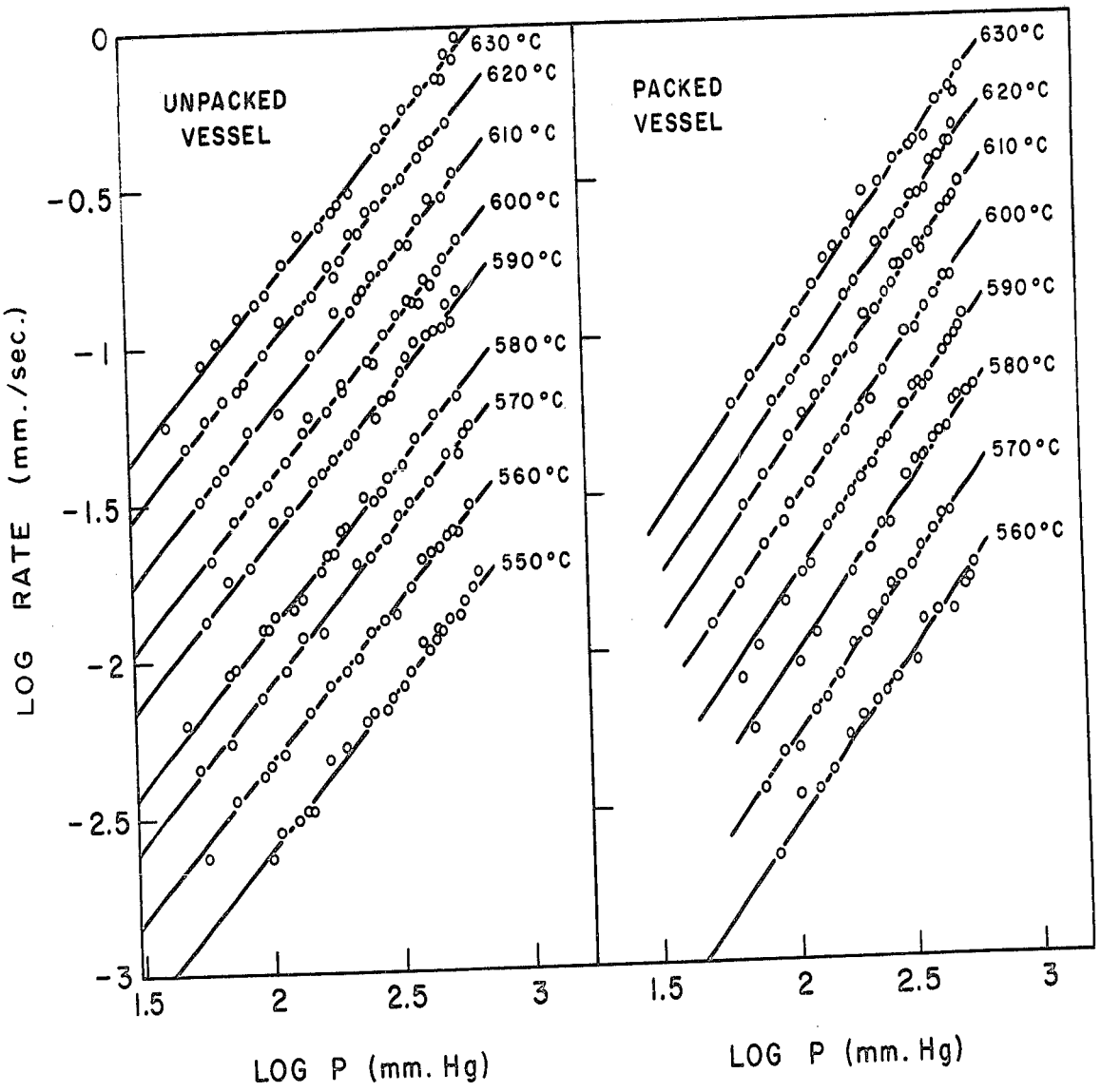


Figure 4 Plots of log rate against log pressure for the uninhibited reaction.

in Table 2. The difference in rates of reaction between the packed and unpacked vessels are shown graphically in Fig. 5.

By plotting the rate constants of the reaction in the unpacked vessel as an Arrhenius plot (Fig. 6), an activation energy of 73.1 kcal $mole^{-1}$ was obtained. This agrees well with results of other investigators, which are shown on the same plot. A similar plot of log (rate at 100 mm.) against 1/T for the packed vessel (Fig. 7) gave a convex curve. The activation energy at high temperatures approached 73 kcal $mole^{-1}$, but at lower temperatures tended to the much higher value of 86 kcal $mole^{-1}$. The rate constant obtained in the unpacked vessel can be represented as

$$k = 1.07 \times 10^{15} e^{-73100/RT} \text{ sec}^{-1}$$

which again agrees quite well with the results of the previous investigators.

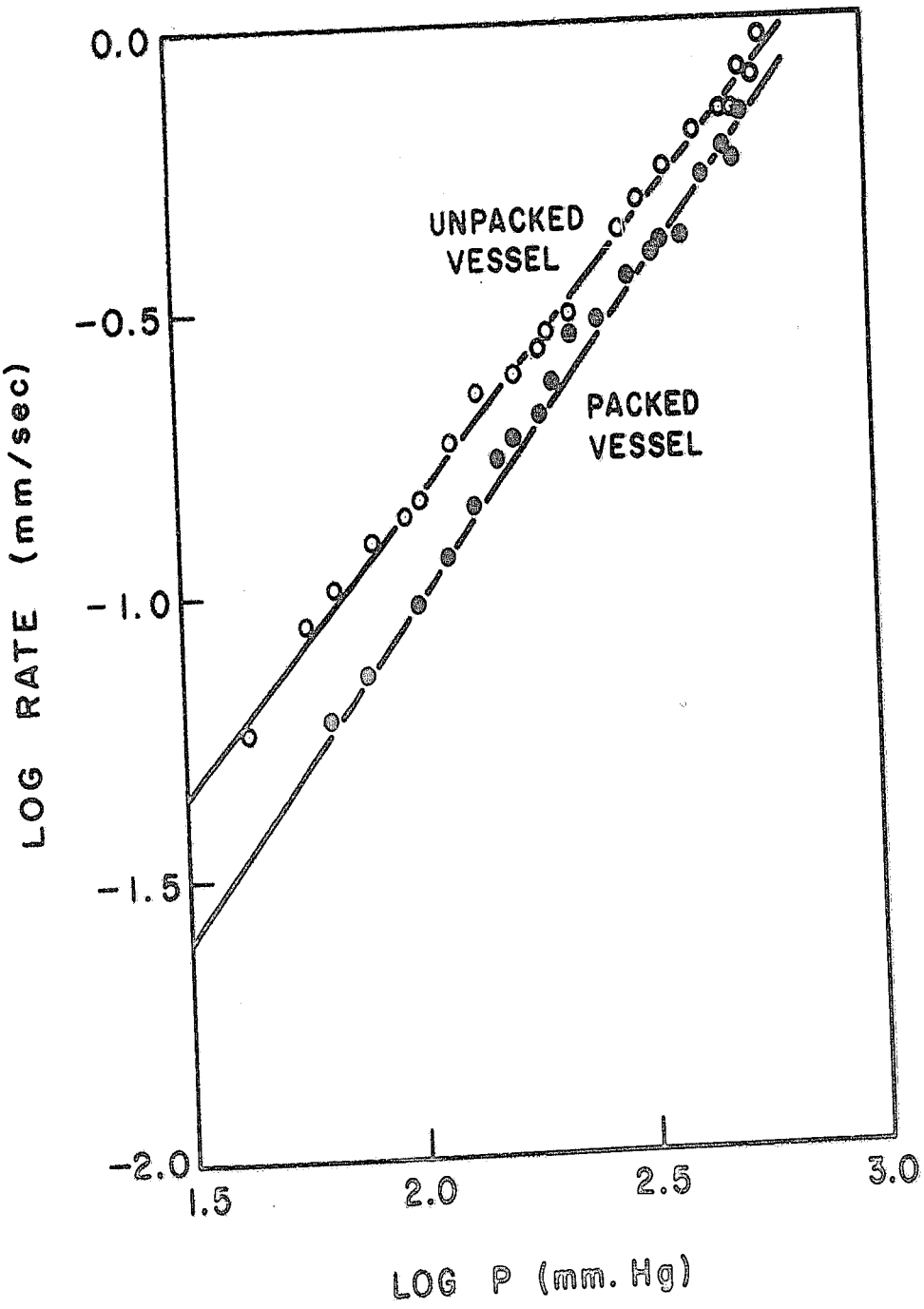


Figure 5 Plots of log rate against log pressure for the packed and unpacked vessels.

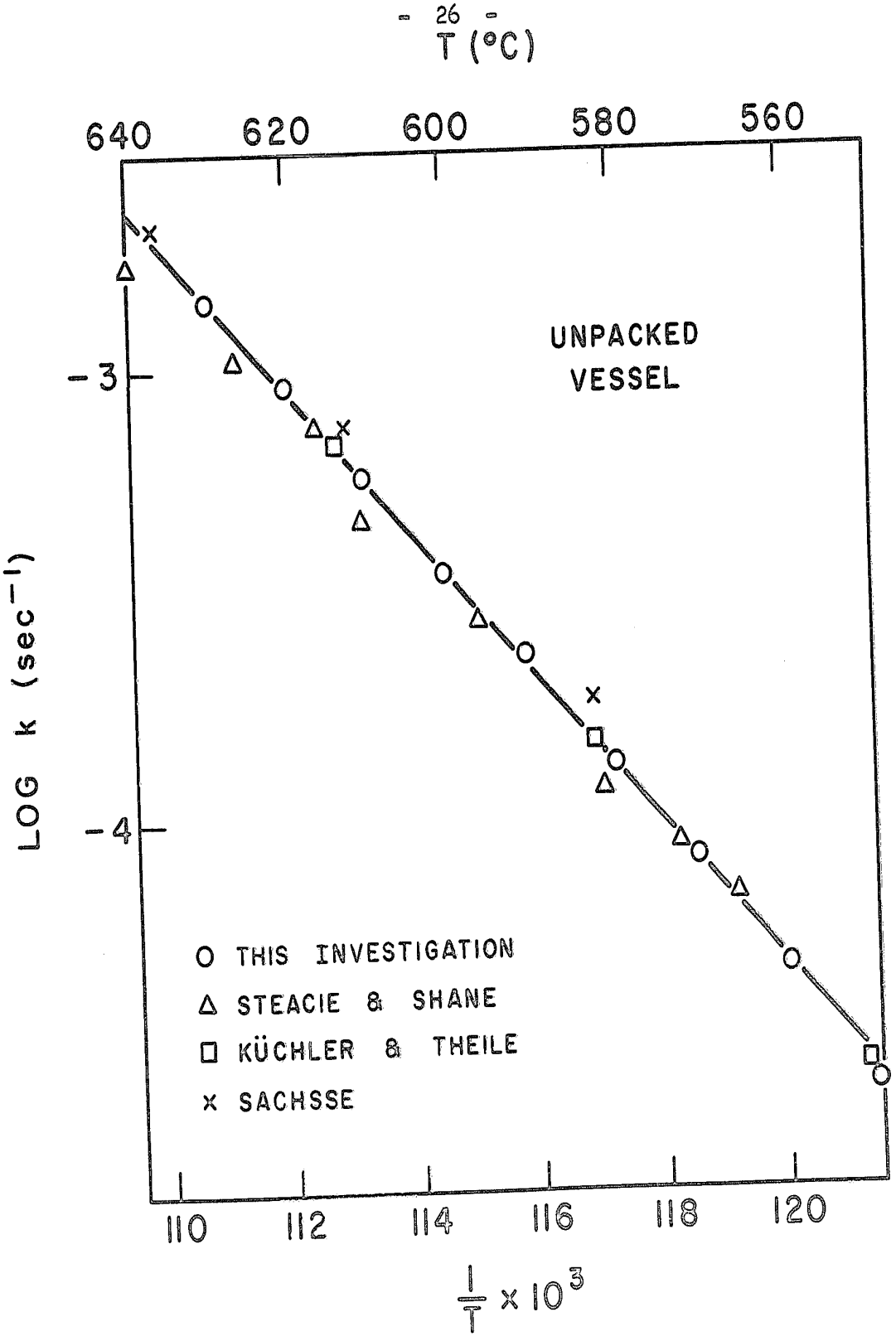


Figure 6 Arrhenius plot for the unpacked vessel, showing the results of various investigations.

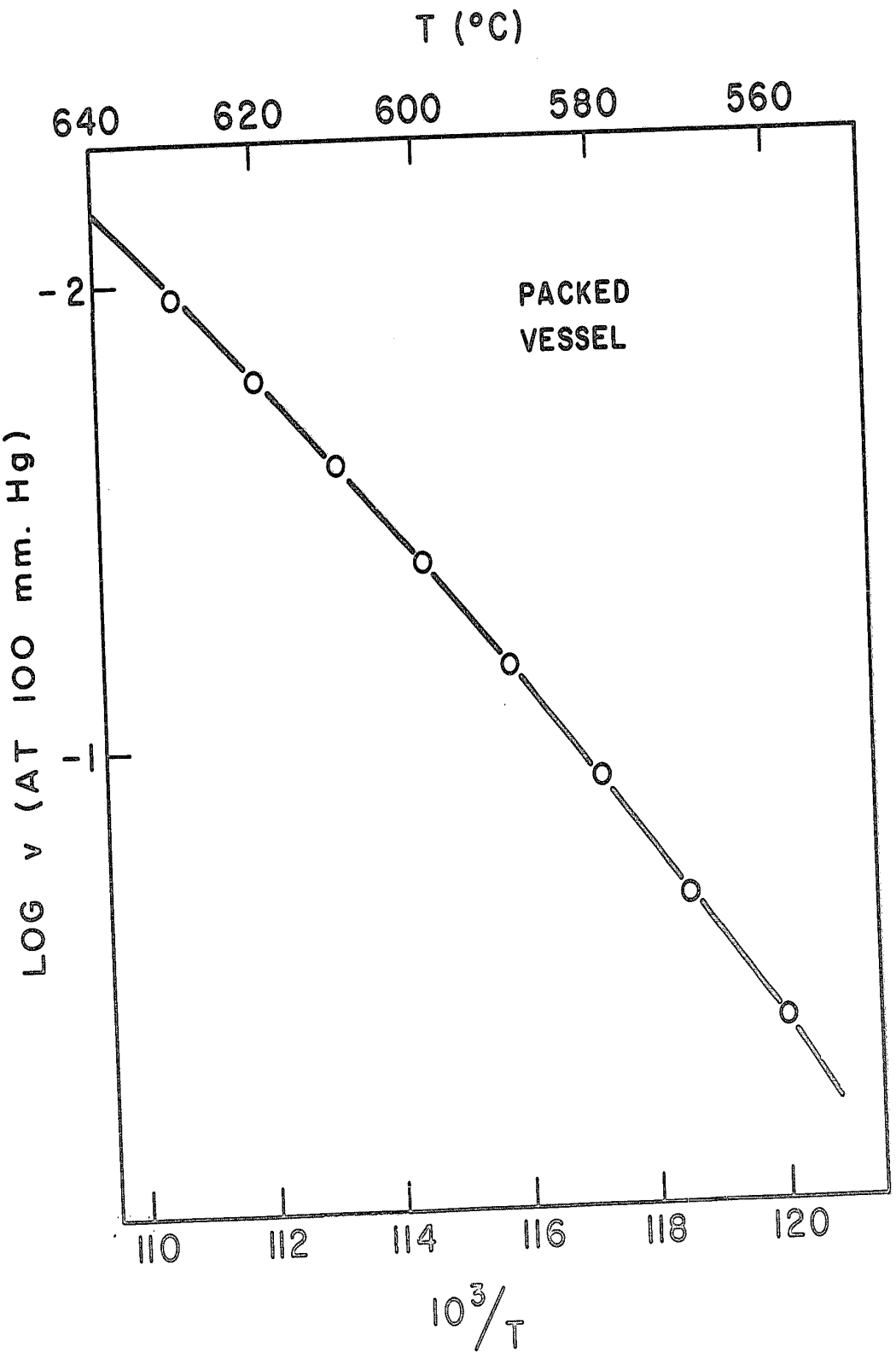


Figure 7 Plot of log (rate at 100 mm. pressure) against 1/T for the packed vessel.

Table 1

Rate constants in unpacked vessel.

T(°C)	T(°K)	k (sec^{-1} x 10^5)
550	823	2.53
560	833	4.70
570	843	8.21
580	853	12.32
590	863	23.07
600	873	35.30
610	883	57.60
620	893	92.40
630	903	141.50

Table 2

Rates at 100 mm initial pressure in packed vessel.

T(°C)	T(°K)	Rate (mm/sec.) x 10^3
560	833	2.44
570	843	4.54
580	853	8.40
590	863	14.50
600	873	24.50
610	883	40.00
620	893	61.00
630	903	93.00

DISCUSSION

The Rice-Herzfeld and Küchler-Theile Mechanisms

The main object of the present work on the uninhibited ethane decomposition was to evaluate, and if possible decide between, the proposed mechanisms of Rice and Herzfeld, and of Küchler and Theile. It was pointed out in the Introduction that the Rice-Herzfeld mechanism can be written as:

1. $C_2H_6 \rightarrow 2CH_3$
2. $CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$
3. $C_2H_5 \rightarrow C_2H_4 + H$
4. $H + C_2H_6 \rightarrow H_2 + C_2H_5$
5. $H + C_2H_5 \rightarrow C_2H_6$ or $H_2 + C_2H_4$

When the usual steady-state treatment is applied to the above scheme we obtain the following radical concentrations:

$$[CH_3] = \frac{2k_1}{k_2} \qquad [3]$$

$$[C_2H_5] = \left(\frac{k_1 k_4}{k_5 k_3}\right)^{1/2} [C_2H_6] \qquad [4]$$

$$[H] = \left(\frac{k_1 k_3}{k_4 k_5}\right)^{1/2} \qquad [5]$$

Since the over-all rate is given by

$$v_{R-H} = k_3 [C_2H_5] \qquad [6]$$

we have

$$v_{R-H} = \left(\frac{k_1 k_3 k_4}{k_5} \right)^{1/2} [C_2H_6] \qquad [1']$$

This must be compared to the predictions of the Küchler and Theile mechanisms:

1a. $X + C_2H_6 \rightarrow 2CH_3 + X$

2. $CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$

3. $C_2H_5 \rightarrow C_2H_4 + H$

4. $H + C_2H_6 \rightarrow H_2 + C_2H_5$

6. $C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$, or $C_2H_4 + C_2H_6$

Initially X is entirely C_2H_6, and in this case the steady-state method gives for the radical concentrations:

$$[CH_3] = \frac{2k_{1a}}{k_2} [C_2H_6] \qquad [7]$$

$$[C_2H_5] = \left(\frac{2k_{1a}}{k_6} \right)^{1/2} [C_2H_6] \qquad [8]$$

$$[H] = \frac{k_3}{k_4} \left(\frac{2k_{1a}}{k_6} \right)^{1/2} \qquad [9]$$

The rate is

$$v_{K-T} = k_3 \left(\frac{2k_{1a}}{k_6} \right)^{1/2} [C_2H_6] \qquad [2']$$

The Order of the Initiating Step.

The Küchler and Theile mechanism requires that initiation is of the second order. The evidence already cited (6, 13, 14) indicates that reaction 1 is second order. Küchler and Theile (6) in their paper report that most inert gases accelerate the rate of decomposition at 609°C. For instance, when the pressure of carbon dioxide is 4.44 times that of ethane, the rate of decomposition is increased by 50%. Other gases bring about a similar effect in varying degrees. The increase in rate occurs not merely in the "fallen-off" pressure region, but also in the region where the over-all decomposition is first order.

Eltenton (14) in the course of his mass spectrometric investigation of the pyrolysis of ethane found that the initiating step was second order under his experimental conditions, up to 110 mm pressure. He reported that, although a definite conclusion as to the order of reaction 1 may be premature, there are good reasons to believe that it is second-order.

Recent theoretical work by Gill and Laidler (20) makes it possible to calculate the transition pressure. It was shown in the above paper that the Hinshelwood theory gives a good approximation of the rate of reaction 1 when s is taken as 9. Using the results of Dodd and Steacie (21) and Steacie (22), Gill and Laidler conclude that the reaction

7. $CH_3 + CH_3 + X \longrightarrow C_2H_6 + X$

is third order at 1 mm pressure and 200°C. The Hinshelwood-Rice-Ramsperger theory of unimolecular reaction rates predicts that the transition pressure will vary as the $(s - \frac{1}{2})$ power of the temperature, where s in this case is probably 9. Thus under the experimental conditions of 600°C, the reaction will be second order at

$$P = \left(\frac{873}{473}\right)^{8.5} \text{ mm} \qquad [10]$$

$$= 180 \text{ mm}$$

if it is accepted that at 200°C the transition occurs at 1 mm pressure. However, if the transition occurs at 10 mm pressure at 200°C, then at 600°C it will occur at 1800 mm. By the principle of microscopic reversibility, this would put all experimental rate measurements in the present investigation safely in the second order region.

The Chain-Terminating Step

It was shown by Steacie (17) that for the Rice-Herzfeld mechanism at high pressures (100-500 mm) reaction 6 will predominate as the chain terminating step. In order to compare the various terminating steps we must first obtain the rate constants for the reactions involved in the mechanisms under discussion. To facilitate comparison of the present calculations with those of Steacie, we will accept most of

the rates given by him (17; see also ref. 23). These are given in Table 3.

A comparison of the rates of various termination steps shows that for the Rice and Herzfeld mechanism

$$\frac{v_5}{v_6} = \frac{k_5 [H] [C_2H_5]}{k_6 [C_2H_5]^2} \qquad [11]$$

$$= \frac{k_5 [H]}{k_6 [C_2H_5]} \qquad [12]$$

By substituting the appropriate steady-state radical concentrations for the Rice-Herzfeld mechanism in equation (12) we obtain

$$\frac{v_5}{v_6} = \left(\frac{k_3 k_5}{k_4 k_6} \right) \frac{1}{[C_2H_6]} \qquad [13]$$

The point where the predominant chain-ending step changes occurs where

$$v_5 = v_6 \qquad [14]$$

The corresponding concentration is

$$[C_2H_6] = \frac{k_3 k_5}{k_4 k_6} \qquad [15]$$

Since in our assigned values in Table 3, $k_5 = k_6$, the transition concentration is given by

$$[C_2H_6] = \frac{k_3}{k_4} = \frac{A_3}{A_4} e^{-32700/RT} \qquad [16]$$

By substituting values from Table 3 we conclude that at 600°C the change will occur at

$$[C_2H_6] = 5.71 \times 10^{-7} \text{ moles cm}^{-3} = 30 \text{ mm.}$$

Table 3

Kinetic Parameters of Reactions Involved in the Uninhibited Pyrolysis of Ethane

Reaction	A*	E	k_{600}	References
1	1.0×10^{17}	85.00	5.01×10^{-5}	23
1a	6.0×10^{17}	70.2	2.28×10^{-1}	calculated(see text)
2	2.0×10^{11}	10.4	5.02×10^{8}	24
3	3.0×10^{14}	39.5	3.96×10^{4}	25
4	3.4×10^{12}	6.8	6.80×10^{10}	26
5	1.6×10^{13}	0.0	1.60×10^{13}	assumed
6	1.6×10^{13}	0.0	1.60×10^{13}	27
8	1.0×10^{12}	2.0	3.16×10^{11}	estimated from ref.28
9	1.0×10^{12}	11.5	1.58×10^{7}	estimated from ref.29

* Frequency factors are in sec^{-1} or $cm^3\ mole^{-1}\ sec^{-1}$

A similar treatment on the basis of the Küchler and Theile mechanism also yields equation [15] and therefore predicts the same change-over pressure. This result agrees qualitatively with Steacie's calculations. Reaction 6 is predicted as the terminating step at high pressures, no matter which of the two mechanisms is used.

The Order of the Over-all Reaction

It has been seen in the previous two sections that the initiating reaction is expected to be of the second order under the conditions of the present experiments, and to become first-order only at higher pressures. The chain-ending step, on the other hand, may change from $C_2H_5 + C_2H_5$ at the higher pressures and become predominantly $H + C_2H_5$ at lower pressures. The various possible combinations of initiation and termination are listed in Table 4.

As far as the over-all order of the reaction is concerned, the facts appear to be consistent only with the above interpretation. If, as proposed in the Rice-Herzfeld mechanism, the initiating reaction were first-order one has to postulate $H + C_2H_5$ as the chain-ending step in order to explain the first-order behaviour; this has been seen to be unlikely. If, as is more probable, chain-ending is by $C_2H_5 + C_2H_5$, the order would be one-half, which is not observed. In fact the

order is unity at the higher pressures and the falling-off of rate constants observed by Küchler and Theile suggests an increase in order. This behaviour is consistent with the suggestion that initiation is always second-order under our conditions, and that termination changes from $C_2H_5 + C_2H_5$ as the pressure is lowered. An order of 3/2 is then expected at the lower pressures.

In order to test this hypothesis rates were measured at high temperatures and low pressures, under which conditions an order of 3/2 is most likely. The results are plotted in Fig. 8, which clearly shows the three-halves order predicted. At 640°C the predicted transition pressure (from eq. [16]) is 76 mm., and the experimental value is 60 mm., in excellent agreement.

Activation Energies and Rate Constants

Using the values given in Table 3 for the activation energies of the elementary reactions we may calculate the over-all activation energies as predicted by the two mechanisms. The Rice-Herzfeld mechanism gives

$$E_{R-H} = \frac{1}{2} (E_1 + E_3 + E_4 - E_5) \qquad [17]$$

$$= 65.6 \text{ kcal mole}^{-1}$$

which is somewhat too low in comparison with the experimental value of 73.1 kcal.

In order to make the calculation for the Küchler-Theile mechanism it is necessary to obtain a value for the

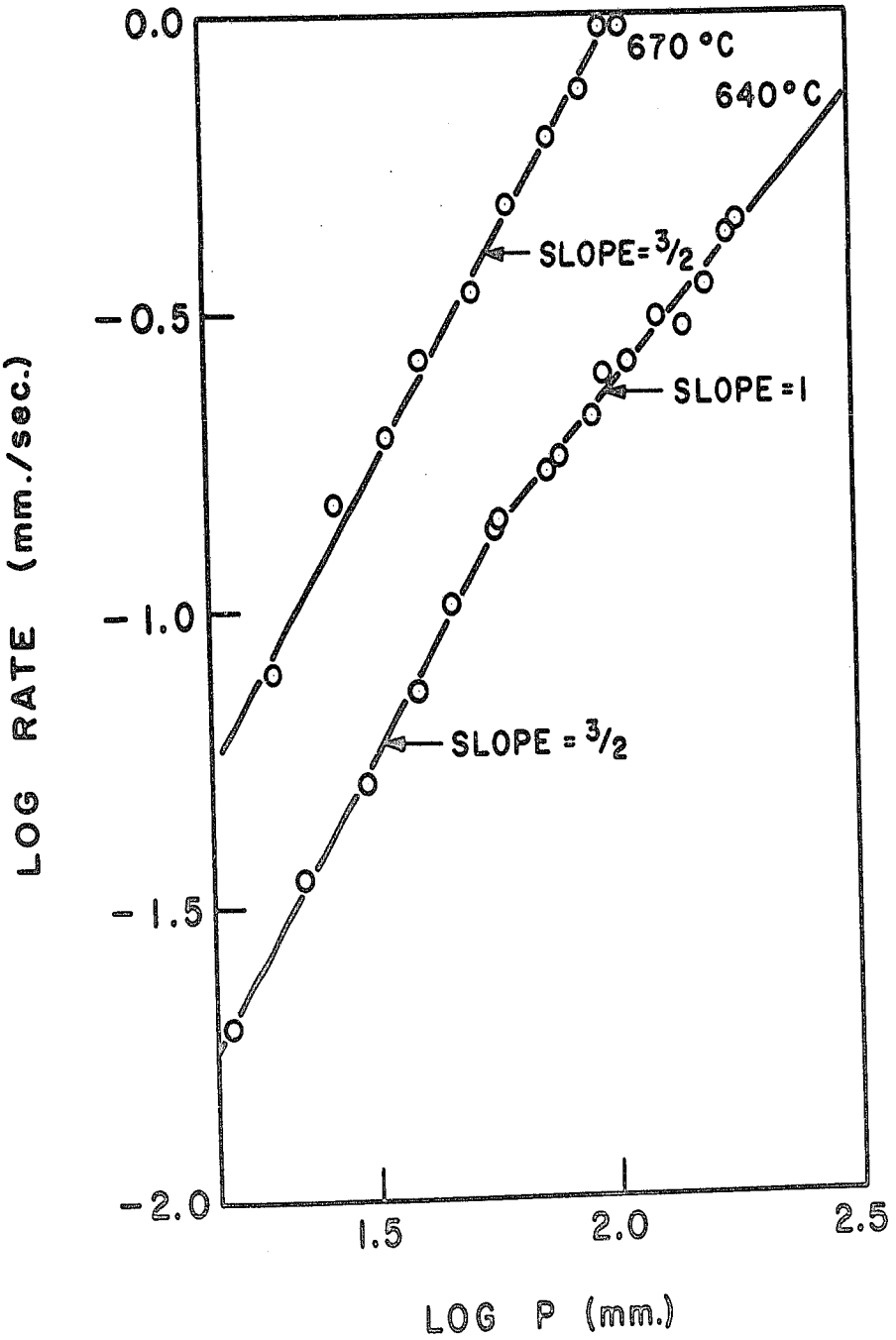


Figure 8 Plots of log rate against log pressure at higher temperatures than in Figure 4, showing the change of order to 3/2 at lower pressures.

Table 4

Possible Combinations of Initiation and Termination in the Uninhibited Pyrolysis of Ethane

Initiation order	Termination	Over-All order
1st	$C_2H_5 + C_2H_5$	1/2
2nd	$C_2H_5 + C_2H_5$	1st
1st	$H + C_2H_5$	1st
2nd	$H + C_2H_5$	3/2

activation energy of the reaction $C_2H_6 \rightarrow 2CH_3$ in the low-pressure region. The value in the high-pressure region, when the rate is given by

$$k = \nu e^{-E_0/RT}, \qquad [18]$$

is equal to 85 kcal. The expression for the second-order rate constant in the low-pressure region is, according to the Hinshelwood-Rice-Hamsperger-Kassel formulations

$$k_1 = Z \left(\frac{E_0}{RT} \right)^{s-1} \frac{1}{(s-1)!} e^{-E_0/RT} \qquad [19]$$

When Z is in pressure units proportional to $T^{-1/2}$, and the temperature-dependence of k_1 is therefore expressed by

$$k_1 \propto \left(\frac{1}{T} \right)^{s-1/2} e^{-E_0/RT} \qquad [20]$$

The low-pressure activation energy is therefore

$$E_{1a} = E_o - (s - \tfrac{1}{2}) RT. \qquad [21]$$

With s = 9, as deduced by Gill and Laidler [2], this gives

$$E_{1a} = 85000 - 8.5\ RT \qquad [22]$$
$$= 70.2 \text{ kcal.}$$

at 609°C, as given in Table 3.

The over-all activation energy predicted by the Küchler-Theile mechanism is

$$E_{K-T} = E_3 + \tfrac{1}{2} (E_{1a} - E_6) \qquad [23]$$
$$= 74.6 \text{ kcal. mole}^{-1}$$

which is in better agreement with the observed value.

The Küchler-Theile mechanism may also be shown to predict a satisfactory value for the rate constant. The procedure that has been adopted has been to calculate a rate constant at 200°C, since a reliable value of k_{1a} is known at this temperature, and there is some uncertainty about calculating k_{1a} at the higher temperatures of the present investigation.

From the results of Dodd and Stoacie (21) Gill and Laidler deduced a value of 3×10^{20} cc^2 mole^{-2} sec^{-1} for the third order rate constant for the methyl radical recombination in the presence of acetone. The equilibrium constant was estimated to be $\sim 10^{-36}$ mole cc^{-1} at this temperature, and

the second-order rate constant for the ethane dissociation is therefore estimated to be $\sim 3 \times 10^{-16}$ cc mole^{-1} sec^{-1}. The rate constants k_3 and k_6 are calculated to be, at 200°C,

$$k_3 = 1.6 \times 10^{-4} \text{ sec}^{-1}$$

and

$$k_6 = 1.6 \times 10^{13} \text{ cc mole}^{-1} \text{ sec}^{-1}$$

and the calculated rate constant for the over-all reaction is then found to be

$$k_{K-T} = k_3 \left(\frac{k_{1a}}{k_6} \right)^{1/2} \qquad [21]$$

$$= 5.0 \times 10^{-19} \text{ sec}^{-1}.$$

The experimental value, calculated from the rate equation, is

$$k = 1.07 \times 10^{15} e^{-73100/198 \times 473}$$

$$= 2.2 \times 10^{-19} \text{ sec}^{-1}.$$

The agreement is better than might have been expected in view of the fact that the activation energy undoubtedly changes over the temperature range from 883°K to 473°K; presumably the frequency factor changes in a way that almost compensates for this change.

An alternative procedure is to calculate the frequency factor. The rate constant of 3×10^{-16} cc mole^{-1} sec^{-1} at 200°C leads to a frequency factor of 1.2×10^{20} at this temperature, and since the frequency factor varies with $T^{-8.5}$ the value at 882°K is 6.0×10^{17}. This leads to an overall frequency

factor, at 882°K, of

$$A = A_3 \left(\frac{A_{1a}}{A_6} \right)^{1/2} \qquad [24]$$

$$= 3 \times 10^{14} \left(\frac{6.0 \times 10^{17}}{1.6 \times 10^{13}} \right)^{1/2}$$

$$= 5.8 \times 10^{16} \text{ cc mole}^{-1} \text{ sec}^{-1}$$

This is in reasonable agreement with the experimental value of 1.07×10^{15} in view of the fact that calculations have had to be made over a wide temperature range.

To summarize the results of the calculations, the individual rate constants lead, on the basis of the Küchler-Theile mechanism, to the following rate expression at 882°K:

$$k_{K-T} = 5.8 \times 10^{16} \; e^{-74600/RT} \text{ cc. mole}^{-1} \text{ sec}^{-1}.$$

This compares favourably with the experimental equation

$$k_{exp} = 1.07 \times 10^{15} \; e^{-73060/RT} \text{ cc mole}^{-1} \text{ sec}^{-1}.$$

At 882°K the rates are

$$k_{K-T} = 1.83 \times 10^{-3} \text{ cc mole}^{-1} \text{ sec}^{-1}$$

$$k_{exp} = 8.4 \times 10^{-4} \text{ cc mole}^{-1} \text{ sec}^{-1}.$$

The agreement was seen above to be equally satisfactory at 200°C.

Summary of Evidence in Favour of Küchler and Theile Mechanism

To sum up the evidence in favour of the Küchler and Theile mechanism, we can cite:

1. The evidence of Küchler and Theile (6), referred to

factor, at 882°K, of

$$A = A_3 \left(\frac{A_{1a}}{A_6} \right)^{1/2} \qquad [24]$$

$$= 3 \times 10^{14} \left(\frac{6.0 \times 10^{17}}{1.6 \times 10^{13}} \right)^{1/2}$$

$$= 5.8 \times 10^{16} \text{ cc mole}^{-1} \text{ sec}^{-1}$$

This is in reasonable agreement with the experimental value of 1.07×10^{15} in view of the fact that calculations have had to be made over a wide temperature range.

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The agreement was seen above to be equally satisfactory at 200°C.

Summary of Evidence in Favour of Küchler and Theile Mechanism

To sum up the evidence in favour of the Küchler and Theile mechanism, we can cite:

1. The evidence of Küchler and Theile (6), referred to

in the discussion on the chain-initiating step, which brings out the fact that inert gases accelerate the rate of the high-pressure reaction.

2. The experiments performed by Eltenton (14) using the mass spectrometer, which indicate that there is a first-order surface reaction producing methyl radicals at very low pressures (below 3 mm) and a second-order homogeneous reaction producing radicals at pressures up to 110 mm, beyond which Eltenton did not pursue the investigation.

3. The calculations of Steacie (17), confirmed here in the discussion on the terminating step, which indicate that the predominant terminating reaction will be:

6'. $C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$ or $C_2H_4 + C_2H_6$.

4. The correct prediction of the falling off of the rate of reaction at low pressures which can be made using the Küchler and Theile mechanism.

5. The satisfactory estimation of activation energies, rate constants and frequency factors that can be made on the basis of the Küchler-Theile mechanism.

In view of the above evidence, we will accept the Küchler and Theile mechanism as correctly representing the over-all reaction, and all further discussion will be based on it.

Inhibition By Products

When reactions

8. $H + C_2H_4 \rightarrow C_2H_5$

9. $C_2H_5 + H_2 \rightarrow C_2H_6 + H$

are included in the Küchler and Theile mechanism, the predicted rate for the reaction is:

$$v = \frac{k_3k_4\left(\frac{2k_{1a}}{k_6}\right)^{1/2}[C_2H_6]^2 - k_8k_9\left(\frac{2k_{1a}}{k_6}\right)^{1/2}[H_2][C_2H_4][C_2H_6]}{k_4[C_2H_6] + k_8[C_2H_4]} \quad [25]$$

At the beginning of the reaction, when $[C_2H_4] = 0$, this reduces

$$v = k_3\left(\frac{2k_{1a}}{k_6}\right)^{1/2}[C_2H_6] \quad [2']$$

This is the initial rate of reaction predicted by the Küchler and Theile mechanism. At the other extreme, when

$$v = 0,$$

equation [23] reduces to

$$\frac{[C_2H_4][H_2]}{[C_2H_6]} = \frac{k_3k_4}{k_8k_9} \quad [26]$$

which is the equation for the equilibrium

10. $C_2H_6 \rightleftharpoons C_2H_4 + H_2$

The values of rate versus pressure of ethane remaining are plotted in Fig. 9 where they are compared with points obtained from equation [25]. The agreement is good up to high conversions, where the predicted rates are lower than

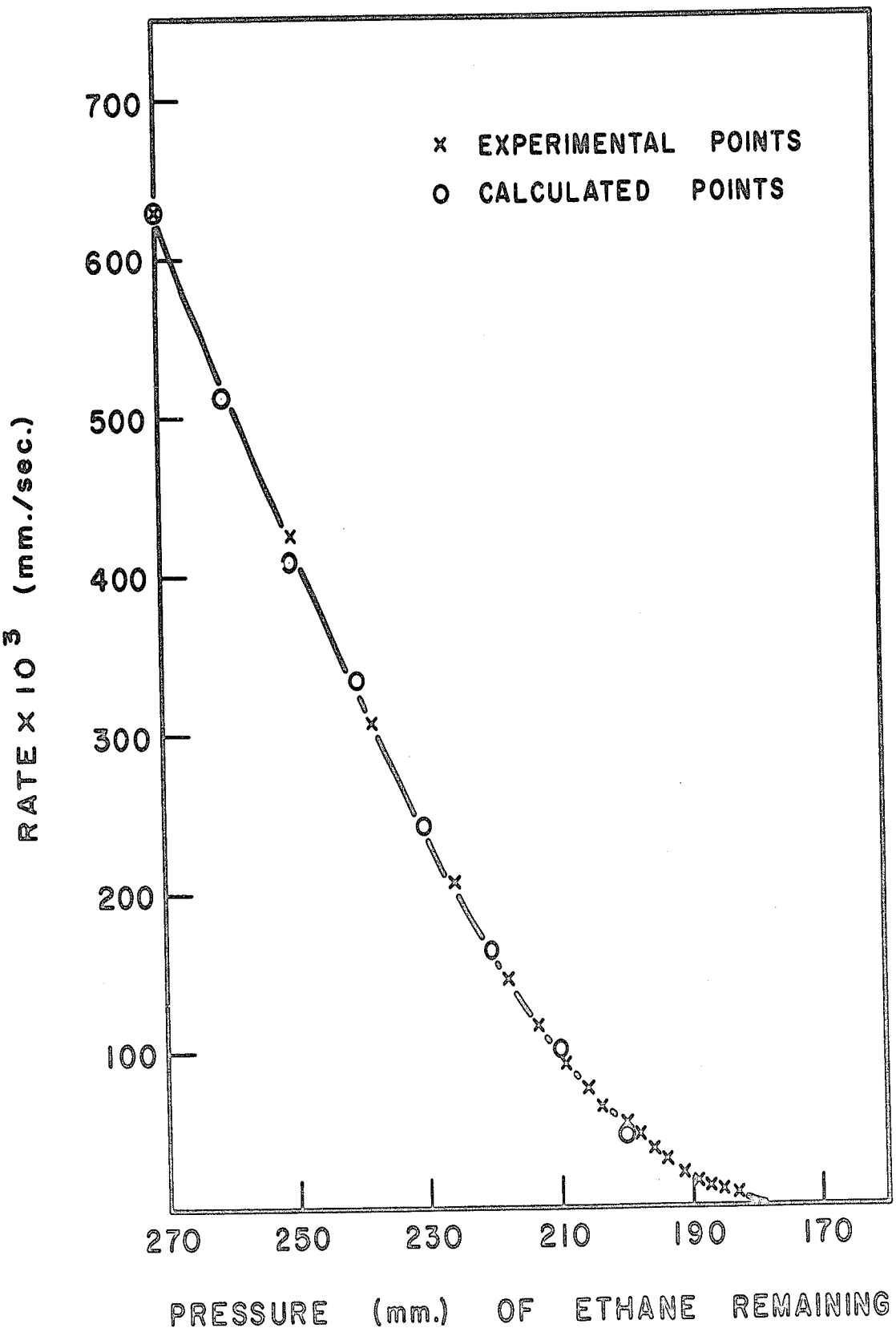


Figure 9 The variation of rate with extent of reaction; the calculated points are based on equation (23).

those observed, The reasons for this are two-fold. The side reaction producing methane (reaction 2) will tend to increase the experimental rate. Secondly, reaction 1a is second-order and thus the numerator in equation [25] should be

$$\left\{ k_3 k_4 \left(\frac{2k_{1a}}{k_6} \right)^{1/2} [C_2H_6]^{3/2} - k_8 k_9 \left(\frac{2k_{1a}}{k_6} \right)^{1/2} [H_2][C_2H_4][C_2H_6]^{1/2} \right\} [X]^{1/2}$$

where

$$[X] = [C_2H_6] + a[C_2H_4] + b[H_2] + \text{----} \qquad [27]$$

Since $a[C_2H_4] + b[H_2] + \text{----}$ is positive, the concentration of X is greater than that of C_2H_6 remaining. The experimental rate will be greater than that predicted since the above is not taken into consideration.

The fact that reaction 1 is second-order and therefore depends on the total pressure explains the reported lack of inhibition by ethylene observed by Frost (30). Indeed the results reported by Dintses (31) indicate that the rate of decomposition is slightly increased by the addition of ethylene. Similar experiments by Stubbs and Hinshelwood (32) indicate that the addition of hydrogen greatly increase the rate of the uninhibited decomposition. In order to explain the observed inhibition at high conversions, Dintses in his paper (31) postulates an imaginary complex which is formed from the products of the decomposition in situ, and inhibits the reaction. This is unnecessary if equation [25] is accepted, since it

states that inhibition will be greatest when both ethylene and hydrogen are present. With most other additives very little inhibition, and perhaps even acceleration, will be observed.

Effects of Surface

The effect of an increased surface-to-volume ratio is to decrease the rate of reaction as shown in Fig. 5. There is also a tendency towards an order higher than the first, as the surface-to-volume ratio is increased. The decrease in rate can be attributed to surface recombination of radicals. On this basis it can be maintained that hydrogen atom recombination will be increased more than that of ethyl radicals by an increase in surface, since the reaction

11. $$H + H \longrightarrow H_2$$

will require a third body, whereas the reaction

6. $$C_2H_5 + C_2H_5 \longrightarrow C_4H_{10} \text{ or } C_2H_4 + C_2H_6$$

can proceed almost as well in the gas phase as on the surface. Also, the relative concentration of hydrogen atoms will increase with decreasing pressure, and reaction 11 will play a greater role at low pressures. This in turn will decrease the rate of the over-all reaction proportionately more at low pressures, and thus cause an apparent increase in order.

The reaction in the packed vessel was also retarded to a greater degree at low temperatures than at high. This is

thought to be due to a greater rate of surface removal of radicals, especially hydrogen atoms, under conditions where surface adsorption is more likely, (i.e. at low temperatures). When the temperature is increased and is no longer favourable for adsorption of radicals, the reaction speeds up, giving an apparent increase in activation energy.

CONCLUSION

The experimental evidence reported here leads us to believe that the over-all reaction is largely homogeneous and first-order under our experimental conditions. Theoretical considerations, coupled with the experimental results reported here and by other workers, indicate that the Kȕchler and Theile free radical mechanism best represents the mechanism of the reaction. The activation energy obtained experimentally was 73.11 kcal $mole^{-1}$ and the rate constant could be represented by

$$k = 1.07 \times 10^{15} \; e^{-73100/RT} \; sec^{-1}.$$

Part II

THE DECOMPOSITION OF ETHANE INHIBITED BY NITRIC OXIDE

INTRODUCTION

The effect of inhibitors such as nitric oxide, propylene, and others, upon the pyrolysis of hydrocarbons has defied satisfactory explanation for the past twenty years. The present work was undertaken in an effort to gather more data and to provide some interpretation of the phenomenon of inhibition. We shall first review the previous work.

Review of Previous Work

In 1937 Staveley (33) found that relatively small amounts of nitric oxide caused profound changes in the rate of decomposition of ethane at 620°C. He suggested that nitric oxide removed free radicals, leaving the unimolecular split

12. $$C_2H_6 \rightarrow C_2H_4 + H_2$$

as the remaining reaction. On this basis Staveley calculated the apparent chain lengths in the uninhibited decomposition, the apparent chain lengths being the ratio of the uninhibited to the inhibited rate.

Staveley found that the apparent chain length varied from 6.4 at 500 mm to 20.6 at 50 mm ethane pressure at 620°C.

The study of inhibition was taken up in 1938 by Hinshelwood and his co-workers. In their paper of 1938, Hobbs and Hinshelwood (34) report an investigation of the nitric oxide inhibition of ethane. The data presented agree qualitatively with the results of Staveley, but differ from it quantitatively. The work of Staveley and of Hobbs and Hinshelwood on the influence of nitric oxide on the decomposition revealed two important points. First it was found that complete inhibition could be obtained with a certain amount of nitric oxide, and that further additions of the inhibitor had no significant effect on the rate of reaction. Secondly it was found that the quantity of inhibitor necessary for complete inhibition depended on the concentration of ethane, and was approximately 10% of the concentration. Using the above evidence Hobbs and Hinshelwood suggest a mechanism of free radical removal eliminating all chains and leaving only a surface reaction and a homogeneous unimolecular split as shown in reaction 12. This conclusion can be questioned on many points, some of which will be discussed later. One of their conclusions, however, is quite acceptable. On the basis of the fact that complete inhibition depends on the relative concentration of inhibitor they suggest that the radical removed is one which can also react with ethane.

Steacie and Shane (35) in 1940 reinvestigated the reaction in the same 15 liter vessel used for the uninhibited reaction (7). They obtained somewhat shorter chain lengths than those reported by Staveley (33); their reported activation energy of 77.3 kcal $mole^{-1}$ is higher than that of Staveley (74.5 kcal $mole^{-1}$) or Ingold, Stubbs and Hinshelwood (74.7 kcal $mole^{-1}$) (36) but is in good agreement with Küchler and Theile (6) who reported 77.0 kcal $mole^{-1}$. All the above workers agree in one respect. The activation energy of the inhibited reaction is a few kcal $mole^{-1}$ higher than that of the uninhibited reaction.

The main argument for the unimolecular hypothesis is the fact that the various inhibitors cause the same limiting rate of reaction. In 1951, Stubbs and Hinshelwood (37) summarized the other arguments for a unimolecular rearrangement and discussed the alternatives. They came to the conclusion that the fact that similar products were obtained in the inhibited and uninhibited reactions was not inconsistent with a unimolecular split in the case of inhibition and with long chains in the uninhibited reaction. They also assumed that the induction period observed in the inhibited reaction was an "inherent property of the reaction". As further proof of the complete suppression of chains they quote the fact that hydrogen accelerates the uninhibited reaction, whereas no such

effect is observed in the inhibited pyrolysis. This of course is easily explained if the Küchler and Theile mechanism is operating in the uninhibited case, and some other form of initiation is predominant in the inhibited reaction.

As early as 1938, Rice and Polly (38) suggested that a free radical mechanism was operating when nitric oxide was present. They proposed the mechanism:

$$M_1 \rightarrow R_1 + M_2$$

$$R_1 + M_1 \rightarrow R_1H + R_2$$

$$R_2 \rightarrow R_1 + M_3$$

$$2\,R_1 \rightarrow R_1R_1$$

$$R_1 + NO \rightarrow \text{Products}$$

$$NO + M_1 \rightarrow NOH + R_2 \rightarrow NOH + R_1 + M_3$$

This required rather drastic approximations in order to yield a rate independent of nitric oxide concentration.

Goldanskii (39) in a lengthy discussion of a modified Rice-Polly mechanism attempted to predict chain lengths and the forms of the ΔP vs. time curves of various reactions. These calculations are not too reliable, since their results are very sensitive to small changes in arbitrarily assigned frequency factors and activation energies, as well as involving drastic approximations.

The suspicions that free radicals were involved in the completely inhibited reaction were supported by Hall and

Moore (40, 41) who studied various inhibited decompositions, Using mixtures of deuterated and undeuterated reagents they found that isotopic mixing occurred even in the early stages of an inhibited reaction. Their results, however, were not convincing, since they were not working under conditions of complete inhibition. Further evidence of isotopic mixing in the inhibited reaction came from Rice and Varnerin (42) who found that in the completely inhibited pyrolysis of mixtures of ethane-d_6 and methane, the ratio

$$\frac{CH_3D}{CH_4}$$

was only dependent on the extent of the reaction and was the same for both the inhibited and uninhibited reactions at the same percentage decomposition.

In 1956, Varnerin and Dooling (43) reported a very convincing series of experiments on isotopic mixing in the inhibited decomposition of ethane. They carried out decomposition of 50-50 mixtures of ethane and methane-d_4, and of ethane-d_6 and methane, both inhibited and uninhibited by nitric oxide. The results clearly indicate that the isotopic mixing is only a function of the percent decomposition and is quite independent of nitric oxide concentration or temperature.

The nature of the mixed products indicates that methyl and ethyl radicals as well as hydrogen atoms continue to play a role in the inhibited decomposition. Unfortunately,

the quantitative results are not accurate enough to permit a more detailed analysis.

Even before the isotopic mixing studies were undertaken Elteton (14) had reported the presence of free radicals in the inhibited decomposition. His mass spectrometric measurements showed the concentrations of methyl radicals to be approximately the same in both the inhibited and uninhibited reactions.

EXPERIMENTAL

Apparatus and Method

The apparatus used was the same as that described in Part I. The method differed slightly, in that mixtures of ethane and inhibitor were prepared in the mixing bulb before each series of runs. The procedure involved condensing about 500 mm of ethane in the mixing bulb and adding to that about 50 mm of inhibitor from the inhibitor storage bulb. The gases were then allowed to reach room temperature, and the total pressure was measured. From the known pressure of pure ethane and the total pressure of ethane plus inhibitor, the percentage of inhibitor in the mixture could be calculated. A series of runs at decreasing initial pressures was then carried out using one mixture. This allowed the investigation of each mixture under various initial pressures, and eliminated any errors due to variation in reagent composition.

The same packed and unpacked vessels described in Part I were used in this investigation.

Results

The reaction was investigated in the region from 610°C to 680°C, and from 20 mm to 500 mm pressure. A typical ΔP vs. time curve for the inhibited decomposition is given in Fig. 10.

Two rates were taken from each curve; the initial and inflection point rates. These are shown for the unpacked vessel as log rate vs. log pressure plots in Fig. 11. The lines drawn through the initial rates have a slope of 1 at high pressures and of 3/2 at low pressures. This interpretation is justified in Fig. 12 where the inflection rates are compared to the initial rates on the same log rate vs. log pressure plot.

The inflection point rates in Fig. 11 have an order higher than 1. The orders corresponding to the various temperatures are given in Table 5.

The activation energy was obtained by plotting the logarithm of the high-pressure first-order rate constant against 1/T in an Arrhenius plot shown in Fig. 13. The activation energy obtained is 77.5 kcal $mole^{-1}$ and the rate is $k = 3.12 \times 10^{15} e^{-77500/RT}$. Results obtained by Steacie and Shane, and by Hobbs and Hinshelwood are shown on the same plot for comparison.

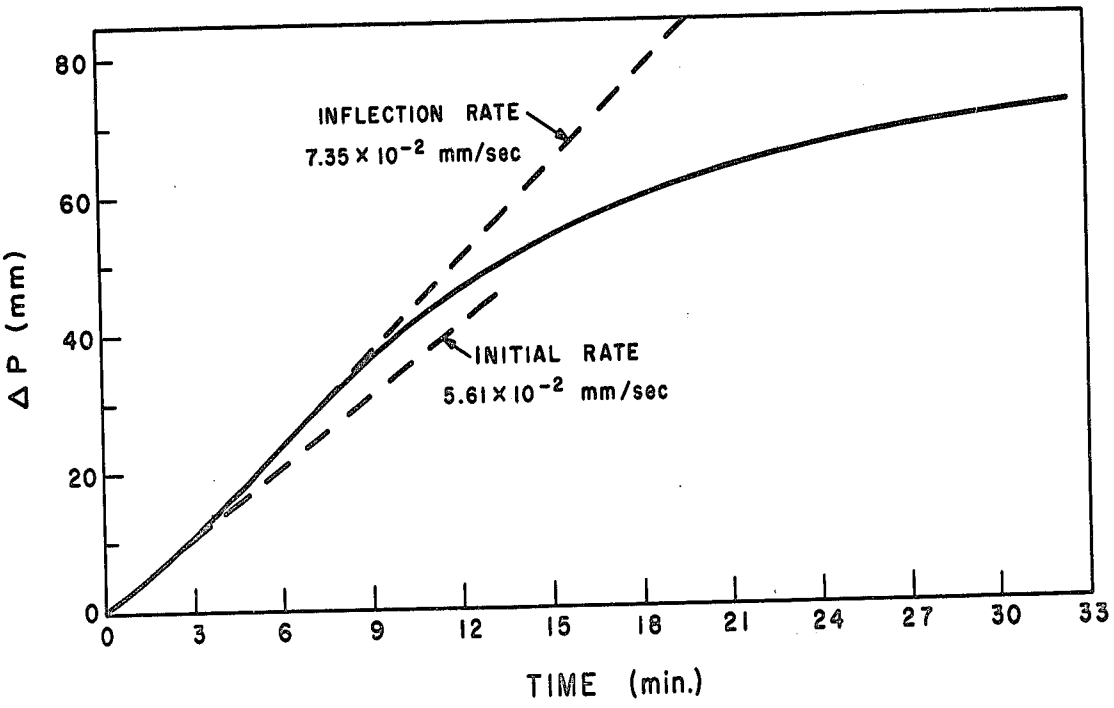


Figure 10 Typical pressure-time curve for the decomposition of ethane inhibited by nitric oxide. Temperature = 640° C; pressure of ethane = 150 mm; 12.5% nitric oxide; unpacked vessel.

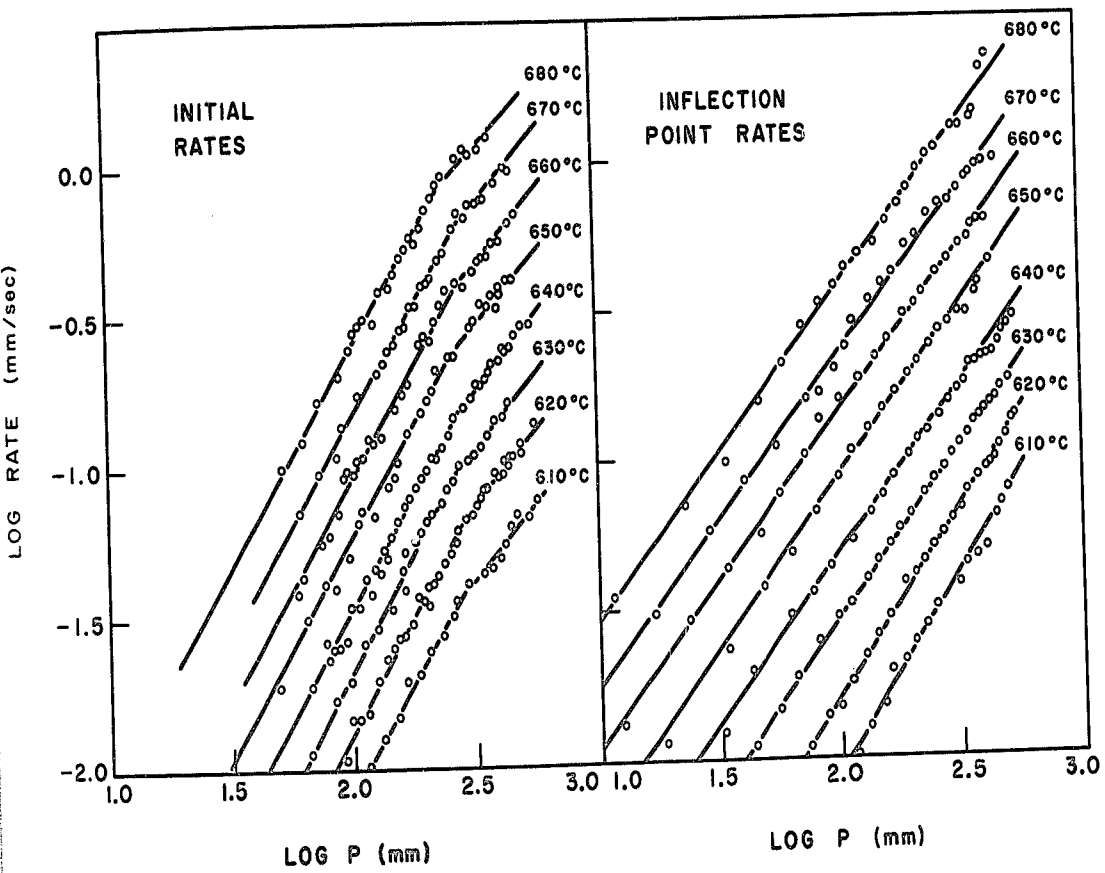


Figure 11 Plots of the logarithm of the rate against the logarithm of the pressure; the left-hand plots are for initial rates, the right-hand for those at the inflection point. Unpacked vessel.

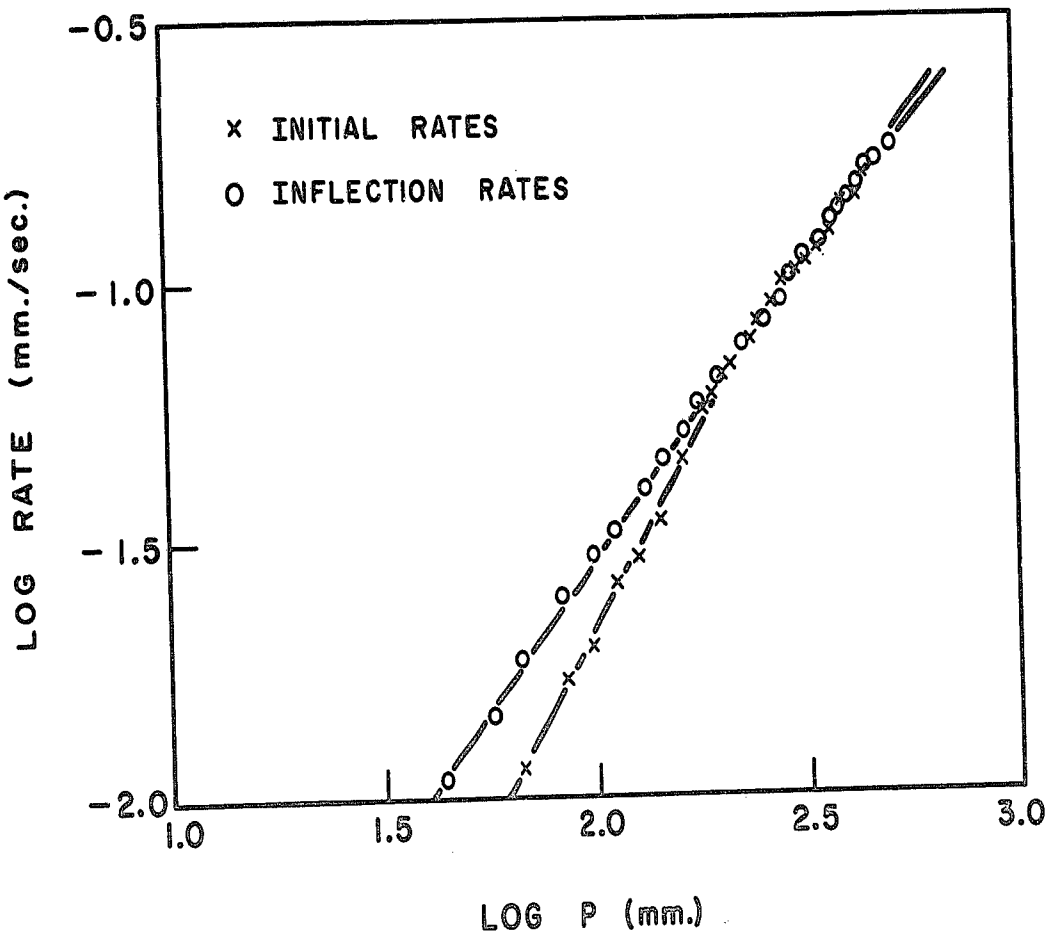


Figure 12 Plots of the logarithm of the rate against the logarithm of the pressure, in the unpacked vessel at 630° C. The crosses (X) denote initial rates, the circles (0) rates at the inflection point.

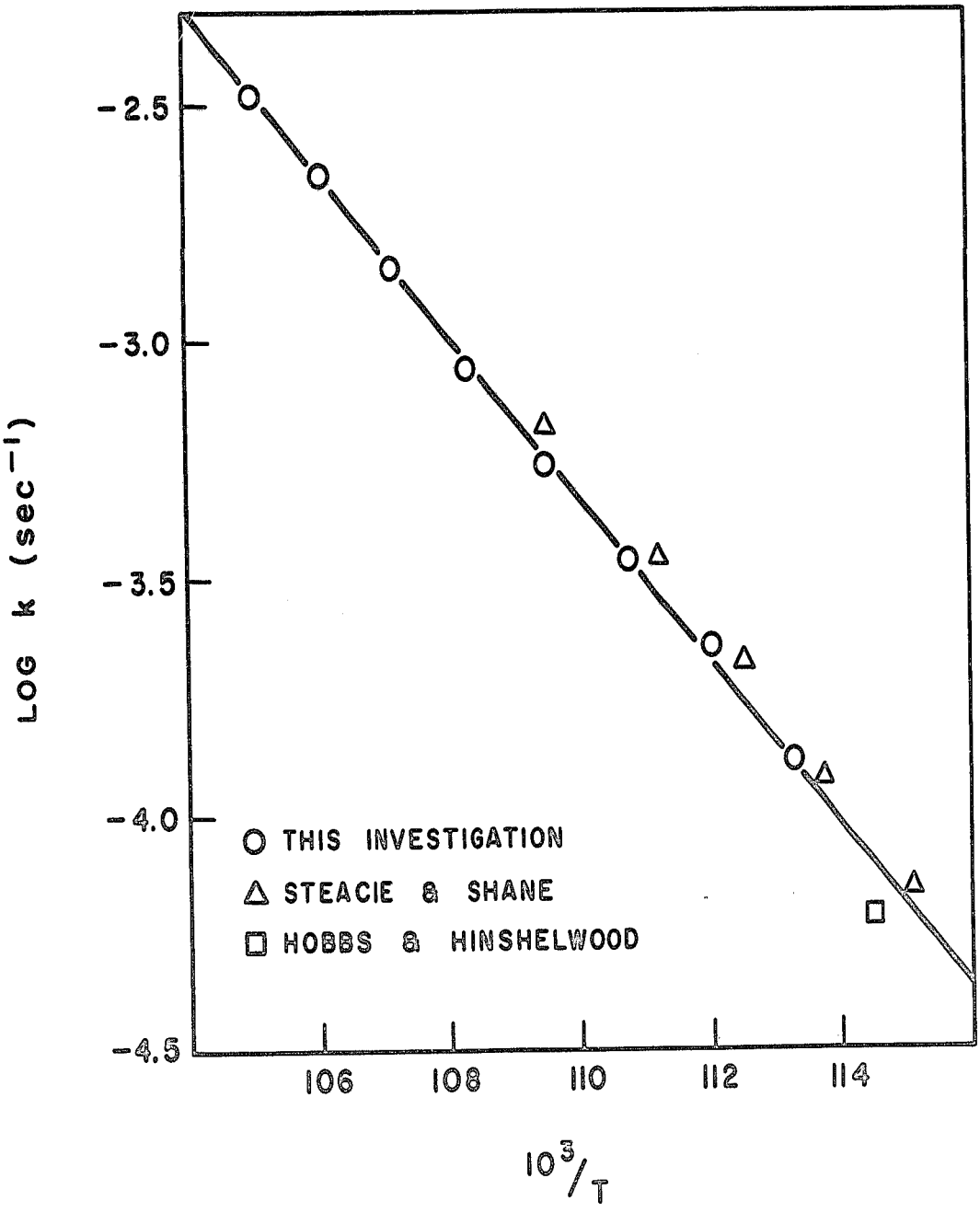


Figure 13 Arrhenius plot for the unpacked vessel, the rate constants being those obtained at high pressures and being the same initially as at the inflection point (compare Fig. 12).

The results from a similar series of runs in the packed vessel at temperatures from 620°C to 680°C are plotted as log rate vs. log pressure in Fig. 14. The ΔP vs. curves were similar to those in Fig. 10. However, the initial rates were not as reproducible as those in the unpacked vessel and are therefore not recorded.

The rate constants were not obtained for the inflection point rates in view of the non-integral orders given in Table 5. The logarithm of the rate at 100 mm is plotted against 1/T for both the packed and unpacked vessel in Fig. 15. From these an apparent activation energy is obtained. In both the packed and unpacked vessels this was ~80 kcal mole^{-1}. This value however is not taken as the true value in view of the fact that non-initial conditions were measured in taking the rate at the inflection point.

In order to ascertain whether 10% nitric oxide in the mixture was sufficient for complete inhibition, a series of runs was carried out using various amounts of nitric oxide. The results obtained are given in Fig. 16 as a plot of log rate vs. log pressure. From this we concluded that inhibition was complete at a 10% nitric oxide concentration. The individual ΔP vs. time curves at various nitric oxide concentrations showed a variation in the induction period which tended to shorten the induction period at high ethane pressures

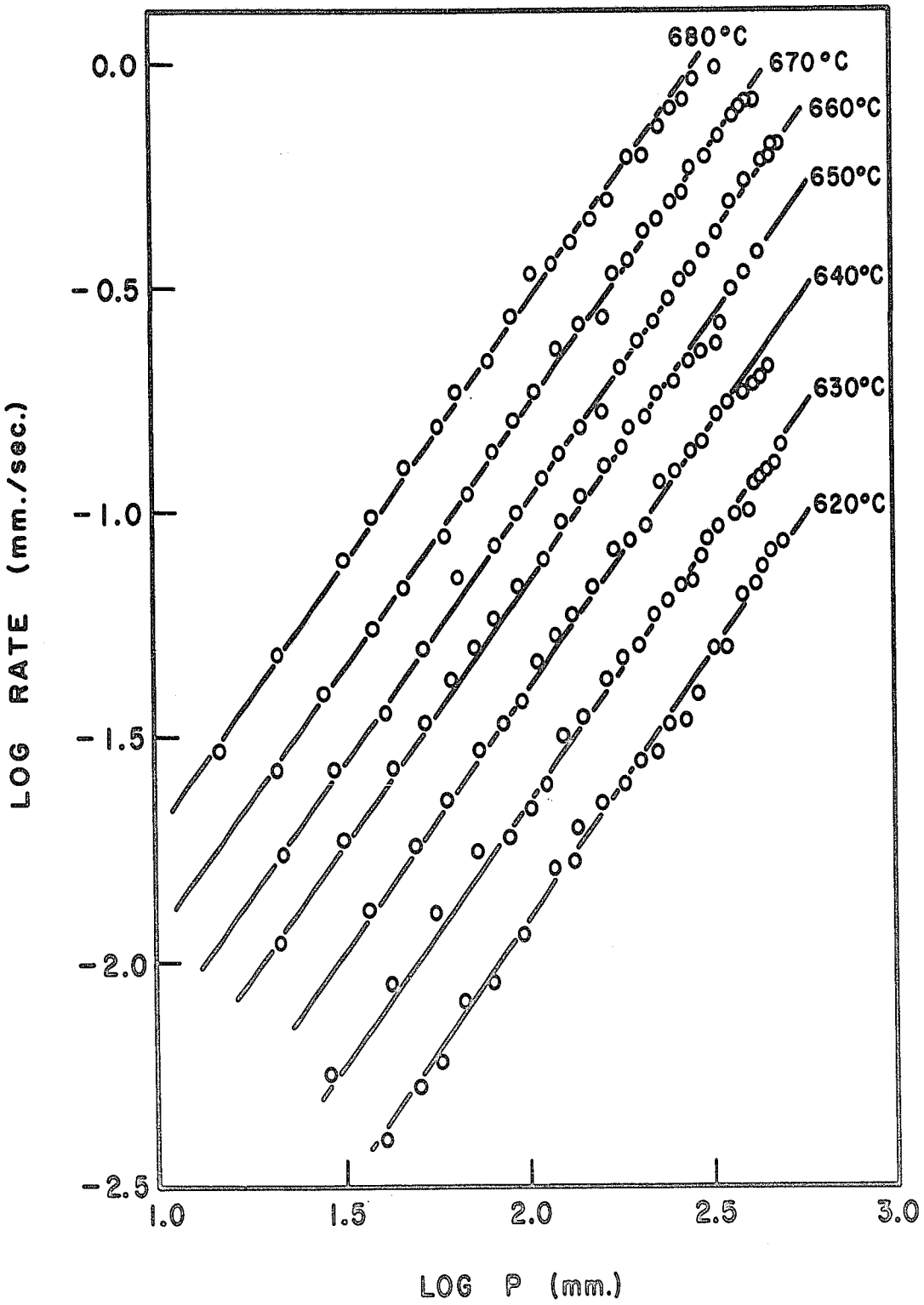


Figure 14 Plots of the logarithm of the inflection-point rates against initial pressure, for the packed vessel.

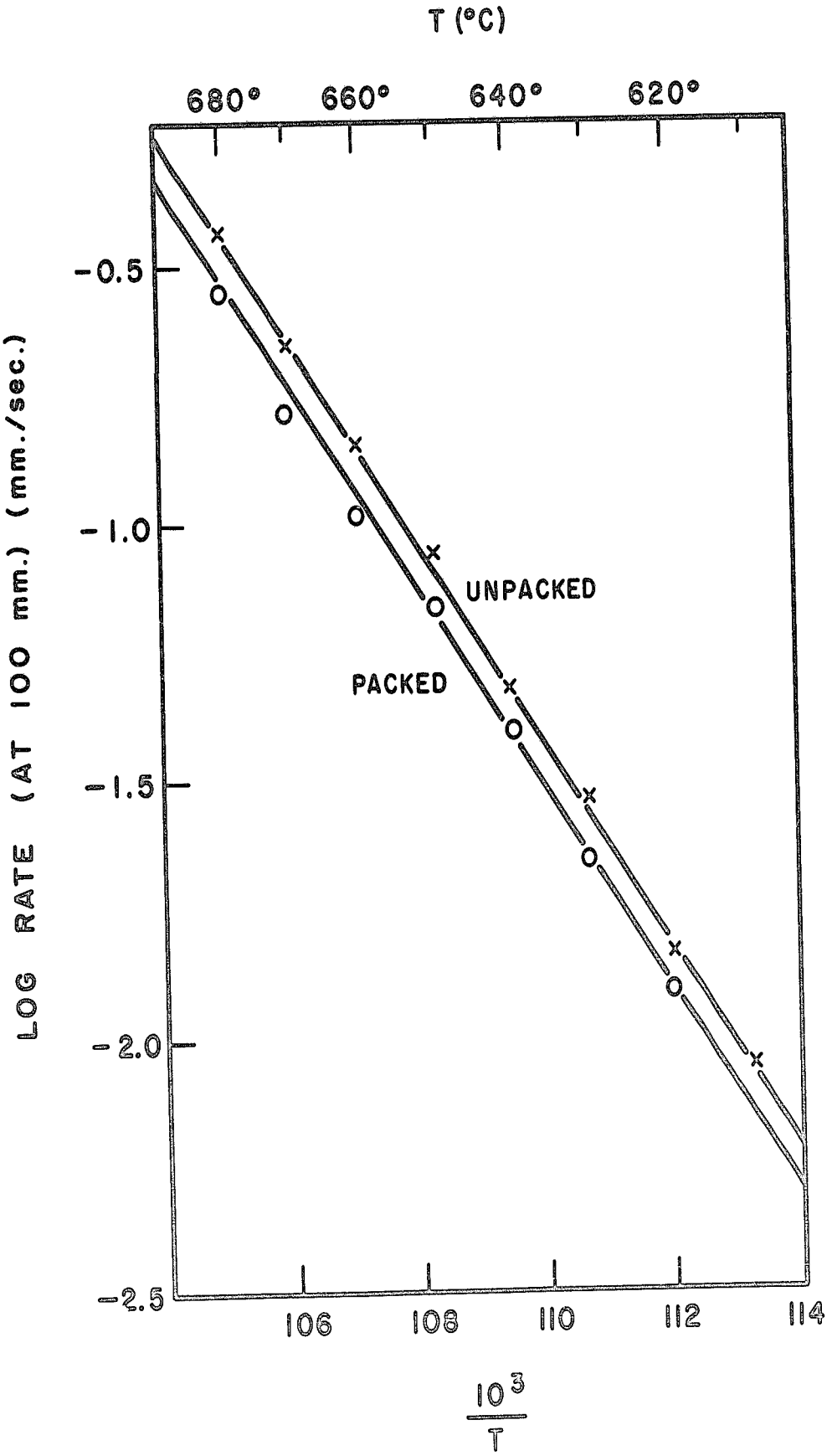


Figure 15 Arrhenius plots for inflection point rates, for the unpacked and packed vessels.

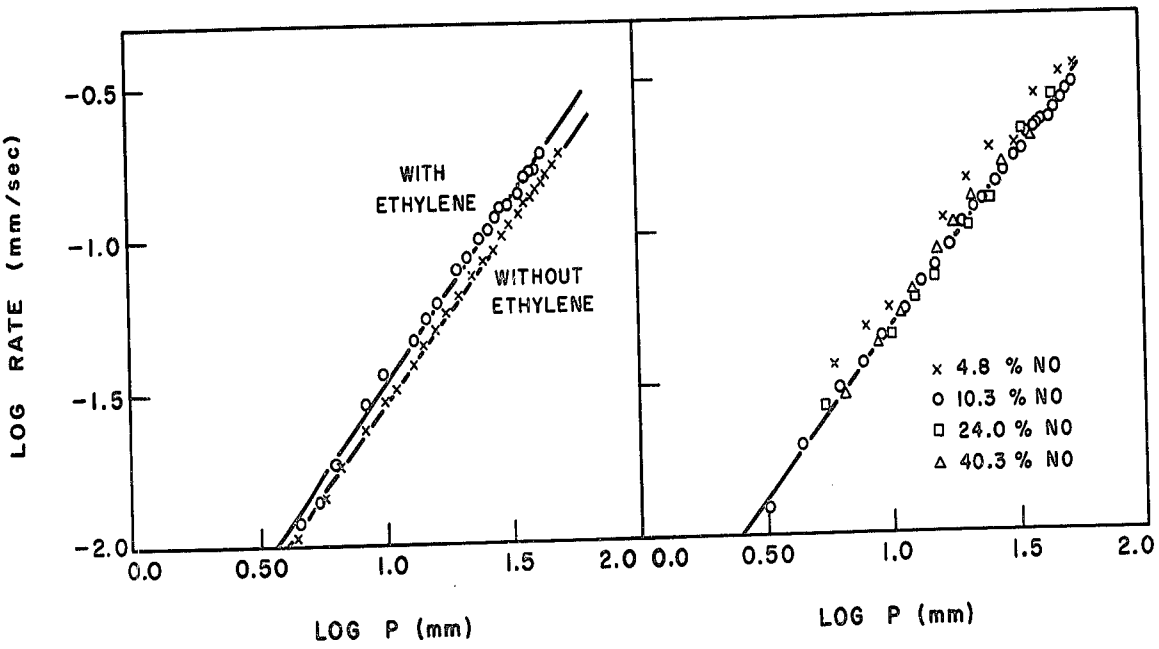


Figure 16 Plots of logarithm of inflection-point rate against logarithm of pressure, for the unpacked vessel. The plots on the left are for 630° C and for 10% nitric oxide, with or without 10% ethylene; those on the right are for 640° C and for various amounts of nitric oxide (no ethylene).

and high temperatures.

The difference in the rate and order of the inhibited reaction as compared with the uninhibited reaction at the same temperature can be seen in Fig. 17, where the two are shown at 630°C. From such comparison the "chain length" can be calculated, and in this case it varied from 3.83 at 500 mm to 5.25 at 50 mm, in good agreement with the values reported by Steacie and Shane.

In order to learn more about the nature of the processes occurring during the induction period, a series of experiments was carried out with 10% ethylene and 10% nitric oxide. The time course of the reaction is shown in Fig. 18. It can be seen that the induction period is no longer in evidence. A comparison of the rates of the inhibited reaction with and without ethylene at 640°C is shown in Fig. 16. The order is slightly higher with added ethylene and the rate is increased by about 10%. Thus ethylene appears to have no inhibitory effect when present without hydrogen.

Finally a comparison is made in Fig. 19 of the inflection point rates in the packed and unpacked vessels. From this it can be seen that increase in surface has a much smaller effect on the inhibited reaction than on the uninhibited, as shown in Fig. 5.

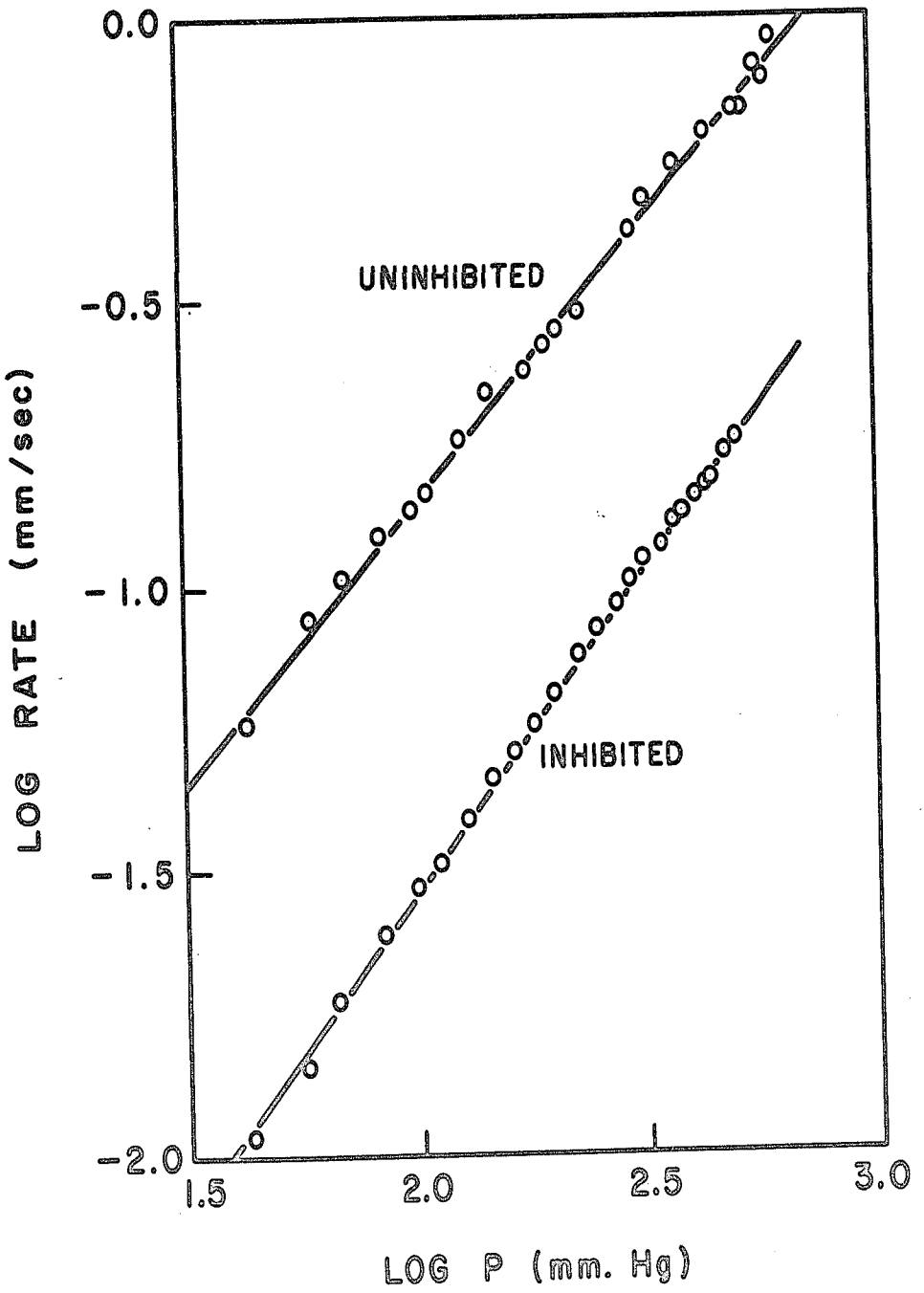


Figure 17 Plots of logarithm of inflection-point rate against logarithm of pressure for the uninhibited and fully inhibited (10% NO) reaction at 630° C.

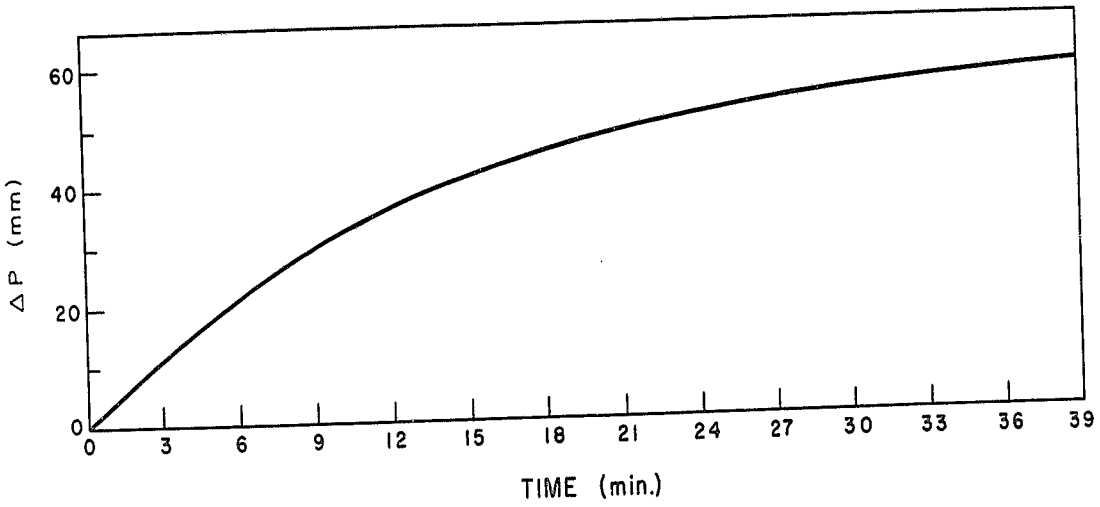


Figure 18 Pressure time curve for the reaction in the presence of both nitric oxide and ethylene, showing that the curve is no longer S-shaped (compare Figure 10). Temperature = 640° C; total pressure 176 mm; 10% nitric oxide and 10% ethylene.

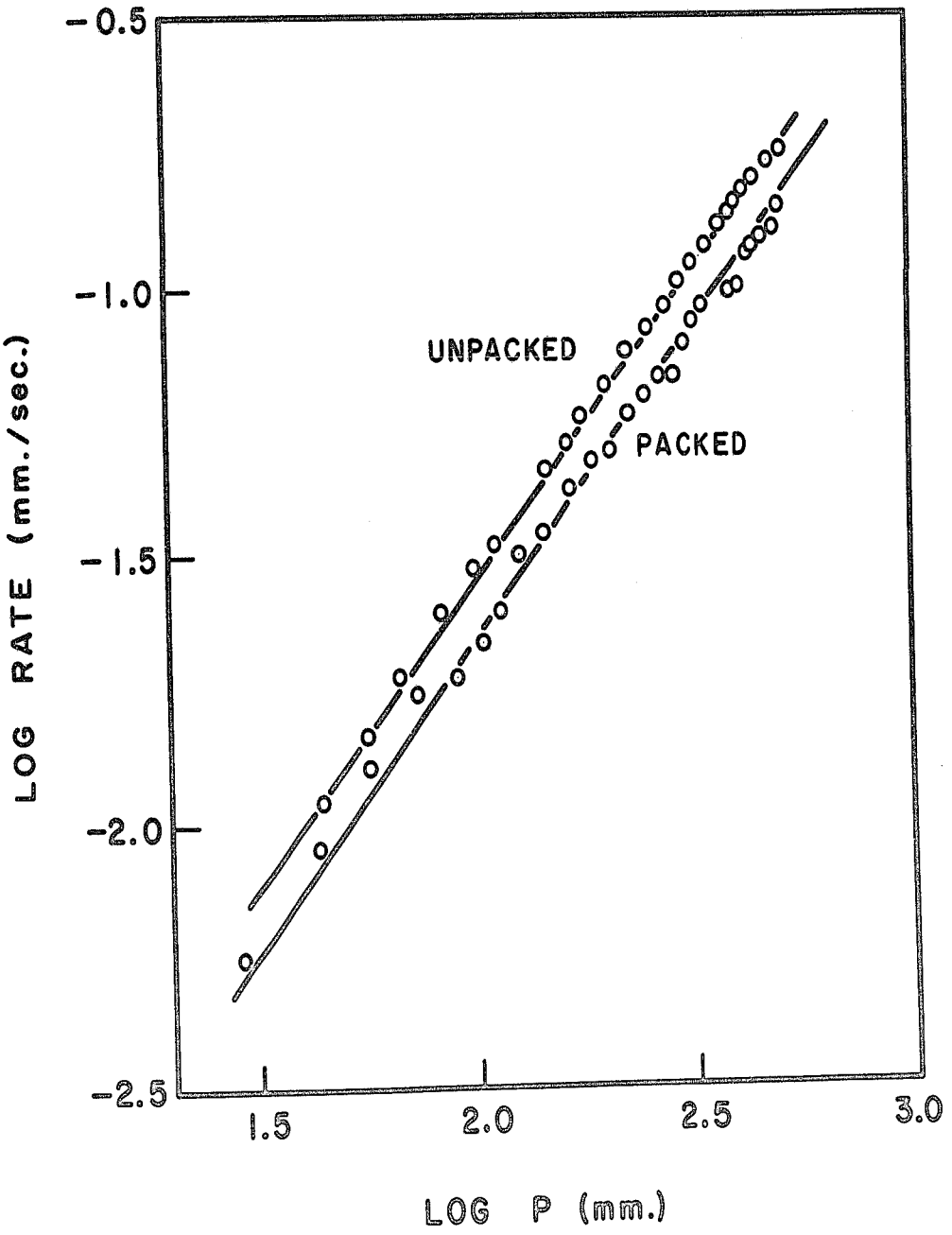


Figure 19 Plots of the logarithm of inflection-point rate against the logarithm of pressure for the packed and unpacked vessels. Temperature 640° C.

Order of the Inhibited Reaction

T° C	Order in Unpacked Vessel	Order in Packed Vessel
610	1.21	1.16
620	1.26	1.16
630	1.14	1.16
640	1.12	1.16
650	1.14	1.16
660	1.10	1.16
670	1.07	1.16
680	1.10	1.16

DISCUSSION

Discussion of Previous Work

As noted in the section on results, two distinct rates can be obtained from a single run; the initial and the inflection point rates. This may well explain the wide divergence in "chain lengths" reported by various investigators. It seems that Staveley (33), who reported the greatest change in "chain length" from high to low pressure, was measuring initial rates, while some other workers measured something approaching inflection point rates. These different approaches have also resulted in a difference in activation energy, with some workers reporting a value around 74 kcal $mole^{-1}$ and others

closer to 77 kcal $mole^{-1}$.

There has also been much discussion about the explanations put forward for the nature of the inhibited reaction. We shall discuss these in some detail below.

a) The Molecular Hypothesis

A number of workers in the field have maintained that the reaction is the unimolecular split

12a. $M \rightarrow M_1 + M_2$.

The arguments which they have put forward in support of their hypothesis have been summarized by Stubbs and Hinshelwood (37). They suggest first that the results obtained by Steacie and Polkins (38), showing that the products of inhibited and uninhibited butane decomposition are very similar, stand in no way in contradiction to the molecular hypothesis, since if chain lengths are sufficiently long the products of both reactions will be the same. This seems rather doutful, in view of the fact that methane should not be observed in the products of the inhibited ethane decomposition as reported by Steacie and Shane (19) if the reaction is unimolecular.

Secondly they consider the induction periods observed to be an "inherent property of the reaction", and suggest that the acceleration is due to secondary decomposition of products. It is hard to imagine why such secondary decompositions would accelerate the inhibited reaction but not the uninhibited

reaction. Also, in the uninhibited reaction, the olefins formed in situ (i.e. the combination of olefin and hydrogen) cause inhibition.

The question of surface effects on the inhibited decomposition is still not clear. However, there is general agreement that there is some decrease of rate with increase of surface-to-volume ratio. Stubbs and Hinshelwood consider this effect secondary. They suggest that in the early stages of a reaction "nitric oxide may catalyze a quite independent condensation reaction" which is also catalyzed by the surface. They do not specify the type of reaction envisioned.

Finally they discuss the question of alternative chain mechanisms and conclude that only a hydrogen propagated chain is likely to be immune to nitric oxide inhibition. This is eliminated as a possibility since addition of hydrogen is known to accelerate the uninhibited reaction, but has no effect on the inhibited reaction. The assumption involved is that an increase in hydrogen atom concentration causes the acceleration. This is not necessarily so. Any additional hydrogen atoms produced in the reacting mixture appear only at the expense of some other radical, and thus contribute nothing to the over-all rate. In addition, if we accept the Küchler and Theilo mechanism we can readily interpret the acceleration of the uninhibited reaction in terms of the pressure effect on the second-order initiation. The fact

this is not observed in the inhibited reaction serves only to strengthen the argument which follows.

It is also worth noting at this point that radicals have been detected in the inhibited decomposition by Eltenton (14) using a mass spectrometer. He reports that no appreciable decrease in the concentration of methyl radicals was observed when nitric oxide was present, compared to the concentration found in the uninhibited reaction. Moreover, work on isotopic mixing (42, 43) has since made it clear that there are radicals present in the inhibited decomposition, and that the rate of reaction is governed by the same radicals in both the inhibited and uninhibited reactions, since the rate of isotopic mixing is a function only of the rate of reaction. The well defined induction period is also taken as an indication of non-steady-state conditions which could not arise in a unimolecular reaction. It is also clear that increase in surface: volume ratio decreases the rate of the inhibited reaction, an effect which was allowed for in the unimolecular hypothesis by a "surface condensation" and is now suggested to be a radical recombination.

In view of the above evidence for a free radical mechanism, and the lack of firm support for a molecular reaction, we are proposing the following free radical mechanism for the inhibited reaction.

Mechanism of the Inhibited Reaction

The suggested mechanism for the inhibited reaction is

13. $C_2H_6 + NO \rightarrow C_2H_5 + HNO$

3'. $C_2H_5 \rightarrow H + C_2H_4$

4'. $H + C_2H_6 \rightarrow C_2H_5 + H_2$

14. $H + NO \rightarrow HNO$

15. $HNO \rightarrow H + NO$

16. $C_2H_5 + HNO \rightarrow C_2H_6 + NO$

This scheme, by the conventional steady-state treatment, yields the radical concentrations:

$$[C_2H_5] = \left(\frac{k_{13}k_4k_{15}}{k_3k_{14}k_{16}}\right)^{1/2} [C_2H_6] \qquad [28]$$

$$[H] = \left(\frac{k_{13}k_3k_{15}}{k_4k_{14}k_{16}}\right)^{1/2} \qquad [29]$$

$$[HNO] = \left(\frac{k_{13}k_3k_{14}}{k_4k_{15}k_{16}}\right)^{1/2} [NO] \qquad [30]$$

and the rate is given by

$$v_1 = k_3[C_2H_5] \qquad [6']$$

$$= \left(\frac{k_{13}k_3k_4k_{15}}{k_{14}k_{16}}\right)^{1/2} [C_2H_6] \qquad [31]$$

It can therefore be seen that, in agreement with experimental results, a first-order reaction is predicted. The observed order of inflection-point rates is found to be 1.15, but this is attributed to the increased length of the induction periods at low pressures. This tends to remove the point of inflection further from initial conditions, and thus gives a lower rate than that which would be observed if the induction period was not present.

Rate of Initiating Reaction

In view of the bond strengths quoted by Szwarc (45) for ClNO (37 kcal mole^{-1}) and BrNO (28 kcal mole^{-1}) we have selected 48 kcal mole^{-1} as the bond strength in HNO. Taking into consideration the bond strength of C_2H_5-H, given as 100 kcal mole^{-1} (45), we arrive at the activation energy for reaction 13. This is taken to be 52 kcal mole^{-1}. The frequency factor is taken as 10^{14} in view of the simplicity of the reactants. The ratio of the rate of the initiating step in the inhibited reaction to that in the uninhibited reaction is therefore:

$$\frac{v_{1a}}{v_{13}} = \frac{k_{1a}[C_2H_6]^2}{k_{13}[C_2H_6][NO]} \qquad [32]$$

$$= \frac{k_{1a}[C_2H_6]}{k_{13}[NO]}$$

since

$$\frac{[C_2H_6]}{[NO]} = 10$$

we have

$$\frac{v_{1a}}{v_{13}} = \frac{10\, k_{1a}}{k_{13}} \qquad [33]$$

Using the values in tables 3 and 6, at 609°C this ratio is 10^{-1}. It is thus seen that reaction 13 is capable of initiating chains.

The assumption that nitric oxide abstracts hydrogen at high temperatures is not new and has been put forward by Rice and Polly (38). Nitric oxide is basically a stable free radical at room temperature and at high temperatures its free radical character will be even stronger. It is therefore not unreasonable to suppose that it will be capable of undergoing free radical reactions.

The Presence of HNO

In 1933 Harteck (46) claimed to have isolated HNO at low temperatures and more recently Dalby (47) analyzed its spectrum, proving conclusively its existence. The reason why it has not been observed in analytical work on inhibited reactionsis its low concentration and its instability. The concentration under steady state conditions can be calculated as follows. In the previous section the activation energy of reaction 15 is taken as 48 kcal $mole^{-1}$, and the frequency

factor is now taken as $\sim 10^{13}$.

The reverse reaction (reaction 14) forming HNO is taken as a typical radical recombination with zero activation energy and a frequency factor that is probably lower than usual, about 1.0×10^{12}. The concentration of HNO is then 10^{-3} [NO] at 609°C. At this low concentration HNO is probably quite stable and thus able to fulfill its role in the free radical mechanism.

Chain Termination

It has been noted by Echols and Pease (48) that very little nitric oxide is used up in the course of an inhibited reaction. This leads us to believe that the chain termination step does not require the removal of a nitric oxide molecule. This eliminates radical removal by such reactions as

17. $R + NO \rightarrow$ Products

However, it does not eliminate the possibility of equilibria such as

18. $R + NO \rightleftharpoons RNO$

being established. These equilibria will not affect the steady-state treatment given in the section on the Mechanism of the Inhibited Reaction, and have therefore been neglected. We are left with two choices for the terminating step:

16. $C_2H_5 + HNO \rightarrow C_2H_6 + NO$

19. $H + HNO \rightarrow H_2 + NO$

Table 6

Kinetic Parameters of Reactions Involved in the Inhibited Pyrolysis of Ethane

Reaction	A*	E	k_{609}	Ref.
13	1.0×10^{14}	52	10	estimated
3	3.0×10^{14}	39.5	3.96×10^{4}	25
4	3.4×10^{12}	6.8	6.80×10^{10}	26
14	1.0×10^{12}	0	1.6×10^{12}	assumed
15	1.0×10^{13}	48	10	estimated
16	1.0×10^{12}	0	1.6×10^{12}	assumed
19	1.0×10^{12}	0	1.6×10^{12}	assumed

* Frequency factors are in sec^{-1} or $cm^3\ mole^{-1}\ sec^{-1}$.

If we compare the rates of the above two reactions we have:

$$\frac{v_{16}}{v_{19}} = \frac{k_{16}\,[C_2H_5]}{k_{19}\,[H]} \qquad [34]$$

Substituting the steady-state concentrations,

$$\frac{v_{16}}{v_{19}} = \frac{k_1 k_{16}}{k_3 k_{19}}\,[C_2H_6]. \qquad [35]$$

Thus the change will occur where

$$[C_2H_6] = \frac{k_3 k_{19}}{k_4 k_{16}} = \frac{k_3}{k_4} \qquad [16']$$

if $k_{19} = k_{16}$.

At 609°C this gives as the transition pressure

$$[C_2H_6] \sim 30.0 \text{ mm}$$

and at 680°C

$$[C_2H_6] \sim 158.0 \text{ mm.}$$

The transition to 3/2 order kinetics is not observed for reasons explained below.

When we compare the rate of reaction 16'

16. $C_2H_5 + HNO \rightarrow C_2H_6 + NO$

to that of reaction 6:

6'. $C_2H_5 + C_2H_5 \rightarrow$ Products

we arrive at the expression

$$\frac{v_{16}}{v_6} = \frac{k_{16}[C_2H_5][HNO]}{k_6[C_2H_5]^2} = \frac{k_{16}[HNO]}{k_6[C_2H_5]} \qquad [36]$$

Substituting the radical concentrations from the inhibited mechanism we obtain

$$\frac{v_{16}}{v_6} = \frac{k_3 k_{14} k_{16}}{k_4 k_6 k_{15}} \qquad [37]$$

Substituting the values for the various constants at 609°C we obtain the rate as

$$\frac{v_{16}}{v_6} = 10^4.$$

Thus we can justify the proposed terminating step as being faster than the corresponding step in the absence of inhibitor.

The Induction Period

As shown in Fig. 11, the initial rates tend to 3/2 order at pressures below 250 mm. This is thought to be a result of non-steady-state conditions in the reaction which are favoured by low pressures and low temperatures. One possible reason for the non-steady-state is a change of termination from

19. $H + HNO \rightarrow H_2 + NO$

back to

16. $C_2H_5 + HNO \rightarrow C_2H_6 + NO$.

This may occur as follows: if k_{19} is greater than k_{16}, the transition pressure will be higher than that calculated in the first section, and may be as high as those observed. Chain termination by reaction 19 will give a 3/2 order reaction whose rate is

$$v_{I_{3/2}} = k_4 \left(\frac{k_{13}k_{15}}{k_{14}k_{19}} \right)^{1/2} [C_2H_6]^{3/2} + k_{13}[C_2H_6][NO] \qquad [36]$$

As the reaction progresses the ethylene formed will tend to sweep up hydrogen atoms and form ethyl radicals. If this occurred only by

8. $H + C_2H_4 \rightarrow C_2H_5$

we would expect no effect, since the presence of the same reaction in the uninhibited pyrolysis produces no induction period. However, the formation of ethyl radicals may also proceed by

20. $C_2H_4 + HNO \rightarrow C_2H_5NO$

which disturbs the equilibrium

21. $C_2H_5NO \rightarrow C_2H_5 + NO$

and produces ethyl radicals. With the increase in ethyl radical concentration, the terminating step would change back to reaction 16 and the reaction would proceed as first-order, but starting at non-initial conditions. This view is supported by the experiments done with ethylene. Fig. 18 shows that the induction period is eliminated by addition of ethylene. Furthermore, the rate is slightly increased due to the removal of the induction period and the achievement of initial conditions. The inhibiting effect of ethylene is quite small, as noted in Part I, and it is therefore not surprising that no further inhibition is brought about by addition of ethylene.

Time Course of the Reaction

The inclusion of reactions

8. $H + C_2H_4 \rightarrow C_2H_5$

9. $C_2H_5 + H_2 \rightarrow C_2H_6 + H$

in the inhibited scheme gives the rate as

$$v_{It} = \frac{(k_{13}k_{15}[C_2H_6])^{1/2}\ (k_3k_4[C_2H_6]-k_8k_9[H_2][C_2H_4])}{(k_{14}k_{16})^{1/2}(k_3+k_9[H_2])^{1/2}(k_4[C_2H_6]+k_8[C_2H_4])^{1/2}} \qquad [37]$$

which reduces to

$$v_I = \left(\frac{k_3k_4k_{13}k_{15}}{k_{14}k_{16}}\right)^{1/2} [C_2H_6] \qquad [31']$$

when $[C_2H_4] = [H_2] = 0$ and

$$\frac{[H_2][C_2H_4]}{[C_2H_6]} = \frac{k_3k_4}{k_8k_9} \qquad [24']$$

when $v_I = 0$.

Inhibition by Other Substances

The rate equation for the inhibited reaction has been given as

$$v_I = \left(\frac{k_3k_4k_{13}k_{15}}{k_{14}k_{16}}\right)^{1/2} [C_2H_6] \qquad [31']$$

In the over-all rate we observe the following relationship:

$$K = \frac{k_{13}}{k_{16}} \cdot \frac{k_{15}}{k_{14}} = \frac{[C_2H_5][HNO].[H][NO]}{[C_2H_6][NO]\ [HNO]}$$

$$K = \frac{[C_2H_5][H]}{[C_2H_6]} \qquad [38]$$

Thus the rate can be written as

$$v_I = (K k_3 k_4)^{1/2}\ [C_2H_6] \qquad [39]$$

and no longer includes any constants which depend on the

inhibitor concentration. Thus any inhibitor which follows the mechanism proposed will give the same limiting rate. The only difference between various inhibitors will be their efficiency in establishing the mechanism: thus the amounts of various inhibitors required for total inhibition.

Activation Energy and Rate

The activation energy for the reaction predicted on the basis of the mechanism and values in Table 6 is:

$$E = 1/2 [E_K + E_3 + E_4] \qquad [40]$$

$$= 1/2 [100 + 39.5 + 6.8]$$

$$= 73.1 \text{ kcal mole}^{-1}.$$

In view of the uncertainties in the individual activation energies, this is in satisfactory agreement with the experimental value of 77.3 kcal mole^{-1}. Moreover since induction periods are longer at lower temperatures the experimental activation energy is higher than the true value.

The predicted frequency factor is

$$A = \left(\frac{A_3 A_4 A_{13} A_{15}}{A_{14} A_{16}} \right)^{1/2} \qquad [41]$$

$$= 1.1 \times 10^{15} \text{ sec}^{-1}.$$

This is also in good agreement with the experimental value of 3.12×10^{15} sec^{-1}.

Effect of Surface

Surface effects are hard to analyze in view of the other complications in the reaction, Nevertheless it can be said that the rate is lowered by increase in the surface-to-volume ratio. The form of the ΔP vs, time curve remains the same with increase in the surface-to-volume ratio, and no increase in order of the reaction is observed. There is also no falling off of rate at low temperature as in the uninhibited reaction. This is due to the fact that the lowest temperature investigated is still above the level at which the falling off was observed.

The reaction is generally less sensitive to increase in surfade-to-volume ratio than the corresponding uninhibited decomposition. This may be understood if we consider that the terminating step in the inhibited reaction is faster than in the uninhibited and thus the extra termination on the surface will have a smaller effect.

It is interesting to compare the above suggestions with those of Voevodsky who interprets the fully inhibited decomposition of hydrocarbons in terms of the idea that initiation and termination both take place on the surface of the vessel. It is proposed by Voevodsky that initiation reactions are caused by irreversible and reversible surface processes of which the former can be suppressed by the inhibitor. Full inhibition corresponds to complete coverage

of the wall. Voevodsky proposes no specific mechanisms and his suggestion is subject to one serious difficulty: the amount of nitric oxide required to give complete inhibition should depend on the surface-to-volume ratio and this is certainly not the case. Also, the sinusoidality of the pressure-time curves, implying abnormally low initial rates, seems inconsistent with Voevodsky's suggestion.

CONCLUSIONS

Although an attempt has been made to assign various rate constants and activation energies to the postulated reactions the calculations should be treated with reserve. The important point is the qualitative interpretation of the observed phenomena. It is worthwhile to mention the major points again:

First, the reaction is held to be of a free radical chain type, and a possible mechanism is postulated.

Second, the induction period is explained in terms of non-steady-state conditions and experimental support is given for our postulates.

Third, it is shown that all inhibitors which obey the postulated mechanism will yield the same limiting rate of the inhibited reaction.

Part III

THE DECOMPOSITION OF PROPYLENE

INTRODUCTION

Investigations of the decomposition of propylene in the temperature range from 550°C to 700°C have, in the past, been concerned mainly with the identification of products. Thus Hurd and Meinert (51) and later Ingold and Stubbs (52) analyzed the products of the decomposition and found that methane, ethylene and hydrogen, in the approximate ratio of 2:2:1, were the major products. A number of minor products, up to C_{12}, including a number of aromatics, were also reported, but no allene was found. Szwarc (53), working in a flow system at lower pressures ($\sim$10 mm.) and higher temperatures ($\sim$800°C) found that allene was then a major product, and proposed a free radical mechanism which accounted for the products and the observed kinetics.

The presence of free radicals, including allyl radicals, was reported by Elteuton (14), who decomposed propylene and analyzed the decomposing mixture in a mass spectrometer. Ingold and Stubbs, however, did not consider that free radicals played any part under their experimental conditions,

and proposed a series of molecular reactions to account for the observed results. They found the order of the reaction to be between unity and 2, which is consistent with the results of the present investigation according to which the order is 3/2 over a considerable range of temperature and pressure.

In view of the importance of the mode of action of propylene in systems inhibited by propylene, we have reinvestigated the kinetics of reaction with the object of arriving at a mechanism.

EXPERIMENTAL

Results

Preliminary investigations were carried out to determine whether measurements of pressure changes gave a reliable indication of the extent of reaction, and to find the precise relationship between pressure change and extent of reaction. Figure 20 summarizes the results of these experiments, done using gas chromatography, and shows that over the entire temperature range the amount of propylene that had reacted varied linearly with the pressure increase, within the experimental error. This conclusion agrees with that of Ingold and Stubbs (52) under the same conditions. A ten per cent pressure increase is seen to correspond to a consumption of about 32 per cent of the initial propylene.

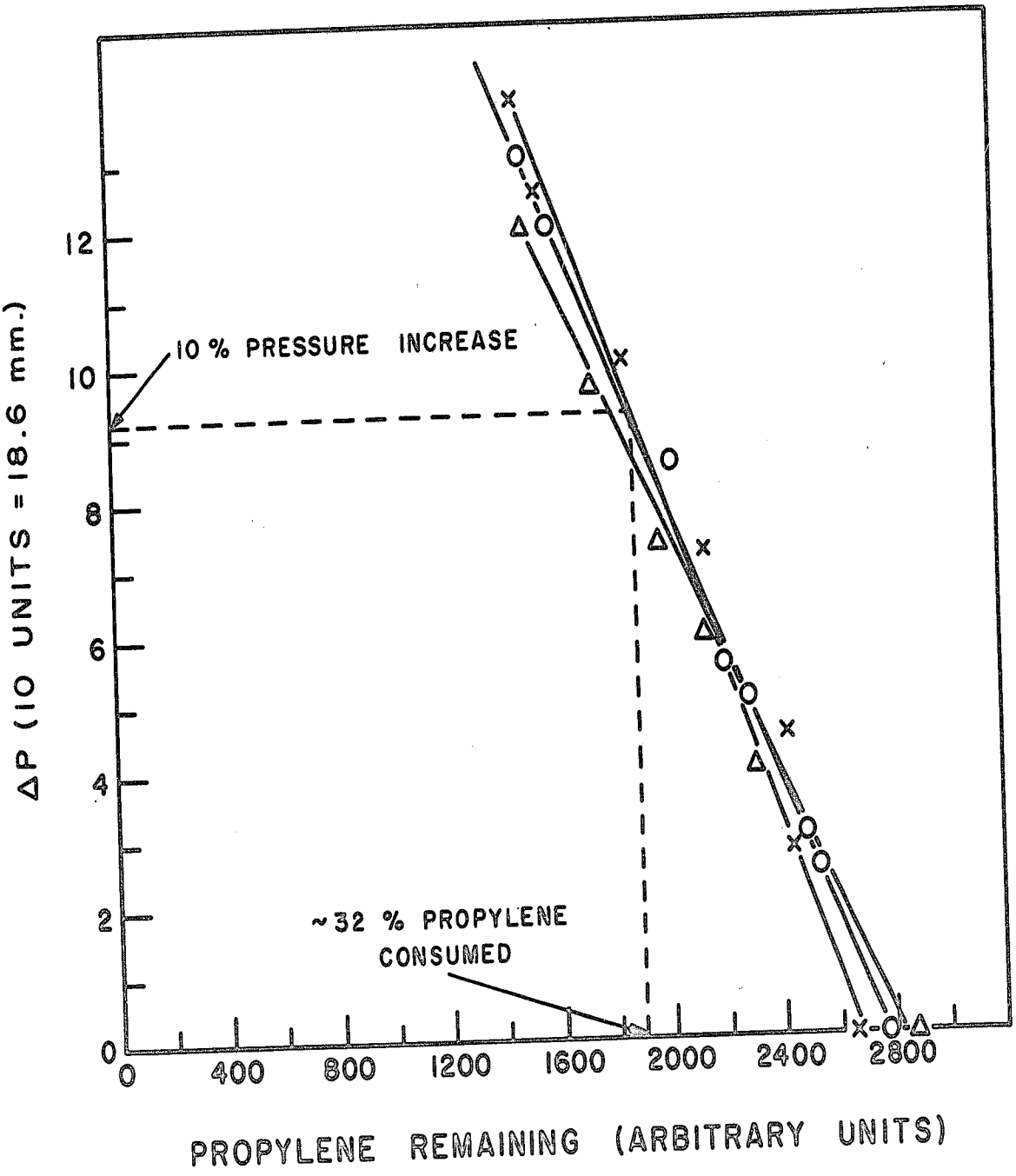


Figure 20 Plot of pressure increase against amount of propylene remaining. The triangles (Δ) correspond to 580°C, the circles (O) to 600°C and the crosses (X) to 640°C.

Product analyses were carried out under various conditions, and table 7 shows the results, which are typical, obtained for a run at 620°C with an initial pressure of 170 mm.; the degree of decomposition was about 10 per cent. The main products ethylene, methane and hydrogen are seen to be very roughly in the ratio 2:2:1, as reported by other workers (Hurd and Meinert, Ingold and Stubbs). The butenes found were partly cis-2-butene and partly trans-2-butenes, with the latter somewhat in excess. The presence of benzene and toluene is of some interest. No allene could be detected using either mass spectroscopy or gas chromatography; this is in agreement with the results of Hurd and Meinert and of Ingold and Stubbs whose conditions were similar to ours.

The kinetics of the reaction were studied using the pressure gauge (fig. 2) at 580°, 600°, 620° and 640°. The form of the curves obtained is shown on Fig. 21. Rates were calculated from the slopes at the inflection point, since before this the steady state has presumably not been established. Fig. 22 shows plots of the logarithm of the rate against the logarithm of the pressure, and the order is found to be 3/2. An Arrhenius plot is shown in Fig. 23, and from it the activation energy was calculated to be 56.7 kcal $mole^{-1}$. The rate constant can be expressed by

$$k = 2.2 \times 10^{13} e^{-56700/RT} \; ml^{1/2} \; mole^{-1/2} \; s^{-1}.$$

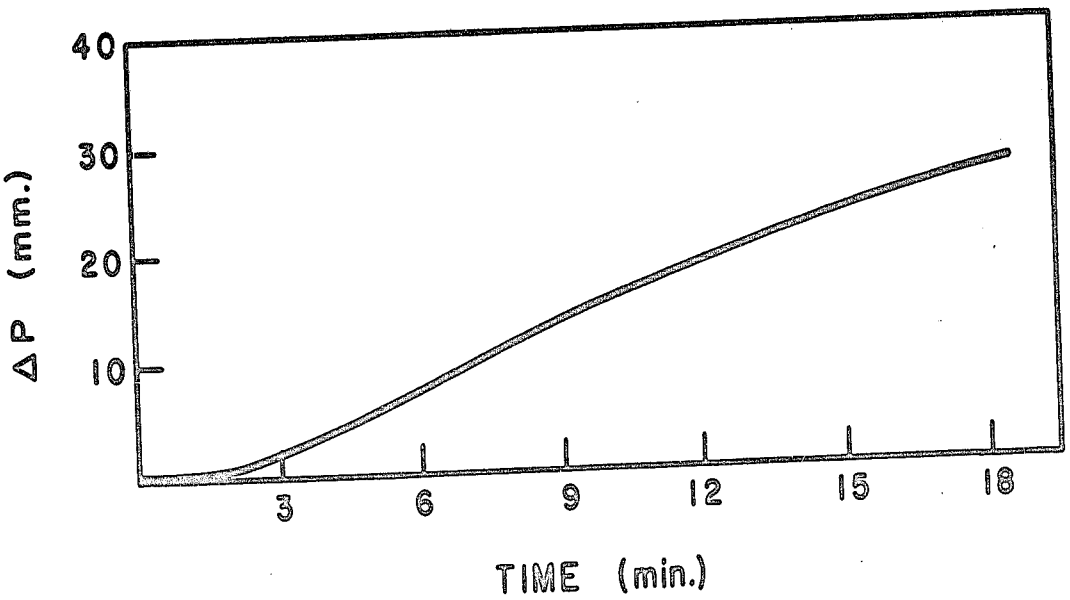


Figure 21 The time course of a reaction at 580°C and 200 mm. initial pressure.

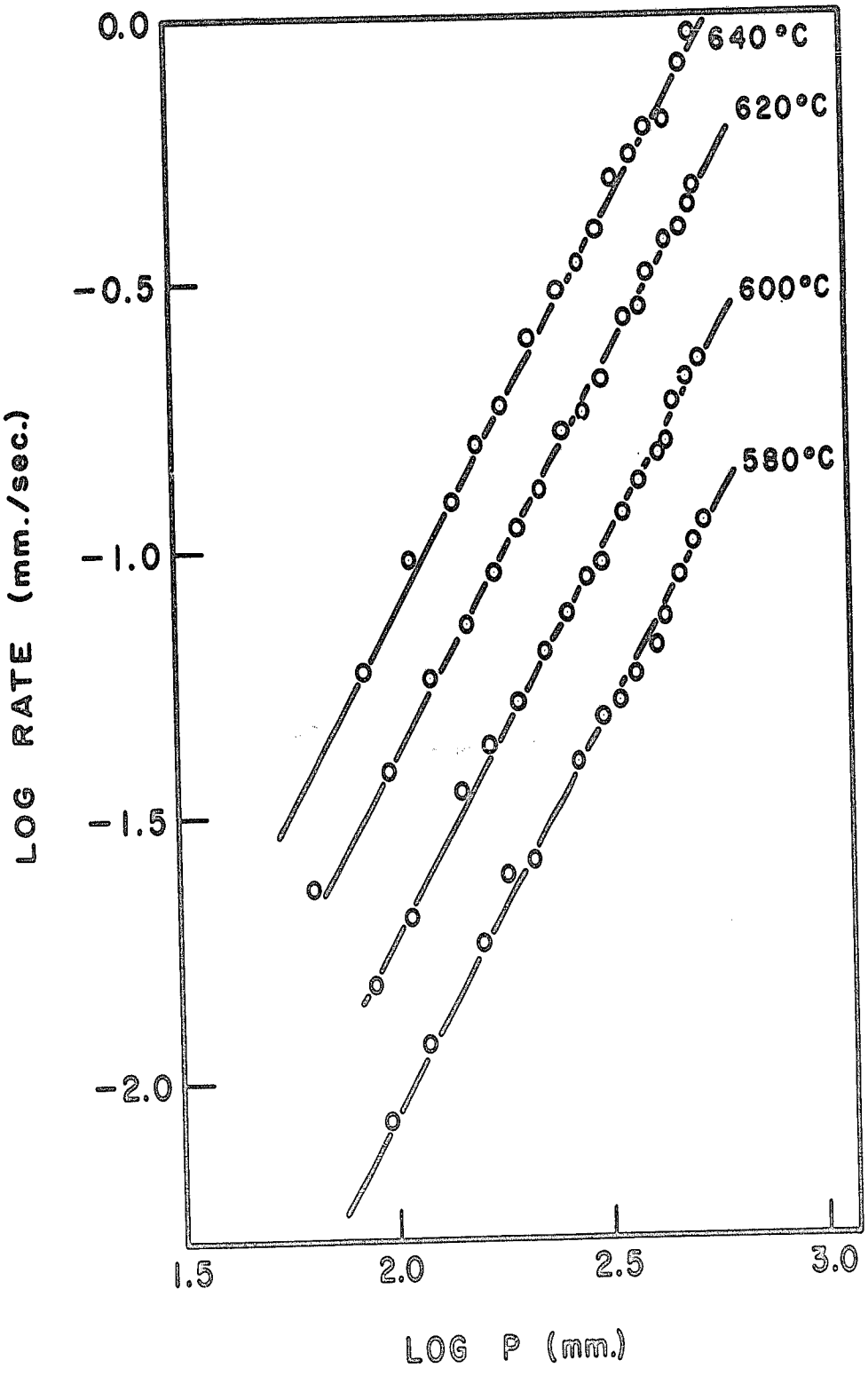


Figure 22 Plots of logarithm of rate against logarithm of pressure for the propylene decomposition. The order is 3/2 at all temperatures.

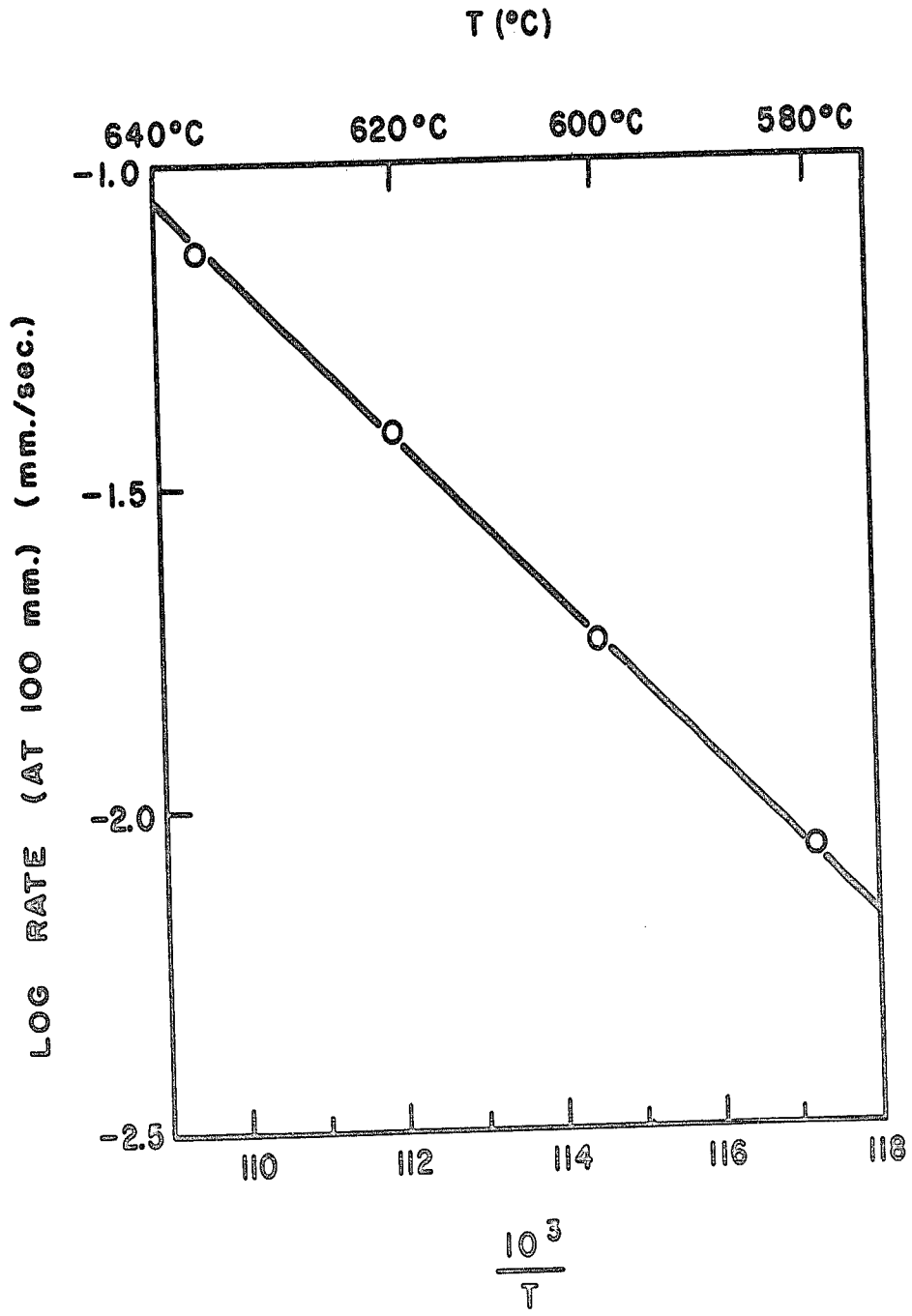


Figure 23 Plot of logarithm of rate at 100 mm. against 1/T. From this an activation energy of 56.7 kcal. was obtained.

Table 7

Relative Amounts of Products obtained in the Pyrolysis of Propylene

Compound	Amount (arbitary units)	Amount relative to hydrogen
Ethylene	32.4	2.02
Methane	25.2	1.57
Hydrogen	16.0	1.00
Propane	6.4	
Butenes	6.4	
Ethane	4.0	
Benzene	3.2	
Cyclohexadiene	2.0	1.65
Cyclopentadiene	2.0	
Toluene	1.2	
Diallyl	1.2	

Some studies were made of the decomposition of propylene in the presence of CD_4, which by itself undergoes no appreciable decomposition in this temperature range. The amounts of CD_3H were measured in the mass spectrometer, and figure 24 shows the percentage of CD_3H produced at various times; the experimental error in the mass-spectrometric determinations is quite large under these conditions, but the results clearly show a steady rise in the amount of CD_3H. In addition, a mass-spectrometric analysis was made of the amount of mono-deuterated propylene, $CH_2D\ CH{=}CH_2$, at various times. The experimental difficulties are now greater and quantitative determinations could not be made. The results did, however, indicate a significant production of this species over the period of the experiment.

A kinetic study of the decomposition of ethane fully inhibited by propylene was also made. The order of the reaction was unity, as shown by the plot in figure 25.

DISCUSSION

Mechanism of Decomposition

In order to explain the three-halves order kinetics it follows from the rules of Goldfinger, Niclause and Letort (54) that one must postulate a chain-ending step involving two p-radicals (i.e., radicals that undergo bimolecular reactions). Hydrogen atoms fall in this category, and our proposal is that

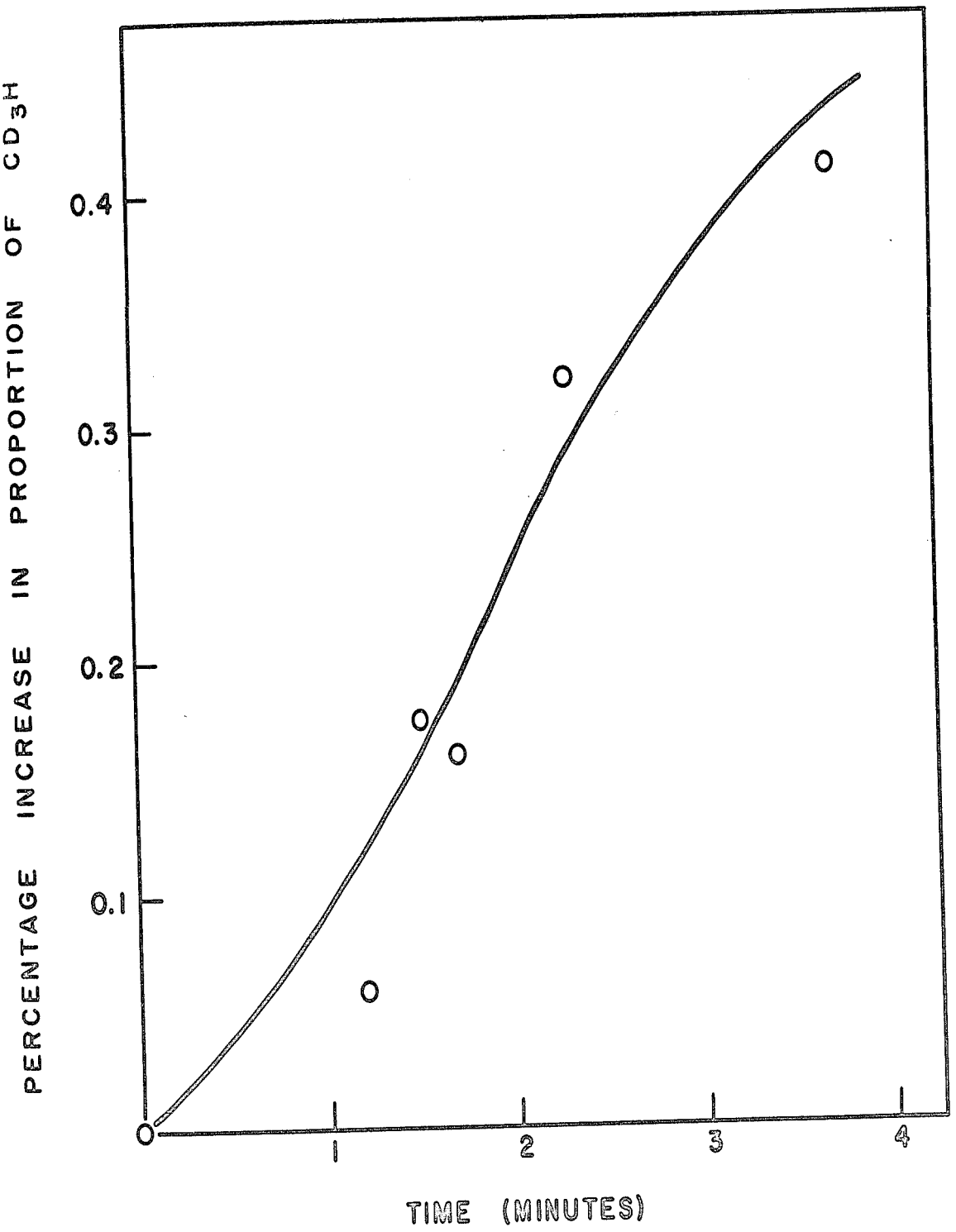


Figure 24 Percentage of CD_3H produced at various times when C_3H_6 decomposes in the presence of CD_4. Temperature = 620°C.

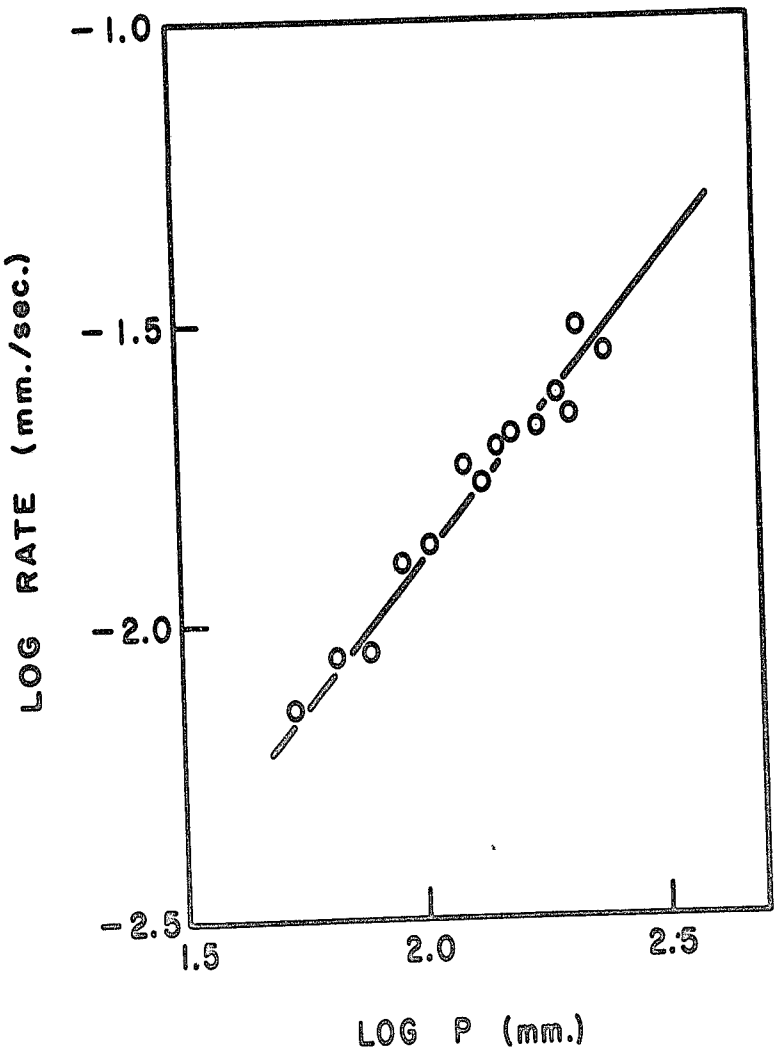


Figure 25 Plot of logarithm of rate against logarithm of initial pressure for the propylene inhibited ethane decomposition at 600°C. The order is unity.

under the conditions of our experiments the allyl radical $\cdot CH_2CH=CH_2$ also acts as a β-radical. That this is so is suggested by the absence of allene, $CH_2=C=CH_2$ which is the most likely product if the allyl radical were to act as a β-radical. At higher temperatures, as employed by Szwarc, allene is found so that allyl is then a μ-radical and the order of the reaction is indeed unity as predicted for βμ recombination. The reason for the transition is discussed later.

The mechanism proposed for the reaction under our conditions, at lower temperatures, is

22. $CH_3CH = CH_2 \rightarrow \cdot CH_2CH = CH_2 + H$

23. $H + CH_3CH = CH_2 \rightarrow CH_3CH_2CH_2\cdot$

24. $CH_3CH_2CH_2\cdot \rightarrow H_2 + C_3H_5$

25. $CH_3CH_2CH_2\cdot \rightarrow C_2H_4 + CH_3$

26. $CH_3 + CH_3CH = CH_2 \rightarrow CH_4 + \cdot CH_2CH = CH_2$

27. $CH_2CH = CH_2 + CH_3CH = CH_2 \rightarrow$ higher products + H

28. $H + \cdot CH_2CH = CH_2 \rightarrow CH_3CHCH_2$

The known and estimated rate constants, activation energies and frequency factors for these and other relevant reactions are shown in table 8.

Table 8

Kinetic Parameters for Elementary Reactions in the Pyrolysis of Propylene

Reaction	Frequency Factor (s^{-1} or ml $mole^{-1}s^{-1}$)	Activation Energy (kcal $mole^{-1}$)	k at 600°C (s^{-1} or ml $mole^{-1}s^{-1}$)	Source
22	1.0×10^{13}	78	3.16×10^{-7}	45
23	1.0×10^{13}	2.5	2.5×10^{12}	60
24	1.0×10^{13}	38	3.16×10^{3}	61
25	6.0×10^{8}	20	6.0×10^{3}	61
26	1.0×10^{10}	7.7	1.2×10^{8}	assumed
27	1.0×10^{9}	15	2.0×10^{4}	assumed
29	1.0×10^{13}	70	3.16×10^{-5}	assumed
28	1.0×10^{11}	0	1.0×10^{11}	assumed
30	1.0×10^{10}	0	1.0×10^{10}	assumed
31	1.0×10^{10}	30	3.16×10^{2}	assumed
32	1.0×10^{12}	44	10	assumed
13	1.0×10^{13}	56	10^{-1}	assumed
4	3.0×10^{14}	39.5	3.96×10^{4}	61
5	3.4×10^{12}	6.8	6.80×10^{10}	26
33	1.0×10^{12}	7	1.80×10^{10}	62

This scheme yields the following steady-state radical concentrations:

$$[H] = \left(\frac{k_{22}k_{27}}{k_{23}k_{28}}\right)^{1/2} [CH_3H_6]^{1/2} \qquad [42]$$

$$[CH_3] = \frac{1}{k_{24} + k_{25}} \left(\frac{k_{22}k_{23}k_{27}}{k_{28}}\right)^{1/2} [C_3H_6]^{1/2} \qquad [43]$$

$$[C_3H_5] = \left(\frac{k_{22}k_{23}}{k_{27}k_{28}}\right)^{1/2} [C_3H_6]^{1/2} \qquad [44]$$

$$[C_3H_7] = \frac{1}{k_{24} + k_{25}} \left(\frac{k_{22}k_{23}k_{27}}{k_{28}}\right)^{1/2} [C_3H_6]^{3/2} \qquad [45]$$

The rate of disappearance of propylene is given by:

$$v = \frac{2k_{24} + 2k_{25} + k_{26}}{k_{24} + k_{25}} \left(\frac{k_{22}k_{23}k_{27}}{k_{28}}\right)^{1/2} [C_3H_6]^{3/2} \qquad [46]$$

The correct three-halves order of the reaction is thus predicted.

If instead of reacting according to reaction 6 the allyl radicals split off hydrogen atoms,

29. $$^{\circ}CH_2CH = CH_2 \longrightarrow CH_2 = C = CH_2 + H$$

the rate equation predicts a first-order reaction with the production of allene. Reactions 27 and 29 will be in competition with one another. Our estimate of the activation energy of reaction 27 is 15 kcal mole^{-1}. The frequency factor will be

small, probably about 10^9 by analogy with similar reactions. Reaction 29, in contrast, will most likely have a normal frequency factor of 10^{13}, but the activation energy will be high; the reaction is endothermic by 68 kcal., and our estimate of its activation energy is 70 kcal mole^{-1}. The ratio of rates of reactions 27 and 29 at 630°C and at a propylene concentration of 10^{-6} moles ml^{-1} ($\sim$100 mm.) is found to be

$$\frac{v_{27}}{v_{29}} = \frac{k_{27}}{k_{29}} [C_3H_6] = 2.5 \times 10^3 \qquad [47]$$

so that reaction 27 is predominant. Szwarc, on the other hand, worked at higher temperatures and lower pressures, and at 850°C and 10 mm pressure, which are within the range of his work, the ratio of rates is found to be 5×10^{-1}. The values therefore explain satisfactorily why allene is absent in Ingold and Stubbs's and our experiments, but is an important product in Szwarc's.

Benzene, cyclohexadiene and cyclopentadiene are probably produced by reaction 27. The presence of cyclohexadiene in the products is significant since it is a necessary intermediate in the formation of benzene by the addition of an allyl radical to propylene.

Propane and ethane are probably secondary products due to addition of hydrogen to the corresponding olefins.

Cis- and trans-butene, of which the latter (which is slightly more stable) is predominant, are probably produced by addition of a methyl radical to propylene, followed by hydrogen elimination. Toluene may be produced in a similar manner from benzene or by addition of allyl to butene followed by hydrogen elimination.

The presence of traces of diallyl is attributed to the initial predominance of chain termination by

30. $$2C_3H_5 \longrightarrow C_6H_{10}$$

rather than by

28. $$H + C_3H_5 \longrightarrow C_3H_6$$

as suggested in the mechanism. Initially, reaction 30 no doubt predominates and thus precludes the continuation of chains and produces the observed induction periods.

Rates of Production of Products

According to the mechanism, whenever an ethylene molecule is produced a methyl radical is formed (reaction 25), and this may give rise to a methane molecule by reaction 26; the rates of formation of ethylene and methane should therefore be equal. This is roughly consistent with the analytical data (table 7). The fact that less methane than ethylene is actually produced is ascribed to other reactions of the methyl radical, such as the production of butenes by reaction with propylene; the sum of the amounts of methane the butenes and toluene is

indeed close to the amount of ethylene.

The rate of formation of ethylene is about twice that of hydrogen, from which it follows that k_{25}/k_{24} is equal to 2. This ratio of products does not vary much with temperature, and it may be that the C_3H_7 is a hot radical which splits into products without requiring any activation by collisions.

Rate of Termination

Three modes of termination are possible; reaction 28 and 30, and reaction

31. $$C_3H_5 + C_3H_5 \rightarrow C_3H_4 + C_3H_6$$

The ratio of the rates of reaction 28 and 30 is

$$\frac{v_{28}}{v_{30}} = \frac{k_{28}[H]}{k_{30}[C_3H_5]} \qquad [48]$$

Substitution of the appropriate radical concentrations gives

$$\frac{v_{28}}{v_{30}} = \frac{k_{27}k_{28}}{k_{23}k_{30}} \qquad [49]$$

Use of the values in table 8 gives rise to

$$\frac{v_{28}}{v_{30}} = 10^{-6}$$

Thus reaction 30 predominates initially but soon ceases to be an important termination step due to establishment of an equilibrium with diallyl. The observed induction periods are

attributed to the initial predominance of reaction 30.

Reaction 31 on a similar basis is 100 times slower than reaction 28.

Kinetic Parameters

If C_3H_7 is taken to be a hot radical, the activation energies of reactions 24 and 25 are negligible. The over-all activation energy of the reaction is:

$$E = E_{26} + 1/2 (E_{22} + E_{23} + E_{27} - E_{28})$$

$$= 55.5 \text{ kcal mole}^{-1},$$

which is close to the experimental value of 56.7 kcal $mole^{-1}$. The frequency factor calculated in the same basis is 2×10^{12}, to be compared with the experimental value of 2.2×10^{13} $ml^{1/2}$ $mole^{-1/2}$ s^{-1}.

If reaction 27 is replaced by reaction 29, which corresponds to the situation under Szwarc's conditions, the predicted activation energy becomes ~ 84 kcal $mole^{-1}$, somewhat higher than Szwarc's value of 72 kcal $mole^{-1}$ but in agreement with the experimental trend to higher values.

The Propylene-Inhibited Decomposition of Ethane

Some evidence for allyl abstraction has already been put forward in this paper. Additional evidence is provided by the work of Mellesby and Gordon (55) and Gordon, Smith and McNeeby (56) who report an activation energy of ~ 32 kcal for the abstraction of hydrogen from cyclopentane. They also

express qualitatively the idea that allyl radicals are chain carriers in propylene-inhibited reactions. Bryce and Ruzicka (57) and Ruzicka and Bryce (58) have further shown that the allyl radical abstracts hydrogen under experimental conditions similar to those of the present work. In view of this evidence we suggest that the propylene-inhibited decomposition of ethane proceeds according to the following mechanism:

32.	C_2H_6	+	C_3H_5	$\rightarrow$	C_2H_5	+	C_3H_6
3.			C_2H_5	$\rightarrow$	C_2H_4	+	H
4.	H	+	C_2H_6	$\rightarrow$	C_2H_5	+	H_2
28.	H	+	C_3H_5	$\rightarrow$	C_3H_6		
22.			C_3H_6	$\rightarrow$	C_3H_5	+	H
33.	C_2H_5	+	C_3H_6	$\rightarrow$	C_2H_6	+	C_3H_5

The conventional steady-state treatment yields

$$[C_2H_5] = \left(\frac{k_{22}k_{32}k_4}{k_{23}k_3k_{33}}\right)^{1/2} [C_2H_6] \qquad [50]$$

$$[H] = \left(\frac{k_{22}k_{32}k_3}{k_{28}k_4k_{33}}\right)^{1/2} \qquad [51]$$

$$[C_3H_5] = \left(\frac{k_{28}k_4k_{33}}{k_{28}k_{32}k_3}\right)^{1/2} [C_3H_6] \qquad [52]$$

The rate of the over-all reaction is given by

$$v = k_3 [C_2H_5] = \left(\frac{k_{22}k_{32}k_3k_4}{k_{28}k_{33}}\right)^{1/2} [C_2H_6] \qquad [53]$$

express qualitatively the idea that allyl radicals are chain carriers in propylene-inhibited reactions. Bryce and Ruzicka (57) and Ruzicka and Bryce (58) have further shown that the allyl radical abstracts hydrogen under experimental conditions similar to those of the present work. In view of this evidence we suggest that the propylene-inhibited decomposition of ethane proceeds according to the following mechanism:

32.	C_2H_6	+	C_3H_5	$\rightarrow$	C_2H_5	+	C_3H_6	
3.			C_2H_5	$\rightarrow$	C_2H_4	+	H	
4.	H	+	C_2H_6	$\rightarrow$	C_2H_5	+	H_2	
28.	H	+	C_3H_5	$\rightarrow$	C_3H_6			
22.			C_3H_6	$\rightarrow$	C_3H_5	+	H	
33.	C_2H_5	+	C_3H_6	$\rightarrow$	C_2H_6	+	C_3H_5	

The conventional steady-state treatment yields

$$[C_2H_5] = \left(\frac{k_{22}k_{32}k_4}{k_{23}k_3k_{33}}\right)^{1/2} [C_2H_6] \qquad [50]$$

$$[H] = \left(\frac{k_{22}k_{32}k_3}{k_{28}k_4k_{33}}\right)^{1/2} \qquad [51]$$

$$[C_3H_5] = \left(\frac{k_{28}k_4k_{33}}{k_{28}k_{32}k_3}\right)^{1/2} [C_3H_6] \qquad [52]$$

The rate of the over-all reaction is given by

$$v = k_3 [C_2H_5] = \left(\frac{k_{22}k_{32}k_3k_4}{k_{28}k_{33}}\right)^{1/2} [C_2H_6] \qquad [53]$$

Since

$$\frac{k_{32}}{k_{33}} \cdot \frac{k_{22}}{k_{28}} = [H] \frac{[C_2H_5]}{[C_2H_6]} = K \qquad [38']$$

one can write

$$v = (K k_3 k_4)^{1/2} [C_2H_6] \qquad [39']$$

so that the rate is independent of the concentration of the inhibitor.

It is obvious from the evidence cited that free radicals play an important role in the decomposition of propylene. Previous workers who have studied the effects of propylene inhibition have taken the view that propylene brings about inhibition only by removing radicals. This point of view can no longer be maintained. The interaction of decomposing propylene with the system undergoing inhibition is probably even more complex than is suggested by the proposed mechanism. The mechanism, however, appears to provide a qualitative explanation which is closer to the truth than one that requires propylene to be solely a radical remover.

The study of the relative efficiency of propylene and nitric oxide as inhibitors in the decomposition of n-pentane carried out by Stubbs and Hinshelwood (59) has revealed that nitric oxide is about twelve times as efficient as propylene in causing inhibition; a similar factor probably applies to ethene. In view of this it is of interest to estimate

the ratio of the rates of initiation for the reactions inhibited by the two substances, the initiation reactions being

32. $C_2H_6 + C_3H_5 \rightarrow C_2H_5 + C_3H_6$

13 $C_2H_6 + NO \rightarrow C_2H_5 + HNO$

The ratio of the rates is

$$\frac{v_{13}}{v_{32}} = \frac{k_{13}}{k_{32}} \quad \frac{[NO]}{[C_3H_5]} \qquad [54]$$

Substitution of the appropriate radical concentration for $[C_3H_5]$ from the inhibited ethane mechanism gives rise to

$$\frac{v_{13}}{v_{32}} = k_{13} \left(\frac{k_{28}k_3}{k_{22}k_{32}k_4k_{33}} \right)^{1/2} \frac{[NO]}{[C_3H_6]} \qquad [55]$$

Substitution of values in table 2 gives

$$\frac{[C_3H_6]}{[NO]} = 10$$

This is close to the experimental value (for n-pentane) of 12. The mechanisms of inhibition thus not only predict the independence of the limiting rate on the inhibitor concentration, but can also be made to yield an estimate of the relative amounts of various inhibitors necessary for the establishement of the proposed mechanisms.

Part IV

MECHANISMS OF OTHER INHIBITED REACTIONS

INTRODUCTION

The inhibition effects observed in a number of other organic decompositions can also be explained in terms of free radical mechanisms of the type discussed above. Hinshelwood (63) has recently reviewed the problem in terms of the molecular hypothesis. However certain characteristics of the fully inhibited decompositions cannot be explained on this basis. These in brief are as follows:

1) Rice and co-workers (42, 43), and Voevodsky and Poltorak (64) have shown that deuterium mixing reactions still occur in the inhibited decomposition.
2) The fully inhibited reactions frequently exhibit a well-defined induction period (65, 66).
3) The rates of the fully inhibited reactions are somewhat decreased by an increase in surface-volume ratio (see Part II).

It would seem to be quite impossible to reconcile these facts with the hypothesis of a simple molecular mechanism, and it is therefore necessary to develop mechanism of the free radical type that will give rise to limiting rates at high

inhibitor concentrations, and will explain the fact that different inhibitors give the same limiting rates in the case of alkane decompositions.

A number of free radical inhibition mechanisms are proposed in the following discussion. The mechanisms are also classified according to the mode of termination and the theoretical approach is thus generalized.

DISCUSSION

The Decomposition of Methane

The decomposition of methane offers an interesting contrast to that of ethane, since both the chain-propagating reactions are of the second-order. The chain carriers are H and CH_3, and one obtains 3/2 order kinetics whether one assumes the chain termination to involve $CH_3 + HNO$, or $H + HNO$. The former is preferred, since the methyl radical concentration is probably usually higher than the concentration of hydrogen atoms. The mechanism to which we are therefore led is as follows:

34. $CH_4 + NO \rightarrow CH_3 + HNO$

35. $CH_3 + CH_4 \rightarrow C_2H_6 + H$

36. $H + CH_4 \rightarrow CH_3 + H_2$

15' $HNO \rightarrow H + NO$

14' $H + NO \rightarrow HNO$

37. $CH_3 + HNO \rightarrow CH_4 + NO$

The expression for the limiting rate is

$$v = \left(\frac{k_{34} k_{35} k_{36} k_{15}}{k_{37} k_{14}} \right)^{1/2} [CH_4]^{3/2} \qquad [56]$$

The conclusion that the order is 3/2 is consistent with the experimental results.

Discussion

This reaction has been studied by Hobbs and Hinshelwood (34), who conclude that the inhibited reaction at 850°C and 100 mm. gives a rate 4.7 times lower than the uninhibited at the same pressure. It is hard to postulate any purely molecular process in this case, since the products are hydrogen, ethane and decomposition products of ethane. We are therefore forced to accept some free radical mechanism to explain the fact that any reaction occurs at all.

The mechanism put forward is essentially that of Kassel (67), modified to allow for nitric oxide participation. From the rate equation 56 we may predict an activation energy of

$$E = 1/2 [E_{34} + E_{15} + E_{35} + E_{36} - E_{37} - E_{14}] \qquad [57]$$

Since the C-H bond in methane is given by Lossing et al.(68) as 103 kcal mole^{-1} we have

$$E_{34} + E_{15} = 103.$$

The activation energy of E_{35} is estimated by Steacie (69) as > 40 kcal mole^{-1}. For present purposes we will accept the value of 42 kcal mole^{-1}.

E_{36} has been calculated (70) to be 10.5 kcal mole^{-1}.

E_{37} and E_{14} we will assume to be 0 kcal mole^{-1}.

We therefore arrive at the predicted activation energy for the reaction:

$$E \sim 78 \text{ kcal mole}^{-1}$$

This cannot be compared to any experimental result, since none is available.

The Decomposition of Ethers

In the reactions discussed above hydrogen atoms were involved in chain-propagating steps. In other decompositions, on the other hand, this is not the case. The chain propagating reactions in the case of dimethyl ether are probably

38. $CH_3OCH_2 \rightarrow CH_3 + CH_2O$

and

39. $CH_3 + CH_3OCH_3 \rightarrow CH_4 + CH_3OCH_2$

In view of this the concentration of HNO is very small, and the participation of HNO in chain termination is therefore unlikely. Our suggestion is that in these reactions chain termination involves nitric oxide itself, reacting with whichever radical is present in greater concentrations; in

the ether decomposition these are the μ radicals. The mechanism to which we are led is therefore as follows:

40. $CH_3OCH_3 + NO \rightarrow CH_3OCH_2 + HNO$

38. $CH_3OCH_2 \rightarrow CH_3 + CH_2O$

39. $CH_3 + CH_3OCH_3 \rightarrow CH_4 + CH_2OCH_3$

15' $HNO \rightarrow H + NO$

41. $H + CH_3OCH_3 \rightarrow H_2 + CH_3OCH_2$

42. $CH_3OCH_2 + NO \rightarrow CH_3OCH_2NO$

Application of the steady-state treatment gives rise to the rate equation:

$$v = \frac{2k_{40}k_{38}}{k_{42}} [CH_3OCH_3] \qquad [58]$$

The result that the reaction is of the first-order is in agreement with experiment.

The proposed mechanism for the diethyl ether decomposition is similar, as follows:

43. $C_2H_5OC_2H_5 + NO \rightarrow C_2H_5OC_2H_4 + HNO$

44. $C_2H_5OC_2H_4 \rightarrow C_2H_5O + C_2H_4$

45. $C_2H_5O \rightarrow CH_3 + CH_2O$

46. $CH_3 + C_2H_5OC_2H_5 \rightarrow CH_4 + C_2H_5OC_2H_4$

15' $HNO \rightarrow H + NO$

47. $H + C_2H_5OC_2H_5 \rightarrow H_2 + C_2H_5OC_2H_4$

48. $C_2H_5OC_2H_4 + NO \rightarrow C_2H_5OC_2H_4NO$

The rate equation is now

$$v = \frac{2k_{43}k_{44}}{k_{48}} [C_2H_5OC_2H_5] \qquad [59]$$

and the order is again first, as found experimentally (71).

Discussion

It is significant that in these ether decompositions the nitric oxide is in no way in competition with the ether molecules themselves. The nitric oxide reacts with a μ radical, and the situation is to be contrasted with that in the case of ethane, where nitric oxide competes with C_2H_6 for reaction with hydrogen atoms. In the ether decompositions the degree of inhibition produced by a given nitric oxide concentration is thus independent of the amount of ether, a prediction that is consistent with experiment.

In contrast to the situation with methane and ethane (and by analogy with the higher paraffins), the mechanism proposed for the ethers does not lead to the general conclusion that the fully inhibited rate should be the same for all inhibitors. Smith and Hinshelwood (72) and Freeman (73) have obtained results that tend to show that the same rates are obtained with both nitric oxide and propylene and this being so it must be assumed, if our mechanisms are correct, that the agreement of rates is fortuitous. It should, however, be pointed out that in the case of the other decompositions there does remain a possibility that the fully inhibited

reactions are molecular processes, since no isotopic exchange experiments have been carried out on these reactions. It should also be borne in mind that the results of Freeman et al, show that the order of the reaction is higher than first and does not indicate a simple molecular process. The mechanism here proposed attempts to explain only the main reaction and dould be subject to distortion by secondary causes as in the ethane reaction.

The activation energy predicted for diethyl ether can be obtained from the following values:

E_{43} = 52 kcal estimated

E_{44} = 19.0 kcal estimated from (74)

E_{48} = 0

This leads to an over-all activation energy of

$E = 71$ kcal $mole^{-1}$

in good agreement with the experimental value of 67 kcal $mole^{-1}$ (75).

The Decomposition of Acetaldehyde

The acetaldehyde decomposition differs from the hydrocarbon decompositions, and is similar to the other decompositions, in that hydrogen atoms are not chain carriers. Chain termination will therefore involve NO rather than HNO. The chain carriers are CH_3 and CH_3CO, of which the former are

in excess; it is therefore postulated that the chain-ending step is reaction between CH_3 (a β radical) and NO.

The mechanism to which we are led is therefore:

49. $CH_3CHO + NO \rightarrow CH_3CO + HNO$

50. $CH_3CO \rightarrow CH_3 + CO$

51. $CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$

15' $HNO \rightarrow H + NO$

52. $H + CH_3CHO \rightarrow H_2 + CH_3CO$

53. $CH_3 + NO \rightarrow CH_3NO$

The rate corresponding to this mechanism is

$$v = \frac{2k_{49}k_{51}}{k_{53}}[CH_3CHO]^2 + 2k_{49}[CH_3CHO][NO] \qquad [60]$$

Discussion

This rate expression, as in previous cases, corresponds to the rate when there is a sufficient excess of nitric oxide: much more complicated expressions result if the uninhibited initiation step is included also. The mechanism in this case leads to initial inhibition, with acceleration at higher nitric oxide concentrations as the second term in the rate equation becomes predominant. This is in fact the behaviour observed experimentally (76). At moderate concentration of nitric oxide the first term will predominate, and the kinetics should therefore be of the second-order, as

is found experimentally.

The activation energy can be estimated from the following data.

E_{49}: The value quoted by Szwarc for the acetaldehyde aldehyde-hydrogen (45) is 85 kcal mole^{-1}. Thus E_{49} is taken to be

$$E_{49} = 85 - 48 = 37 \text{ kcal mole}^{-1}.$$

E_{51}: Similarly, Steacie (77) quotes the value

$$E_{51} = 7.5 \pm 1.5 \text{ kcal mole}^{-1}.$$

E_{53}: This is taken as zero, as in the previous mechanisms.

Thus the over-all activation energy is predicted to be

$$E \sim 45 \text{ kcal mole}^{-1}$$

and is in good agreement with the experimental value of 47 kcal mole^{-1} (76).

The Decomposition of Acetone

The nitric oxide inhibited decomposition of acetone is very similar to that of acetaldehyde (there is again catalysis at high concentrations) and a similar mechanism is therefore probably involved.

54. $CH_3COCH_3 + NO \rightarrow CH_3COCH_2 + HNO$

55. $CH_3COCH_2 \rightarrow CH_3 + CH_2CO$

56. $CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_3COCH_2$

15. $HNO \rightarrow H + NO$

57. $H + CH_3COCH_3 \rightarrow H_2 + CH_3COCH_2$

53. $CH_3 + NO \rightarrow CH_3NO$

The resulting rate expression is

$$v = \frac{2k_{54}k_{56}}{k_{53}}[CH_3COCH_3]^2 + 2k_{54}[CH_3COCH_3][NO] \qquad [61]$$

which is consistent with experiment.

Discussion

The fact that the proposed mechanisms for these last two examples lead to the conclusion that there is catalysis at high nitric oxide concentrations, as observed experimentally, provides valuable support for the general scheme of reactions presented here.

The lack of experimental data concerning the activation energy of the NO inhibited reaction as well as the C-H bond strength makes any prediction of the activation energy highly speculative.

GENERAL DISCUSSION

The suggestion that the initiating processes in reactions fully inhibited by nitric oxide involve a hydrogen atom abstraction by NO is not new; it was first made by Rice and Polly (18) and was discussed by Goldanskii(10). The postulation of reactions between radicals and HNO as chain-terminating steps seems to be required in order to account for the observed kinetics, and more particularly to explain

the causes of limiting rates at high nitric oxide concentrations. Our view is that in the paraffin decompositions, where rather high temperatures are involved, reactions such as

$$C_2H_5 + NO \rightleftharpoons C_2H_5NO$$

merely proceed to equilibrium and do not disturb the steady-state concentrations of radicals; they therefore need not be included in the reaction schemes. In reactions at lower temperatures, however, such reactions are important chain-ending steps.

This mechanism of chain-ending by NO agrees also with the experimental evidence of Mitchell and Hinshelwood (78) and other workers, who found that at low temperatures, nitric oxide removes all radicals produced.

The mechanisms here proposed are mainly concerned with inhibition by nitric oxide. Only in the case of alkanes does the mechanism of propylene inhibition yield the same rate equation. The fact that both propylene and nitric oxide give the same limiting rate for the inhibited decomposition of diethyl ether is therefore left unexplained.

The idea that HNO plays an important role in reaction mechanism is reasonable in view of the fact that this substance has been prepared and its spectrum analyzed (47). Since the molecule is iso-electronic with O_2, it may be expected to be quite stable with respect to H + NO.

It may be seen that the reaction mechanisms discussed

above fall into four main classes. Table 9 summarizes the main features and gives examples of each type.

Table 9

Summary of Reaction Types for Inhibition by Nitric Oxide

Case	H as chain carrier	Chain Ending step	Order of Reaction	Examples	Chain carriers (most abundent) given first)	Chain-Ending Step
I	yes	μ + HNO	1	C_2H_6	C_2H_5, H	C_2H_5 + HNO
II	yes	β + HNO	$\frac{3}{2}$	C_2H_6 (initial rates)	H, C_2H_5	H + HNO
				CH_4	CH_3, H	CH_3 + HNO
III	no	μ + NO	1	CH_3OCH_3	CH_3OCH_2, CH_3	CH_3OCH_2 + NO
				$C_2H_5OC_2H_5$	$C_2H_5OC_2H_4$, CH_3	$C_2H_5OC_2H_4$ + NO
IV	no	β + NO	2	CH_3CHO	CH_3, CH_3CO	CH_3 + NO
				CH_3COCH_3	CH_3, CH_3COCH_2	CH_3 + NO

Part V

FREE RADICAL MECHANISMS FOR INHIBITED ALKYL HALIDE DECOMPOSITIONS

INTRODUCTION

In spite of the considerable amount of work that has been done on the decomposition of alkyl halides, there are certain puzzling features of the reactions which have not been fully explained. The most significant of these is that for certain of the reactions there are clear indications that free radical processes occur to a considerable extent, but at the same time there is little or no inhibition by nitric oxide, propylene or cyclohexene. For example, the thermal decomposition of ethyl bromide (79, 80) exhibits an induction period, and is very sensitive to the nature of the surface, so that it seems clear that free radicals are involved. The reaction is inhibited by cyclohexene but there is no inhibition by nitric oxide. Lack of inhibition by nitric oxide is commonly regarded as an indication that free radical reactions are not important, so that something of a paradox is involved in this case. Other reactions of the same type show similar peculiarities. In Chapter IV it was suggested that the effect of substances such as nitric oxide, propylene and cyclohexene is not merely to remove free radicals, but also to initiate free radical

processes. It has been proposed, for example, that nitric oxide can abstract hydrogen atoms from organic compounds, with the formation of HNO and a free radical, and that chain ending occurs by reaction between either NO or HNO and one of the radicals involved in the chain-propagating steps. These ideas will now be applied to the alkyl halide decompositions, and it will be suggested that the initial step is now the abstraction of the halide atom from the organic molecule, and that the chain-ending step involves a radical such as BrNO and a free radical. The significant conclusion that has emerged from these considerations is that under certain circumstances the rates of the reactions occurring in the presence of nitric oxide are exactly the same as those occurring in its absence. This result arises when the chain-ending step in the uninhibited reaction involves the reaction between a β radical and a μ radical. It is also concluded that the olefins sometimes bring about inhibition by removing hydrogen atoms, but not halide atoms, which means that they abolish one part of the chain reaction but leave another.

These conclusions are of some significance in view of the commonly held belief that lack of inhibition by nitric oxide is an indication that free radical processes are not involved, and that the reactions occurring in the presence of excess of nitric oxide are molecular reactions. This view can no longer be maintained.

DISCUSSION

The Pyrolysis of Ethyl Bromide

The uninhibited decomposition of ethyl bromide has been studied by Goldberg and Daniels (79), and the inhibited reaction by Thomas (80). In both cases the reaction showed induction periods and was very sensitive to the state of the surface. That free radicals are involved in the reaction was shown by the work of Roof and Daniels (81, 82), who found that ethyl bromide can sensitize the decomposition of acetaldehyde at temperatures around 370°C. In spite of this, however, nitric oxide has no effect on the rate of decomposition. Cyclohexene, which is usually a less powerful inhibitor than nitric oxide, did produce a significant amount of inhibition. The results with ethyl chloride are quite similar (83, 84, 85); in spite of evidence for free radicals, no inhibition is observed with propylene.

It will now be shown that certain mechanisms for the decomposition of these molecules, both uninhibited and in the presence of inhibitors, can explain these results. For the uninhibited decomposition of ethyl bromide the following mechanism, which is somewhat over-simplified, probably explains the main results:

54. $C_2H_5Br \longrightarrow C_2H_5 + Br$ (E_1 = 65 kcal.)

55. $Br + C_2H_5Br \longrightarrow HBr + C_2H_4Br$ (E_2 = 17 kcal.)

56. $C_2H_4Br \longrightarrow C_2H_4 + Br$ (E_3 = 18 kcal.)

57. $Br + C_2H_4Br \longrightarrow C_2H_4Br$ ($E_4 = 0$ kcal.).

The estimated activation energies for these reactions are shown. That for reaction 54 is calculated from thermochemical data, while those for 55 and 56 are estimated on the basis of similar reactions; the values are probably reliable within a few kilocalories. The radicals occurring in the chain propagating steps are Br and C_2H_4Br, and since the activation energies for reaction 55 and 56 are quite similar their concentrations will be comparable. In view of this the most likely chain-ending step is reaction 57; the reaction Br + Br may be excluded as requiring a third body, while the reaction $C_2H_4Br + C_2H_4Br$ probably has a considerably smaller frequency factor than has reaction 57. The scheme above corresponds to first-order kinetics, as observed experimentally, and the rate expression is

$$v = \left(\frac{k_{54} k_{55} k_{56}}{k_{57}} \right)^{1/2} [C_2H_5Br] \qquad [62]$$

Chain propagation may also occur <u>via</u> the reactions

58. $H + C_2H_5Br \longrightarrow HBr + C_2H_5$ ($E_5 = 5$ kcal.)

3. $C_2H_5 \longrightarrow C_2H_4 + H$ ($E_6 = 39.5$ kcal.).

The activation energy for reaction 3 is well established, but that for 58 is an estimate. It is to be seen that the sum of the activation energies for reactions 58 and 3 is significantly higher than that for reactions 55 and 56, and from this follows

that the part played by H and C_2H_5 in the reaction will not be as important as that played by Br and C_2H_4Br. Unfortunately the rate equation when all six reactions are included, together with all of the chain-ending steps of the β-μ type, is much too complicated to be of any value.

The activation energy for the reaction proceeding via steps [1] to [4] is given by

$$E = \frac{1}{2} (E_{54} + E_{55} + E_{56} - E_{57}) \qquad [63]$$

$$= 50 \text{ kcal.}$$

and this agrees with the experimental value. The activation energy for reactions 54, 58, 3 and 57 is a few kilocalories larger.

The Reaction in the Presence of Nitric Oxide

We proposed in Chapter IV that nitric oxide can abstract hydrogen atoms from organic compounds to form HNO and an organic radical. In the present case we suggest that there is abstraction of a bromine atom with the formation of BrNO. The mechanism to which we are led is therefore as follows:

59. $NO + C_2H_5Br \longrightarrow NOBr + C_2H_5$

60. $NOBr \longrightarrow NO + Br$

61. $NO + Br \longrightarrow NOBr$

55. $Br + C_2H_5Br \longrightarrow HBr + C_2H_4Br$

56. $C_2H_4Br \longrightarrow C_2H_4 + Br$

62. $BrNO + C_2H_4Br \longrightarrow NO + C_2H_4Br_2$

The rate expression corresponding to this mechanism is

$$v_{NO} = \left(\frac{k_{55}k_{56}k_{59}k_{60}}{k_{61}k_{62}} \right)^{1/2} [C_2H_5Br] \qquad [64]$$

The ratio of the rates in the presence and absence of nitric oxide is therefore

$$\frac{v_{NO}}{v} = \left(\frac{k_{57}k_{59}k_{60}}{k_{54}k_{61}k_{62}} \right)^{1/2} \qquad [65]$$

This ratio of rate constants is related to the equilibrium constants for certain reactions, as follows:

$$C_2H_5Br \rightleftharpoons C_2H_5 + Br \qquad \frac{k_{54}}{k_{57}} = \frac{[C_2H_5][Br]}{[C_2H_5Br]} \text{ eq.} \qquad [66]$$

$$NO + C_2H_5Br \rightleftharpoons BrNO + C_2H_4Br \qquad \frac{k_{59}}{k_{62}} = \frac{[BrNO][C_2H_4Br]}{[NO][C_2H_5Br]} \text{ eq.} \qquad [67]$$

$$NOBr \rightleftharpoons NO + Br \qquad \frac{k_{60}}{k_{61}} \quad \frac{[NO][Br]}{[NOBr]} \text{ eq.} \qquad [68]$$

The ratio of rates is therefore

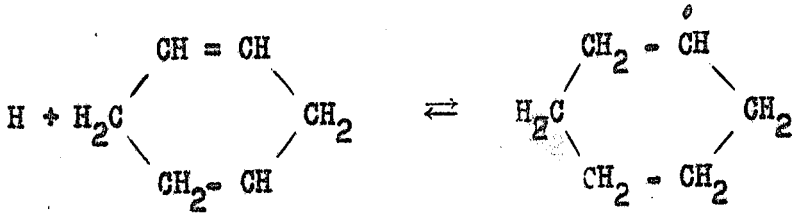
$$\frac{v_{NO}}{v} = \left(\frac{[C_2H_5Br]}{[C_2H_5][Br]} \cdot \frac{[BrNO][C_2H_4Br]}{[NO][C_2H_5Br]} \cdot \frac{[NO][Br]}{[NOBr]} \right)^{1/2} \text{eq.} \qquad [69]$$

$$= 1$$

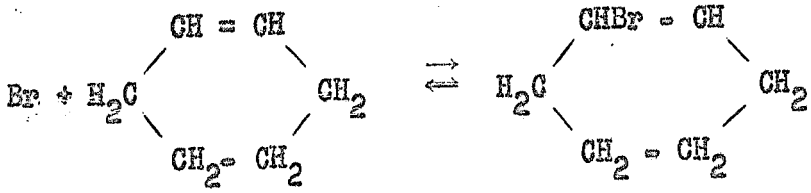
The rate is therefore the same in the presence and absence of nitric oxide, in spite of the fact that a completely different mechanism is involved. This result is only obtained when the chain-ending step involves interaction between a β and a μ radical; it is not found with the ethane decomposition, for which a $\mu\mu$ recombination is believed to be predominant.

The Influence of Weak Inhibitors

Thomas's result that cyclohexene, although normally a weaker inhibitor than nitric oxide, does somewhat inhibit the ethyl bromide decomposition, requires that a different type of process is involved. Our explanation is that cyclohexene is able to add on hydrogen atoms,



and that at the temperatures involved the equilibrium lies well over to the right, since the reaction is exothermic by about 35 kcal. On the other hand the analogous reaction



is much less exothermic (compare the activation energies for reactions 56 and 3) and the equilibrium at the temperatures of the bromide decomposition probably lies over to the left. It is therefore postulated that cyclohexene effectively removes hydrogen atoms but hardly touches the bromine atoms. It therefore removes that part of the reaction that proceeds via reactions 54, 58, 3 and 57, but leaves untouched that part that proceeds via 54, 55, 56 and 57.

In general the weaker an inhibitor the stronger the bond that it will form with hydrogen atoms, so that weak

inhibitors will greatly reduce the concentration of the hydrogen atoms. At lower temperatures the resulting radicals will not effectively bring about hydrogen atom abstractions, so that they will not initiate chains by reactions analogous to reaction 59. At higher temperatures, however, as discussed in the previous Chapter, olefinic substances probably inhibit by a mechanism that is similar to that with nitric oxide inhibition; thus the propylene inhibition of the ethane decompositions is believed to involve a hydrogen atom abstraction by an allyl radical.

Support for our explanation for the olefin inhibitions of halides is that propylene does not inhibit the decomposition of ethyl chloride, which occurs at a higher temperature than that of ethyl bromide, and for which bromine atom abstraction by allyl radicals probably occurs.

CONCLUSIONS

The main conclusion which can be drawn is that when an organic decomposition involves a $\beta\mu$ chain-ending step there may be no inhibition by nitric oxide (and, at sufficiently high temperatures, by the olefins) even though the reaction in the presence of these substances involves a completely different mechanism.

When other types of chain-ending step occur, however, there will be inhibition. It is significant that, as noted by

Semenov (86), bromide decompositions that are first-order are uninhibited by nitric oxide, while those that are three-halves order are inhibited. Some examples are shown in Table 10. The data are those of Maccoll et al (87). Semenov's explanation is that the three-halves order reactions are free radical process, and the first-order reaction molecular processes. It is not denied that molecular mechanisms may play important roles in these reactions, but the preceding discussion has shown that lack of inhibition cannot be regarded as evidence for the absence of chain reactions.

Table 10

Summary of Kinetic Data for Organic Halides

Compound	Order of uninhibited reaction	Temperature	Inhibitor employed	Inhibition
C_3H_5Br	1	300-380°	Propylene	No
n-C_3H_7Br	3/2	300-380°	Propylene	Yes
iso-C_3H_7Br	1		Propylene	No
n-C_4H_9Br	3/2	370-420°	Cyclohexene	Yes
sec-C_4H_9Br	1	300-350°	Propylene	No
Tert-C_4H_9Br	1	230-280°	Cyclohexene	No
Tert-C_4H_7Br	1	220-270°	Cyclohexene	No
Cyclo-C_5H_9Br	1	300-360°	Cyclohexene	Yes
Cyclo-$C_6H_{11}Br$	1	300-350°	Cyclohexene	No
2 Bromo, 2:3-dimethyl butane	1	210-260°	Cyclohexene	Yes
C_2H_5Br	1	400°	Nitric Oxide Propylene Cyclohexene	No Yes Yes
C_2H_5Cl	1	500°	Propylene	No

Claims to Original Research

1. A new type of apparatus capable of recording the time-course of reaction was designed and built.
2. The pyrolysis of ethane was reinvestigated and it was noted that there is a transition from first-order to three-halves order at high temperatures and low pressures.
3. Theoretical consideration of the uninhibited reaction has led to the conclusion that initiation occurs by a second-order unimolecular process.
4. It has been shown that the Küchler and Theile mechanism is consistent with the experimental facts.
5. A more detailed experimental study of the nitric oxide inhibited decomposition of ethane has been carried out. It was noted that an induction period was present in the reaction; the order of the initial rates was three-halves under most conditions, whereas the order at the inflection points was first.
6. A mechanism of inhibition has been proposed which is consistent with all the known facts.
7. The decomposition of propylene was restudied and the order found to be three halves under all experimental conditions.
8. A mechanism is proposed for the decomposition of propylene which is consistent with all the known facts.

9. A generalized theory of inhibition is proposed which can be used to explain the observed inhibition phenomena.

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