THE THERMAL DECOMPOSITION OF VINYL ETHYL ETHER

by

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Thesis submitted to the Faculty of
Graduate Studies and Research of
McGill University in partial
fulfillment of the requirements for
the degree of Doctor of Philosophy.

McGill University April, 1942.

The author desires to express his gratitude to Dr. C.A. Winkler, whose kind supervision and sympathetic criticism have been greatly appreciated.

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INTRODUCTION

It is now generally conceded that the decomposition of an organic compound can be realized in two different ways: First, the products may be formed by a single process of rearrangement of atoms. In such case, the activation energy E and the frequency factor A contained in the rate equation

$$k = Ae^{-E/RT}$$

as determined from experimental data convey real physical significance. Secondly, the products may be only formed through a series of steps in which the free radicals play the role of an intermediate, i.e., a chain mechanism. Both kinds of mechanism are, of course, possible. In fact, they may be operative simultaneously. The task facing a physical chemist in studying the decomposition of an organic compound, therefore, not only consists of the determinatoon of the chemical change taking place and the rate expression of the over-all process, but also whether the process comes through a rearrangement mechanism or a chain mechanism or both.

The thermal decomposition of formaldehyde into H_2 and CO, for instance, may be a case of rearrangement process. The process may be pictured as the closing together of the two hydrogen atoms and the simultaneous spreading out of the C-H links with the subsequent formation of CO and H_2. The lowest energy barrier involved is, in the light of London-Polanyi-Eyring theory, the activation energy. In principle, all the characters of such a process should be predictable from the molecular constants of the initial and final states.

A chain process, on the other hand, represents no other than a combination of several individual rearrangement processes, among the participants of which are free radicals. The free radical mechanism for the decomposition of organic compounds was first advocated by Rice (1) who, as admitted by himself in his paper, was prompted by the isolation of free methyl and free ethyl radicals by Paneth and his collaborators (2) as well as other suggestive experiment like the polymerization of ethylene initiated by ethyl groups formed in the decomposition of lead or mercury alkyls (3). A little later, Rice and Herzfeld (4) were able to show that the chain mechanism is capable of accounting for the kinetic behavior of the total reaction by assuming suitable consecutive steps.

For example, the decomposition of dimethy ether at moderate pressure was originally represented by Rice and Herzfeld by the following scheme:

No.	Chemical equation	Rate constant	Act. Energy assigned (kcal)
1	$CH_3OCH_3 = CH_3 + CH_3O$	k_1	80
2	$CH_3O + CH_3OCH_3 = CH_3OH + CH_2OCH_3$	k_2	15-25
3	$CH_3 + CH_3OCH_3 = CH_4 + CH_2OCH_3$	k_3	15
4	$CH_2OCH_3 = CH_3 + HCHO$	k_4	38
5	$CH_3 + CH_2OCH_3 = C_2H_5OCH_3$	k_5	8
6	$CH_3 + CH_3O = CH_3OCH_3$	k_6	

For the sake of clarity, we give indices to the different substances

$$\begin{array}{cccc} CH_3OCH_3 & CH_3 & CH_3O & CH_2OCH_3 \\ 1 & 2 & 3 & 4, \end{array}$$

and use x with the corresponding subscript to denote concentration.

The steady state conditions are as follows:

$$CH_3 \qquad \frac{dx_2}{dt} = k_1x_1 - k_3x_1x_2 + k_4x_4 - k_5x_2x_4 - k_6x_2x_3 = 0 \qquad (1)$$

$$CH_3O \qquad \frac{dx_3}{dt} = k_1x_1 - k_2x_3x_1 = 0 \qquad (2)$$

$$CH_2OCH_3 \qquad \frac{dx_4}{dt} = k_2x_3x_1 + k_3x_2x_1 - k_4x_4 - k_5x_2x_4 = 0 \qquad (3).$$

From these equations we can obtain

$$x_3 = \frac{k_1}{k_2} \quad (4), \qquad x_2 = \sqrt{\frac{k_1k_4}{k_3k_5}} \quad (5), \qquad x_4 = x_1\sqrt{\frac{k_1k_3}{k_4k_6}} \qquad (6)$$

with the approximations involved in

$$k_2x_1x_3 \gg k_6x_2x_3 \qquad \text{and} \qquad k_3x_1x_2 \gg k_6x_2x_3$$

The rate of decomposition of ether is given by

$$\frac{dx_1}{dt} = -kx_1 = -2k_1x_1 - \sqrt{\frac{k_1k_3k_4}{k_5}}\, x_1$$

a first order equation, whence

$$k = 2k_1 + \sqrt{\frac{k_1k_3k_4}{k_5}}$$

Since k_1 is negligibly smaller than $\sqrt{\frac{k_1k_3k_4}{k_5}}$,

$$k = \sqrt{\frac{k_1k_3k_4}{k_5}} \qquad (7),$$

and the activation energy E is equal to 1/2 $(E_1 + E_3 + E_4 + E_5)$, i.e., 62.5 kcal. from the assigned values while the experimental value obtained by Hinshelwood and Askey (5) is 58.5 kcal..

It should be pointed out, however, that in the above scheme several possible reactions like the combination of two methyl or two CH_2OCH_3 groups are entirely neglected. If they are assumed instead of equation (5) as the major chain ending process, quite different rate expressions would be obtained. Moreover, the activation energies of these radical reactions were so chosen to make the whole picture consistent. To test the various detail features of such a scheme one must know very definitely about the activation energies of these radical reactions. Despite much work done toward this end, there are still a great many data lacking. For the moment, such a scheme must be regarded as little more than speculation. Nevertheless, the work of Rice and Herzfeld did a great service in pointing out the possibility of a chain mechanism. It showed that the complexity of a reaction which had been always attributed to the intrinsic nature of rearrangement process may well be due to the presence of certain chain processes. Therefore, in the experimental study of a thermal decomposition, an important point to establish is the extent to which free radicals are formed in the course of the reaction.

The presence of free radicals can be demonstrated in four main ways: the para- and ortho-hydrogen conversion method, the sensitization method, the inhibition method and the Paneth mirror method.

Para- and Ortho-hydrogen Conversion Method

The para- and ortho-hydrogen which differ from each other in the nuclear spin can not change into each other directly, but only by metathesis (6), e.g.

$$H + pH_2 = oH_2 + H$$

or by collision with a paramagnetic molecule such as O_2, NO and NO_2 (7). Now if some comparatively pure para- or ortho-hydrogen is mixed with the reactant, acceleration of conversion may occur if some free radicals, which are paramagnetic, or some hydrogen atoms are present. The hydrogen atoms may be produced by reaction of the free radical with the H_2 present. The method is useful, since the composition of an para- and ortho-hydrogen mixture may be easily determined by specific heat measurements. This method has been applied by Patat and Sachsse for the examination of the thermal decompositions of HCHO (8), CH_3CHO and CH_3COCH_3 (9). It seems not out of place to consider the general way in which the concentration of methyl groups in the case of CH_3CHO, CH_3COCH_3, etc. decompositions has been estimated. It is assumed that when the hydrogen is present with thereaction mixture, a stationary concentration of hydrogen atom is produced through the operation of the following reactions

$$CH_3 + H_2 = CH_4 + H \qquad k_1$$

$$\underset{\text{(org. subs.)}}{H + CH_3COCH_3} = H_2 + CH_3COCH_2 = H_2 + CH_2CO + CH_3 \qquad k_2 .$$

Between the concentrations of hydrogen atoms and free methyl radical, there exists the relation

$$\frac{(CH_3)}{(H)} = \frac{k_2 \text{ (org. sub.)}}{k_1 \ (H_2)}$$

The ortho-para conversion is assumed to be due mainly to H atoms. The CH_3 concentration is then calculated by estimating the ratio k_2 / k_1. However, it must be remembered that the free methyl radical, being paramagnetic, is capable of catalyzing the conversion itself. As the efficiency of this process is unknown, the free radical concentration obtained from the above manner must be regarded as upper limit (10).

Sensitization Methods

The most important sensitization method consists in the study of the effect of the compound in question on the decomposition rate of some other substance. If a conspicuous acceleration is produced which can be shown to be not due to any cross collisional activation, then it may be concluded that the compound in question yields some free radicals which serve to initiate chains in the latter. For example, the production of free radicals in the decomposition of ethylene oxide was demonstrated by Fletcher and Rollefson (11) by its large catalytic effect on the decomposition of acetaldehyde.

Any polymerization reaction which can be induced by certain free radicals may also be made use of for the present purpose. For instance, the polymerization of ethylene was found greatly accelerated in the presence of thermally decomposing mercury dimethyl (3), or azomethane (12), or lead tetramethyl (13). Since the total polymerization induced in all these cases are far greater than can be accounted for by the amounts of these substances introduced on a stoichiometric basis, it is evident that free radicals are produced in the thermal decompositions of these three compounds which initiate polymerization chains in ethylene.

On the other hand, by some artificial means such as decomposition of certain compounds either thermally or photochemically, free radicals may be introduced into the substance in question. If a chain is set up in this way, pure thermal decomposition may proceed through chain mechanism. If there is no effect at all, then any possibility of chain mechanism is precluded. We shall illustrate these two principles with the cases of acetaldehyde and acetone.

Leermakers (14), from his study of the photochemical decomposition of acetaldehyde, concluded that the free radicals produced from the first act of absorption of radiation initiate a chain process above 80°C. While the quantum yield is only 0.03 at room temperature, it rises to 300 at 310° under otherwise similar conditions. The results were confirmed by Allen and Sickman (15) in their study of the sensitized decomposition of acetaldehyde by azomethane at 245°- 330°C. These authors showed further that Rice-Herzfeld chain mechanism with the main chain propagating steps

$$R + CH_3CHO = CH_4 + CH_3CO$$

$$CH_3CO = CH_3 + CO$$

is satisfactory in accounting for their experimental results. As the chain length, presumably, would continue to increase with temperature, we can say that around 500°C where normal thermal decomposition takes place, the average chain length would be greater than 300 once it is started. In fact, however, the methyl radical concentration as estimated by o- and p-hydrogen conversion method (9) is much lower than is to be expected from Rice-Herzfeld scheme, and the reaction rate is not affected by nitric oxide (16). Therefore, whether acetaldehyde decomposes in a rearrangement process or in a chain process remains an open question.

The resistance of a substance to the setting up of a chain is well exemplified by the acetone case. The photodecomposition of acetone was studied by Leermakers (17). The quantum yields of CO production were, within their experimental accuracy, unity from 200 - 400°C. Over the same temperature range, the carbon monoxide in the measured reaction products decreased from 50% to approximately 33%. This means that at 400°C two molecules of gas not condensed in liquid air are found for each molecule of CO. At 200°C one molecule of non-condensed gas is formed for each CO. The non-condensed gas is either ethane or methane. The interpretation given is that: at 400°C the two radicals resulting from

$$CH_3COCH_3 + h\nu = CH_3 + CH_3CO \tag{8}$$

$$CH_3CO = CH_3 + CO \tag{9}$$

react bimolecularly with acetone molecules to form methane and the comparatively stable CH_2COCH_3 radicals. The radicals do not further decompose, at least to yield a non-condensable gas, but disappear by recombination in the gas phase or on the wall. At 200°C the radicals liberated in the primary act do not react with the acetone molecule but disappear according to reactions (9) and (10)

$$2\ CH_3 = C_2H_6 \tag{10}$$

, that is, a molecule of ethane is formed for each molecule of CO.

The stability of CH_3COCH_2- radical is further substantiated by the work of Rice, Rodowskas and Lewis (18). They heated acetone containing approximately 1% dimethyl mercury in the range 350-400°C. No ketene was found in the product. Instead, a high boiling substance identified as acetylacetone $CH_3COCH_2CH_2COCH_3$ was found in amounts approximately corresponding to the amount of dimethy mercury added. The evidence suggests that the followong reactions occur

$$CH_3COCH_3 + CH_3 = CH_4 + CH_3COCH_2$$

$$2\ CH_3COCH_2 = 2CH_3COCH_2CH_2COCH_3$$

Pure acetone decomposes thermally at 540-620°C into methane and ketene (19). If a chain mechanism plays a part here, the important propagating steps would be

$$R + CH_3COCH_3 = RH + CH_3COCH_2$$

$$CH_3COCH_2 = CH_2CO + CH_3$$

Thus a rapid unimolecular decomposition of CH_3COCH_2 radical is the prerequisite for the propagation of a chain. From the two studies mentioned previously, it appears that this radical is stable up to 400°C. Whether it still remains quite stable at 550°C is not known. Nevertheless, a lower limit of activation energy for the decomposition of CH_3COCH_2 radical may be estimated from the results at lower temperature. A comparison of this value with the one necessary for the success of the chain scheme may tell some more about the possibility of such a mechanism.

Inhibition Method

If a minute amount of some compound has a marked inhibiting effect on the rate of homogeneous decomposition of a second compound, then the decomposition of the second compound must take place, at least in part, by chain mechanism. In a chain mechanism a considerable inhibiting effect can be produced by a small amount of foreign substance, if it can react with the chain carrier and destroy it.

NO Inhibition

Most important of the inhibition agents is nitric oxide. Staveley and Hinshelwood (20) discovered that a small amount of nitric oxide can reduce the rate of decomposition of lower members of ethers to a steady limit of only a small fraction of the original value. For instance, 1 mm. of NO was found to be enough to reduce the rate of decomposition of hundreds mm. dimethyl ether to about 6% of its normal value at 540°C, while further increase of NO up to 20 mm. produced no more effect. The nitric oxide was gradually used up but usually only slowly. For example, 2 mm. NO was sufficient for the decomposition of 400 mm. diethyl ether which, in the mean time, reacted at about one third the normal rate. If NO was used up before decomposition was complete, the rate rose rather abruptly to the normal value.

This phenomenon was explained by Hinshelwood on the basis that the ethers decompose by a chain mechanism, and that NO is capable of reacting, hence destroying, the chain carrier with the result that the length of the chain is shortened and the total rate of decomposition decreased.

Hinshelwood, in fact, goes further. He interprets the steady limit obtained as corresponding to an entirely inhibited reaction. This is tantamount to assuming that NO combine with each free radical produced beforeit can react further with other molecules. In case the chains are few but long, the part of the inhibited reaction due to chains would be negligible, and the rate of inhibited reaction would be little different from the rate of rearrangement process.

In table I the reactions which have been tested with NO are listed.

Table I

Substance	Effect of Small Amount of NO	Reference
Hydrocarbons		
Methane	Inhibition	(21)
Ethane	Inhibition	(22)
Propane	Inhibition	(21)
Butane	Inhibition	(23) (24)
Hexane	Inhibition	(21)
Ethers		
Dimethyl	Inhibition	(16)
Methyl ethyl	Inhibition	(16)
Diethyl	Inhibition	(16) (25)
Methyl butyl	Inhibition	(26)
Ethyl propyl	Inhibition	(16)
Dipropyl	Inhibition	(16)
Diisopropyl	Inhibition	(16)
Aldehydes		
Acetaldehyde	No inhibition	(16)
Propionaldehyde	Inhibition	(16)
Butaldehyde	Inhibition	(16)
Chloral	No inhibition	(16)
Ketones		
Acetone	No inhibition	(16)
Methyl ethyl	No inhibition	(16)
Esters		
Methylformate (heterogeneous)	No inhibition	(16)

Table I (continued)

Substance	Effect of Small Amount of NO	Reference
Alcohol		
Methyl	No inhibition	(16)
Cyclic ethers		
Ethylene oxide	Inhibition	(11) (24)
Propylene oxide	Inhibition	(27)
Dioxane	Inhibition	(28)
Miscellaneous		
Iodine-catalyzed decompositions of aldehydes and ethers	No inhibition	(16, Mitchell's unpublished result)
Polymerization of ethylene	Inhibition	(29)
Hydrogenation of ethylene	Inhibition	(29)

The above explanation of function of nitric oxide is substantiated by several more observations:

(1) Mitchell and Hinshelwood (30) observed a reduction of the quantum yield in the photochemical decomposition of acetaldehyde from several hundred to about nearly unity by the addition of nitric oxide with 1 mol nitric oxide used up by about 1 mol of radical produced.

(2) Thompson and Meissner (31) followed the change in the absorption spectrum during reaction of a mixture of NO and dimethyl ether. It was found that the NO bands progressively weakened as ether decompositions progressed and that NH_3 bands appeared. The disappearance of the NO bands paralleled the resumption of normal ether decomposition. Using diethyl ether in a similar experiment, new bands appeared which could be attributed to methyl amine.

(3) The admission of minute amounts of nitric oxide into a stream of ether issuing from a furnace at 800°C inhibits the removal of tellurium mirrors (32).

A quantitave treatment of the NO inhibition phenomenon has been attempted by Hobbs and Hinshelwood (21, 22) and Hobbs (25).

In the case of ethane, the theory is as follows:

Let <u>a</u> be the concentration of the activated ethane molecules which yield radicals, <u>n</u> that of the normal ethane molecules, R that of the radicals or atoms which propagate the chain. In the stationary state:

$$dR/dt = k_1 a - k_2 R^2 n^y - k_5 R(NO) = 0$$

whence

$$R = \frac{-k_5(NO) + \left\{(k_5(NO))^2 + 4k_1 k_2 a n^y\right\}^{1/2}}{2k_2 n^y}$$

The term $k_2 n^y$ allows for the operation of either binary or ternary recombination mechanism, *a* is an unknown function of the ethane concentration, which we will represent approximately by n^x. In addition to the chain reaction there is a rearrangement process the rate of which is $k_3 f_2(n)$ and possibly a surface reaction of rate S. The total rate, V, is $k_3 f_2(n) + k_4 R\, n + S$, it being assumed that the chain propagating reaction is proportional to the product of the ethane and of the radical concentrations.

$$V = S + k_3 f_2(n) + \frac{k_4 n}{2k_2 n^y} \left(-k_5(NO) + ((k_5(NO))^2 + 4k_1 k_2 n^x n^y)^{1/2} \right)$$

When $(NO) = 0$, rate $= V_0$,

$$V_0 = S + k_3 f_2(n) + \frac{k_4 n}{2k_2 n^y} (4k_1 k_2 n^x n^y)^{1/2}$$

Let V_∞ be the limiting value when (NO) is large,

$$V_\infty = S + k_3 f_2(n)$$

whence

$$\frac{V - V_\infty}{V_0 - V_\infty} = ((\gamma(NO))^2 + 1)^{1/2} - \gamma(NO) \qquad (11)$$

where

$$\gamma = c(C_2H_6)^{-(x+y)/2} \qquad (12)$$

When ethane is constant, γ is also a constant, while for different ethane pressures γ varies according to (12).

The mean chain length being measured by V_0/V_∞ is

$$V_0/V_\infty = 1 + K \sqrt{\frac{(C_2H_6)^{2+x}}{(C_2H_6)^y (k_3 f_2(n) + S)}} \qquad (13).$$

For four different pressures of ethane, initial rates were measured with different proportions of NO at 600°C. The relation (11) was found to be obeyed with γ equal to values listed below corresponding to different initial pressures of ethane.

$P_{C_{2H6}}$	57	100	300	454	mm
γ	3.60	2.10	1.15	0.65	

The mean chain length was also found to vary with C_2H_6 as represented by equation (13).

$P_{C_2H_6}$	57	100	300	454	mm.
Mean chain length	9.8	6.5	5.9	4.1	

By comparing the experimental data with these equations it was found that $x=1$, $y=0.66$ yield the best fit. $x=1$ signifies that the rate of production of free radicals is nearly proportional to the concentration of ethane. That $y=0.66$ suggests two possibilities: There may be two independent chain-ending mechanisms, one involving binary collisions and one ternary. The exact expression $k_2 + k_2'(C_2H_6)$ can be made to vary with ethane pressure as well as $(C_2H_6)^{0.66}$ by a suitable choice of the ratio k_2'/k_2. On the other hand, there is also the possibility of a single chain-ending process, the order of which depends upon the pressure. If the time between collisions is comparable with the mean life of the activated association product of the radicals, then it is easy to show that the rate of chain breaking will depend upon the ethane concentration according to an expression of the form $(C_2H_6)/(b+(C_2H_6))$ which can also be represented over the range in question by a fractional power 0.66, if a suitable value of b is chosen.

Equation (11) was found also to be valid for methane, propane and hexane. The mean chain length of each, as in the case of ethane, decreases as the initial pressure increases.

The behavior of diethyl ether is, however, markedly different. Here the $(V - V_{\infty})/(V_0 - V_{\infty})$ vs. p_{NO} curve is the same for all the different initial pressures of ether, while the mean chain length is also independent of pressure within the pressure range 51 mm. to 400mm. at 504°C.

According to Hobbs, this may be explained by assuming the following chain mechanism

(1)	$C_2H_5OC_2H_5 = CH_3 + CH_2OC_2H_5$	k_1
(2)	$CH_3 + C_2H_5OC_2H_3 = C_2H_6 + CH_2OC_2H_5$	k_2
(3)	$CH_2OC_2H_5 = CH_3 + CH_3CHO$	k_3
(4)	$CH_3 + CH_2OC_2H_5 =$ Product	k_4
(5)	$NO + CH_2OC_2H_5 =$ Product	k_5

To make it more general, the large radical $CH_2OC_2H_5$, which is removed by the NO, will be called S; the small radical CH_3, which reacts with the ether, will be called R; and the etherwill be called A. The conditions for stationary state are

$$\frac{d(R)}{d\,t} = k\,(A) + k_3(S) - k_2(R)(A) - K_4(R)(S) = 0$$

$$\frac{d(S)}{d\,t} = k_1(A) + k_2(R)(A) - k_3(S) - k_4(R)(S) - k_5(S)(NO) = 0$$

whence
$$(R) = \frac{-k_2k_5(NO) + ((k_2k_5(NO))^2 + 8k_2k_4(k_1k_5(NO) + 2k_1k_3))^{1/2}}{4k_2k_4}$$

In addition to the chain reaction there is a rearrangement process and possibly a surface reaction, the joint rate of which may be written as k' f(A). The total rate is therefore

$$V = k'f(A) + k_2(R)(A) \quad ,$$

it being assumed that the chain propagating reaction is proportional to the ether and radical concentrations.

$$V = k'f(A) + \frac{k_2(A)}{4k_2k_4}\left(\left((k_2k_5(NO))^2 + 8k_2k_4(k_1k_5(NO) + 2k_1k_3)\right)^{1/2} - k_2k_5(NO)\right).$$

When (NO) = 0, rate = V_0

$$V_0 = k'f(A) + \frac{k_2(A)}{4k_2k_4}\left(16k_1k_2k_3k_4\right)^{1/2} \quad .$$

The rate of the uninhibited chain reaction, $(A)\,(k_1k_2k_3/k_4)^{1/2}$ is thus proportional to the first power of the ether pressure.

V_∞ is the limiting rate when (NO) is large, then

$$V_\infty = k'f(A) \quad , \text{ and}$$

$$\frac{V - V_\infty}{V_0 - V_\infty} = \left((\alpha(NO))^2 + \beta(NO) + 1\right)^{1/2} - \alpha(NO)$$

where $\alpha = (k_2k_5)/4(k_1k_2k_3k_4)^{1/2}$ and $\beta = k_5/2k_3$.

$(V - V_\infty / V_0 - V_\infty)$ is thus independent of the concentration of the ether.

The mean chain length is given by

$$V_0 / V_\infty = \frac{k'f(A) + (A)\,(k_1k_2k_3/k_4)^{1/2}}{k'\,f(A)} \quad .$$

Staveley and Hinshelwood (20) found that the rate of the uninhibited part of the reaction, k'f(A), was of the first order with respect to the ether concentration, so that the above expression shows the mean chain length to be independent of the ether concentration.

It is to be noted that in this connection the real characters of the small and large radicals are not important. It might be, as well, C_2H_5 and $C_2H_4OC_2H_5$. In fact, this type of chain mechanism was first postulated by Rice and Herzfeld (4) to get the first order character of the over-all reaction. An interesting point here is that reaction between NO and the light radical is relatively ineffective. According to Hobbs, it may be due to the greater abundance of the large radical.

Much work has been done to ascertain the product of the reaction between NO and the free radicals. In many pyrolyses inhibited by NO, tests for cyanides in the reaction products have been obtained. In others the presence of NH_3 has been demonstrated. In still other cases, a white solid has been isolated and it has been suggested that this solid was formaldoxime (33, 34, 35).

On the other hand, however, reactions have been followed in presence of NO and no positive tests for cyanides or ammonia were found (36) wherefore decomposition of CH_3NO, the complex postulated, into CH_4, CO, N_2 and H_2O was proposed. Further it has been suggested that the stability of the complex relative to the reactants forming it is small. Echols and Pease (37) suggested that an equilibrium is set up between the complex, NO and radicals in butane pyrolysis even at 520°C.

Thompson and Meissner, from their spectroscopic study mentioned above, suggested formation of formaldoxime might occur between CH_3 and NO and the reaction

$$C_2H_5 + NO = CH_3NH_2 + CO$$

might occur for the ethyl radical.

It may be mentioned in passing that if Hobbs' suggestion that the main reaction of NO is with the heavy radical is true, these respective products may be the direct products of such processes.

The pyrolysis of formaldoxime has been studied by Taylor and Bender (38). It dissociates first into hydrogen cyanide and water which reacts further, but more slowly, to produce chiefly CO and NH_3. According to them, formaldoxime is more satisfactory as the intermediate between methyl group and NO than the isomeric formamide, although isomerization between these two at elevated temperature might occur.

Inhibition by Propylene

The inhibiting action of propylene on thermal decompositions of organic substances was first observed by Rice and Polly.(39) Its effect was explained by them by assuming it to remove some of the active chain propagating radicals R by reaction to give RH and the allyl radical, which combined with itself to form diallyl instead of propagating any chain. The decompositions of propane, n-butane, acetaldehyde, acetone, dimethyl ether, trimethyl amine and ethylene oxide were all found to be inhibited. It would be really interesting if the reported behavior of acetaldehyde and acetone are true, for they both show a negative result toward NO. But, as the authors themselves admit, the measurement of initial rates was not accurate owing to complications arising from the strong catalytic effect of traces of oxygen present as well as the decomposition of propylene itself. The whole issue, therefore, must be viewed with interest but with reserve.

However, inhibition of the decomposition of n-butane by propylene was confirmed by Echols and Pease (40), although the effect was found to be only about one twentith to one thirtith that with nitric oxide.

The phenomenon of inhibition is, in fact, a very general one. Nitric oxide distinguishes itself only because of its particular effectiveness in deactivating the free radicals. But any substance like propylene which can react with the chain propagating radical to form less active radicals would have the effect of inhibition. For example, by virtue of the stability of the CH_2COCH_3 group, acetone acts as an inhibitor in the sensitized decomposition of acetaldehyde by ethylene oxide. (11)

Paneth's Mirror Method of Direct Detection

The most direct method of detecting the existence of free radical is that developed by Paneth and others. It is based upon the ability of the free radicals to combine with the metals such as lead and mercury etc. to form some volatile compounds which can be collected and identified. The nature of free radical combining with the metal can at once be known when the identity of the compound is known. In this way, Paneth and his collaborators (2) first proved in a direct way the existence of free methyl and ethyl radicals. However, the successful detection of these simple free radicals had been restricted to the organic decompositions at high temperatures in which cases their concentrations may be rather high. Recently, radioactive lead has been used to increase the sensibility of this method (41,42).

The modification consists only in measuring radioactivity instead of identifying the metallic compound by chemical means. It was claimed by Burton and others that they had succeeded in this way in establishing the formation of free radicals in the pyrolysis of acetaldehyde at 500°C. This modified method seems to have a great possibility of development. In view of the accuracy of the radioactive measurement, it may not be too much to hope that before long this method will become most useful in measureing the concentration of free radical in organic decompositions.

After free radicals have been shown to be produced in a decomposition, there remains the problem of determining the part they play in generating short or longchains. The number of chains initiated depends upon the free radical producing capacity of the substance. But the length of the chain depends upon the chain propagating capacity of the substance. These two different qualities are by no means always associated. For instance, we have already seen that acetaldehyde can propagate a chain of hundreds in length around 300°C without being able to initiate it in the same temperature region. On the other hand, there are compounds which can produce free radicals readily but cannot act as a medium for chain propagation. A typical example is azomethane. Because of its various interesting aspects we shall discuss this case in some length as a good illustration.

The decomposition of azomethane was first studied by Ramsperger (43) at temperatures between 279° - 330 °C and at pressures from

0.26 - 708 mm.. The reaction is homogeneous and of first order. The rate constant starts to fall down at low pressure.

Heidt and Forbes (44) showed that although the final pressure is always nearly twice the initial pressure, the composition of gaseous product changes steadily with the course of reaction.

Riblett and Rubin (45) studied the reaction at 340°C by an analytical method in different stages of reaction. The main products were found to be nitrogen, methane, ethane and a liquid with a higher carbon-nitrogen ratio than that in azomethane. The percentage of nitrogen and, more markedly, that of methane increases as reaction proceeds, the percentage of liquid decreases, while ethane shows little variation in its percentage. Furthermore, they showed that if the number of moles of each component produced by the decomposition of 100 moles of azomethane is plotted against the percent reaction, the liquid and nitrogen lines are straight and may be extrapolated to yield fifty moles of nitrogen and fifty moles of liquid as the primary products.

The work was extended by Taylor and Jahn (35) who studied the decomposition of azomethane in the temperature range 290°C - 340°C by an analytical method. They confirmed that methane, instead of ethane, is the main hydrocarbon product, and suggested $(CH_3)_2N\ N(CH_3)_2$ to be the liquid in accordance with the approximate value of its composition obtained through carbon and hydrogen balances. The reaction mechanism was considered as consisting of mainly

$$CH_3N=NCH_3 = N_2 + 2CH_3$$

$$CH_3N=NCH_3 + 2CH_3 = (CH_3)_2N\ N(CH_3)_2$$

and the subsequent decomposition of the hydrazine derivative to yield hydrocarbons and other products. The activation energy of the total reaction was found to be 52500 cal..

The supposition that azomethane decomposes into 1 molecule of N_2 and two free methyl groups as the primary step was confirmed by the same authors (46) through the study of azomethane decomposition in presence of large amonnt of NO. The reaction was accompanied by small pressure increase and yielded insignificant quantities of hydrocarbons in the volatile products. This was interpretated as indicating an initial dissociation of azomethane into nitrogen and free methyl groups which for the most part combined with nitric oxide. The energy of activation of azomethane decomposition in presence of NO is the same as that for pure azomethane -- a coincidence suggesting that the same process is the rate-determining step in both cases.

The capacity of azomethane to produce free radicals and its inability to propagate chains are supported by many other studies.

Leermakers (47) and Rice and Evering (48) both demonstrated the presence of free radicals in the azomethane decomposition by the mirror method.

Allen and Sickman (15) found that azomethane can sensitize the decomposition of acetaldehyde.

Leermakers (49) showed that up to 275°C the ethyl radical does not react with azomethane.

Forbes, Heidt and Sickmann (50), in studying the photodecomposition of azomethane, found that up to 260°C the quantum efficiency lies below 2. Davis, Jahn and Burton (34) concluded from the effect of NO on the photolysis that the primary process involves only the formation of a methyl radical and that dissociation by a single act into ethane and nitrogen does not occur. Together, these two seperate facts shows that the methyl radical does not start chains in azomethane.

Of course, the cases of acetaldehyde and azomethane as presented above are extreme ones among various possible combinations and gradations. In every actual case it is necessary to determine whether the chains are short or long after free radicals have been shown to be present.

The most direct way of determining the chain length is to study the quantitative effect upon the substance in question of definite number of free radicals produced among its molecules from the decomposition of other substance either thermally or photochemically. Aside from this, there are a few criteria from which, occasionally, useful information to this end may be drawn.

In a long-chain case the products are practically those given by the chain propagating steps. In a short chain case, the products from both the chain initiating step and the chain ending step are important. Thus a detailed study of the products might be helpful.

If the free radical is of the type which can react with NO, a detailed study of the reaction in the presence of NO and its comparison with normal decomposition should be informative. If the activation energy of the inhibited reaction is far smaller than corresponds to any bond strength in the compound, there must be only a very small fraction of the primary process which leads to the formation of free radicals.

This knowledge, together with the mean chain length would make possible a rough estimate of the true chain length.

In considering here the length of the chain, it is perhaps not out of place to examine the validity of Hinshelwood's assumption that the inhibited process corresponds to an entirely non-chain process. There is ample evidence to show that the ability of nitric oxide to combine with methyl, ethyl and, perhaps, some other radicals makes it capable of reducing the chain length to a very small value. However, evidence also exists to indicate that the chain may still propagate a few steps before the chain carrier is caught up by nitric oxide. Jahn and Taylor (51), in studying the decomposition of azomethane in the presence of large amounts of nitric oxide, found that there was still appreciable reaction of methyl radicals with azomethane, the upper limit of the ratio of nitric oxide to azomethane reacting being about 2. This is not difficult to understand. The reaction of nitric oxide and methyl radicals, presumably, involves also an activation energy of a few kilocalories. As the activation energy of this association reaction must be also very low, it is natural that part of the methyl radicals would react with azomethane rather than with nitric oxide. The same situation should be expected to exist in other NO inhibition cases, since the activation energies of radical-molecule reactions are, in general, quite low. Thus it is quite probable that the inhibited reaction still involves chains of few steps. When the chains are long, this part would be negligible, and in such cases Hinshelwood'S approximation is essentially correct. When the chains are short, however, serious error may be involved in the approximation.

Therefore, before the relative extent of chain process and rearrangement can be fixed by this method, a knowledge about the length of the chain is necessary.

On the experimental side, the ultimate solution of a thermal decomposition problem is only considered to be reached when we know all about the individual process involved, — not only the chemical changes invovled but also the rate equations governing them.

In fact, because of the experimental difficulty, except for a few simple rearrangement processes, by far the majority of studies of organic compound decompositions is still far short of such a goal.

Among all groups of organic compounds the aliphatic ether group is one of the few which have recieved extensive studies. As the present research is concerned with the thermal decomposition of vinyl ethyl ether, which is different in type from the ethers formerly studied on account of its double bond, it seems necessary to make a review of the kinetic studies that have been made upon the aliphatic ethers, It serves not only for drawing comparison with the results of the present study, but also helps to illustrate how inadquate our general knowledge still is even in such an extensively studied series.

Comparatively well studied among the ethers are dimethyl-, diethyl- methyl ethyl- and methyl butyl ether. The review will be confined to mainly these compounds. However, the case of divinyl ether will be added to the list because of its particular character in possessing two double bonds.

Thermal Decomposition of Dimethyl Ether

This reaction has been studied over the temperature range 400 - 600°C (5). It is a first order reaction, yeilding CH_4, CO and H_2 as the final products. Formaldehyde was found to be the intermediate. Thus the main changes are

$$CH_3OCH_3 = CH_4 + HCHO$$
$$HCHO = CO + H_2 \quad .$$

It was found that the ratio of the amount of formaldehyde to the initial amount of ether is independent of the initial pressure, and only dependent upon the percentage decomposition of the ether. The relation can only be understood if the decomposition of formaldehyde is also of the first order. Kassel (51) calculated from the experimental data that the rate constant for the decomposition of formaldehyde was five times that for the ether.

The reaction rate begins to fall when initial pressure goes below 350 cm.. Since the rate constant does not fall during the course of a run, the product must play some part in the activation process. It has been shown by Hinshelwood that nitrogen, helium, carbon monoxide and carbon dioxide have very small activation effect. Therefore, the activation can only be due to hydrogen. This inference was verified by separate experiments in the presence of hydrogen. The rate constant at in finite pressure, k_∞, obtained by extrapolation of $1/k - 1/p$ curve, conforms to the following equation:

$$k_\infty = 1.55 \cdot 10^{13} \cdot 10^{-58500/RT} \text{ sec.}^{-1} \quad .$$

Increase in surface decreases the reaction rate. Hinshelwood and Askey found that the rate in a silica bulb half-filled with powdered silica was appreciably lower than that in an empty bulb. At about 535°C and 175 mm. initial pressure, the decrease was about 14 %. Pease (52), using two pyrex tubes, one empty and the other filled with 5 mm. pyrex chips coated with potassium chloride, also found 11.5 % decrease in rate of pressure increase in packed bulb at 481°C. He considered this as evidence of the presence of chains in dimethyl ether decomposition.

Strong confirmation of the existence of a chain process came form NO inhibition work. Staveley and Hinshelwood (53) found that 1 mm NO reduced the initial rate of ether decomposition to a small fraction of the normal value which was not changed by further addition of NO up to 20 mm. partial pressure. As previously discussed, this phenomenon was attributed to the chain character of the reaction, and the consistent value of the minimum rate was assumed to correspond to a fully inhibited reaction. The mean chain length, defined as the ratio of normal rate to fully inhibited rate, was about 17 at 565 °C. The activation energy of the fully inhibited reaction was found to be 62000 cal..

The above postulated scheme of chemical change as well as the inhibiting effect of nitric oxide was confirmed in detailed analytical work of Gay and Travers (54). This method of study consisted of enclosing a definite amount of the ether in a glass bulb, which was heated rapidly to the temperature desired and maintained at that temperature for a definite period of time, after which the bulb was cooled rapidly to arrest the reaction and the content taken out for analysis. Two experiments with pure dimethyl ether were carried out by them at 490°C at concentration corresponding to 0.04 gram mols per liter. The reaction tubes were heated for 15 and 45 minutes respectively, when the amount of decomposition corresponded to 48 and 92 % of the dimethyl ether present. The following tables record their results

Table II (in gram moles per liter)

	Sample I			Sample II		
	C	H	O	C	H	O
$(CH_3)_2O$	0.08000	0.24000	0.04000	0.08000	0.24000	0.04000
H_2	-----	0.02476	------	------	0.06180	------
CO	0.01381	------	0.01381	0.03454	------	0.03454
CH_4	0.01813	0.07252	------	0.03525	0.14100	------
$(CH_3)_2O$ (unreacted)	0.04156	0.12468	0.02078	0.00645	0.02529	0.00321
CO_2	0.00039	------	0.00078	0.00027	------	0.00054
C_2H_4	0.00026	0.00078	-------	0.00022	0.00066	-----
Non-volatile at -80°C	0.00570	0.01156	-------	0.00332	0.00904	------
Unaccounted for	0.00015	0.00570	0.00463	0.00003	0.00221	0.00171

Table II (g.mol per li.)

	I	II
CH_4	0.01813	0.03525
$(CH_3)_2O$ decompd.	0.01922	0.03678
Difference	0.00109	0.00153

Table III (g.mol. per li.)

	I	II
CO	0.01381	0.03454
H_2	0.01238	0.03093
Difference	0.00142	0.00361

Many other experiments were made with packed and unpacked bulbs. In all these experiments the amounts of carbon monoxide and hydrogen were always found to be approximately the same. The rate of decomposition of the ether, as determined from the amount of methane formed, was found to be much slower in packed bulbs than in unpacked bulbs.

The results of some typical experiments with ether-NO mixture are listed in the following table.

Table V

T 520°C Initial $(CH_3)_2O$ 0.00458 g.mol/liter . t 15 minutes.

Serial	NO(initial)	NO(final)	H_2	CO	CH_4	CO_2	Final $(CH_3)_2O$
1	0.00000	0.00000	0.00203	0.00216_5	0.00250	0.00006_5	0.00233
2	0.00005_5	------	------	0.00011	0.00014	0.00004_5	0.00442
3	0.00015	-------	-------	0.00003_5	0.00015	0.00001_5	0.00441
4	0.00026	0.00011	0.00003_5	0.00005	0.00014	0.00005	0.00451

The above results establish the chemical changes that take place, and that a large part of the decomposition takes place by a chain mechanism. The effect of increased surface indicates that the chain may be quite long. Very little is revealed, however, about the mechanism of the chain process. Much light was thrown upon this aspect by Leermakers' study of chain decomposition of dimethyl ether photosensitized by acetone (17). The reaction was followed by the amount of methane produced which was, in turn, obtained by substracting from the amount of non-condensable gas twice the volume of CO found. At temperature range 160 - 400°C, the following equation was found to hold

$$\frac{d\,(CH_4)}{d\ t} = k\sqrt{\frac{I_{abs.}}{(CH_3)_2CO}}\,(CH_3OCH_3)$$

where $I_{abs.}$ is the product of the incident light intensity and the fraction of light absorbed by acetone, and $k = 7.3 \cdot 10^{3} e^{-16000/Rt}$ $\mathrm{moles}^{1/2} \mathrm{einst}^{-1/2}$ sec^{-1}. The quantum yield of methane production or what was assumed to be the equivalent of ether decomposition, was as high as 230 at 400°C for experiments of lowest light intensity and was about 11 at 270°.

For the detail mechanism, Leermakers suggested the following scheme

$$
\begin{array}{rcllll}
CH_3COCH_3 + h\nu & = & CH_3 + CH_3CO & (1) & & \\
CH_3CO & = & CH_3 + CO & (2) & & \\
CH_3 + CH_3COCH_3 & = & CH_4 + CH_3COCH_2 & (3) & Q_3 & 20\ \mathrm{kcal.} \\
CH_3 + CH_3OCH_3 & = & CH_4 + CH_3OCH_2 & (4) & Q_4 & 15\ \mathrm{kcal.} \\
CH_2OCH_3 & = & HCHO + CH_3 & (5) & Q_5 & 35\ \mathrm{kcal.} \\
CH_2COCH_3 + CH_3OCH_3 & = & CH_3COCH_3 + CH_3OCH_2 & (6) & Q_6 & 20\ \mathrm{kcal.} \\
CH_2OCH_3 + CH_2COCH_3 & = & X & (7) & Q_7 & 10\ \mathrm{kcal.}
\end{array}
$$

The activation energy values were chosen to justify the following approximations: $I_{abs.}$ is small compared to $k_3(CH_3)(CH_3OCH_3)$, $k_6\ (CH_2COCH_3)\ (CH_3OCH_3)$ and $\dfrac{k_5 k_6\ I_{abs.}\ (CH_3OCH_3)}{k_3 k_7 (CH_3)\ (CH_3COCH_3)}$;

and $k_4(CH_3OCH_3)$ is large compared to $k_3(CH_3COCH_3)$. The choice of (7) as a chain ending process was made because it led to the right rate expression. The final expression for the rate of decomposition of dimethyl ether is

$$
-\frac{d(CH_3OCH_3)}{d\quad t} = \sqrt{\frac{k_4 k_5 k_6}{k_3 k_7}\ \frac{I_{abs.}}{(CH_3COCH_3)}}\ (CH_3OCH_3) + \sqrt{\frac{k_5 k_3 k_6}{k_4 k_7} I_{abs.} (CH_3COCH_3)},
$$

the second term on the right side of the equation being negligible. Considering only the first term, and assuming with Rice and Herzfeld (4) that the coefficient of the exponential in first order reactions is 10^{14} and in second order reaction is 10^{13}, we have

$$k = \sqrt{\frac{k_4 k_5 k_6}{k_3 k_7}} = 10^{7} e^{-20000/RT}$$

whereas the experimental value is $k = 10^{4} e^{-16000/RT}$.

From this it can be concluded that the chain in the normal dimethyl ether decomposition must be very long. As the mean chain length is only about 17 at 565°C, it is probable that only a small fraction of the inhibited reaction results in the production of free radicals, the major part of it being a rearrangement process.

A very interesting point here is the way in which the formaldehyde decomposes. Fletcher and Rollefson (11), on strength of the fact that the decomposition rate of formaldehyde as an intermediate in this reaction is fifteen times as great as that of pure formaldehyde, suggested that formaldehyde was decomposed here by a sensitized reaction in the presence of free radicals produced by the ether. This explanation has been rendered of quite doubtful value by an interesting study made by Steacie and Alexander (55). They decomposed mixtures of deutero-acetone and ordinary dimethyl ether at 590°C. If the decomposition of formaldehyde is not a chain process, the hydrogen obtained should be all light. On the other hand, if formaldehyde decomposes through a radical mechanism such as

$$R + HCHO = RH + CHO$$

$$CHO = H + CO \quad ,$$

then as the hydrogen atom must have a good chance of extracting a deuterium atom from the deutero-compound and the hydrogen gas obtained should have a high content of deuterium. In fact, they found that within an experimental error of about 2 % the hydrogen from the mixture was entirely light. This result rather indicates that the higher rate of decomposition of formaldehyde as an intermediate in dimethyl ether decomposition is not due to the action of free radicals, but may be due to the presence of some energy chains.

Thermal Decomposition of Diethyl Ether

Since the first work by Hinshelwood in 1927 (56), the thermal decomposition of this ether has been repeatedly studied by various investigators.

The reaction at normal pressure i.e. around and below 1 atm. may be considered first. It is essentially homogeneous and is inhibited by nitric oxide. Aldehyde was found as an intermediate product. Davoud and Hinshelwood (57), working with ether at 300 mm. both pure and in the presence of 5 mm. NO at 547°C, found that in both cases the amount of aldehyde increased at first with time, passed through maximum, and then decreased. The maximum for the inhibited reaction appears in a later period than that for the normal reaction. The rate of decomposition of aldehyde in both cases can be inferred from the curve. The ratio of rates thus inferred at corresponding pressures of aldehyde withand without nitric oxide is 2.9 .

Fletcher and Rollefson (58), however, carried out quantitative estimation of both formaldehyde and acetaldehyde at 507° and 552°C for an initial pressure of 200 mm. and at 552° for an initial pressure of 20 mm. Their results on total aldehydes are similar to those of Davoud and Hinshelwood, but the amount of formaldehyde was found in each case to constitute from 20 - 25 % of the total aldehyde.

The results of gas analyses from these two separate studies are as follows:

Fletcher and Rollefson

p_o 200 mm. T 507 °C

$\Delta p / \Delta p_\infty$	Hydrocarbon % Unsat.	Hydrocarbon % Satd.	H_2 %	CO %	Pressure increase %
0.05	7.6	77.4	7.4	7.6	10
0.075	10.0	74.8	7.0	8.2	15
0.25	9.5	68.2	5.3	17.0	50
0.40	8.5	68.5	4.0	19.0	80
0.50	10.5	60.9	4.3	24.3	100
0.90	8.5	57.9	4.3	29.3	180

Davoud and Hinshelwood

p_o 300 mm. T 547°C

Pressure increase %	CO_2	O_2	C_2H_4	CO	H_2	$CH_4+C_2H_6$	Ratio $\frac{CO_2}{Gas}$ on combustion
25	1.9	1.9	8.4	24.1	3.1	60.6	1.38
35	0.7	1.5	8.1	23.7	6.2	59.8	1.24
50	0.9	1.7	6.9	27.8	4.0	58.7	1.41
60	0.6	0.6	4.4	29.4	5.2	59.8	----
75	0.9	1.6	5.0	26.1	2.7	62.7	1.47
85	0.8	0.4	5.6	29.0	6.2	58.0	1.31
100	1.1	1.6	8.7	28.6	6.5	53.5	1.35

(continued)

Pressure Increase %	CO_2	O_2	C_2H_4	CO	H_2	$CH_4+C_2H_6$	Ratio $\frac{CO_2}{Gas}$ on combination
110	0.5	0.8	5.1	31.4	3.6	58.6	1.31
125	0.8	0.6	4.3	33.1	3.4	61.8	1.38
135	0.3	0.2	4.0	32.0	4.9	58.6	1.37
150	0.0	2.2	6.2	32.5	4.9	54.2	1.36

p_o 300 mm. T 547°C p_{NO} 5 mm.

Pressure Increase %	CO_2	O_2	C_2H_4	CO	H_2	$CH_4+C_2H_6$	Ratio $\frac{CO_2}{Gas}$ on combination
19.8	1.7	1.5	20.6	25.2	4.8	46.1	1.41
30.6	1.8	2.2	16.5	25.5	3.7	49.7	1.45
41.0	1.5	1.8	15.0	24.8	3.8	53.1	1.30
49.8	1.7	2.1	12.9	24.5	3.7	55.1	1.26
60.4	2.1	1.7	8.6	29.7	4.5	53.4	1.40
70.2	1.8	1.0	7.4	30.3	3.1	56.4	1.43
80.0	1.4	1.0	6.6	32.6	2.4	56.0	1.35
90.1	1.7	2.3	5.6	31.0	3.1	56.3	1.47
100	1.3	0.6	4.5	32.2	3.2	58.2	1.45
110	0.9	0.5	6.0	32.8	3.6	56.2	1.33
120	1.4	0.6	6.8	31.2	3.7	56.3	1.38
130	1.5	0.6	7.7	34.3	3.2	52.7	1.40
1.40	0.9	1.2	8.0	34.2	3.4	51.5	1.43

Davoud and Hinshelwood proposed the following equations to represent the change:

(1) $C_2H_5OC_2H_5 = CH_3CHO + C_2H_6$

(2) $C_2H_5OC_2H_5 = CH_3CHO + C_2H_4 + H_2$

(3) $CH_3CHO = CH_4 + CO$

(4) $C_2H_5OC_2H_5 = 2C_2H_4 + H_2O$ (Surface reaction) .

(1) and (3) are the major changes, (2) is postulated to account for the presence of H_2 and C_2H_4, and (4), considered as a surface change, is postulated to account for the disparity between the amounts of H_2 and C_2H_4. They postulated reaction (4) as a surface reaction since , when the surface of the reaction vessel was poisoned by a carbonaceous film obtained by decomposing acetone vapor at 800°C, the amount of ethylene formed was found to be appreciably decreased.

Fletcher and Rollefson, on the other hand, postulated a different set of minor changes. Their scheme is

(1) $C_2H_5OC_2H_5 = CH_3CHO + C_2H_6$

(3) $CH_3CHO = CH_4 + CO$

(5) $C_2H_5OC_2H_5 = C_2H_4 + CH_4 + HCHO$

(6) $HCHO = H_2 + CO$.

Although the scheme of Davoud and Hinshelwood must have some deficiency for failing to take account of the presence of HCHO. It appears that Fletcher and Rollefson's scheme also is not satisfactory, since their scheme indicates that

$$(CH_4) - (C_2H_4) = (CO) - (H_2)$$

which is, however, far from being the case according to Davoud and Hinshelwood's results.

The difficulty involved in clarifying these minor reactions is immediately apparent. The accuracy of present experimental methods used in the analysis of small amounts of complex organic mixture is, in general, poor. Furthermore, if the minor reaction is of heterogeneous nature, it is even difficult to reproduce the change. With a meagre experimental information in hand, it is naturally very difficult to decide upon the right course of minor reactions among numerous plausible alternatives.

That a chain mechanism is involved in the reaction is borne out by the following facts:

(1) The rate of decomposition of acetaldehyde as an intermediate is greater than in the pure state (58).

(2) The aldehyde, as an intermediate in the ether decomposition, decomposes slower in presence of nitric oxide (57).

(3) The decomposition of the ether is inhibited by nitric oxide (20).

(4) The decomposition of acetaldehyde is accelerated by the presence of small amount of ether (58).

(5) This sensitized decomposition is inhibited by nitric oxide (57).

Kinetically the first order constant rises with pressure and approachs a limiting rate around 600 mm. or higher. The addition of hydrogen at lower pressures of ether restores the rate to what it would be at higher partial pressures.(58) The effect of deuterium is uncertain (59).

The dependence of the reaction rate upon the ether pressure is nearly the same for the NO inhibited reaction as for the uninhibited reaction. The same effect of hydrogen is also observed here as in the uninhibited case.(20) It is thus evident that the fall of rate with decrease in initial pressure has little to do with the chain character of the reaction, but is due to the failure to attain Maxwell-Boltzmann equilibrium concentration for the activated species by collisional activation.

There is quite a range among various activation energy values determined by different workers. This is partly due to the different ways in which the rate constant of the ether decomposition is taken, and, of course, partly due to the unavoidable experimental error.

Activation Energy for Uninhibited Reaction

Activation Energy	Method of Determination	Author
62,000 cal.	Initial rate of pressure change	Rice and Sickmann (60)
58000 cal.	Aldehyde factor corrected	Fletcher and Rollefson (58)
53,000 cal.	50 % pressure increase	Hinshelwood (56)

Activation Energy for NO INhibited Reaction

Activation Energy	Method of Determination	Author
67,000 cal.	Pressure change	Staveley and Hinshelwood (20)
62,000 cal.	Aldehyde corrected	Davoud and Hinshelwood. (59)

Our knowledge about the extent and character of the chain part is comparatively meager, but may be briefly outlined.

(1) An estimate of the concentration of free radicals has been made by Davoud and Hinshelwood (57). From 300 mm. ether at 546°C, the maximum pressure of aldehyde formed was 60 mm., and the rate of decomposition of this aldehyde in presence of ether alone was 2.9 times as great as at the corresponding pressure in presence of ether and NO. It is assumed that

the increased rate is caused by free radicals from the ether, there being good evidence that none is due aldehyde itself. Thus the rate of the radical-catalyzed reaction is 1.9 times the normal rate, found at this pressure to be 1.85 mm. / sec.. The number of molecules reacting per c.c. per sec. is $4.2 \cdot 10^{15}$. It is assumed equal to the number of collisions between aldehyde molecules and free radicals, multiplied by $e^{-E/RT}$, where E is the activation energy for the reaction between acetaldehyde and free radicals, known from the study of the photochemical reaction of CH_3CHO at 300 - 400°C to be 9700 cal.. At 60 mm. and 540°C, the number of collisions between acetaldehyde molecules and radicals is $4,5 \cdot 10^8 n_1$, where n_1 is the number of radicals per c.c.. According to the assumption made $4.5 \cdot 10^8 n_1 e^{-9700/1.98 \cdot 813} = 4.2 \cdot 10^{15}$ whence $n_1 = 3.6 \cdot 10^9$, which is equivalent to $1.35 \cdot 10^{-10}$ gram mol /li.. It is pointed by the authors that there are two sources of uncertainty. First, some of the aldehyde might be formed in an activated condition, decomposing immediately. Secondly, the value of E derived from the photochemical experiments depends upon the assumption that there is no appreciable activation energy for the combination of two free radicals, which is nearly, but may not be quite true.

(2) The sensitized decomposition of diethyl ether by ethylene oxide has been studied by Fletcher and Rollefson (11).With a mixture containing 5 % of ethylene oxide the initial rate at 441°C for an ether pressure of 180 mm. was increased by a factor of twenty, and the reaction went 82 % toward completion. If the chain length of the ethylene oxide-catalyzed reaction is not very different from that of the chains in the normal ether decomposition , it is apparent that the proportion of free radicals produced

directly from ether is only about one four hundredth of the proportion from ethylene oxide: Considerably less than one ether molecule in a thousand, therefore, forms a free radical.

Now the mean chain length at 550°C is about 3.7 (59). If the fully inhibited reaction corresponds practically to the rearrangement process, the chain part in the normal reaction would be (3.7 - 1)/ 3.7, i.e. 73 % of the total reaction.

Viewing these two pieces of information together, it may be inferred that the chains propagated in the ether decomposition are quite long.

The mechanism of the chain part of the ether decomposition into ethane and acetaldehyde has been postulated as:

(1) $C_2H_5OC_2H_5 = CH_3 + CH_2OC_2H_5$
(2) $CH_3 + C_2H_5OC_2H_5 = C_2H_6 + CH_2OC_2H_5$
(3) $CH_2OC_2H_5 = CH_3CHO + CH_3$
(4) $CH_2OC_2H_5 + CH_3 = R$

It yields the correct products and gives the correct first order for the chain part. But it is easily seen that the same conditions may be fulfilled by suitable variation of the above scheme. The primary chain initiating step may be carbon-oxygen split instead of carbon-carbon split. In the reaction of methyl or ethyl radicals with ether, the free radical may simply take one hydrogen atom away from the ether instead of breaking the carbon-carbon bond as postulated in the above scheme. The bond energies of carbon-carbon and carbon-oxygen do not differ largely from each other. It may be that in the primary process both carbon-carbon and carbon-oxygen splits take place. As to the propagating process, it appears theoretically that an attack upon the well-shielded carbon-carbon linkage by the free radical is quite unlikely as compared with an attack upon the outer carbon-hydrogen linkage (61).

It is interesting to note that same indication can be obtained from a comparative study of the deutero-compound and hydrogen compound. According to Davoud and Hinshelwood (59), the rate of decomposition of H-ether is about twice that of the D-ether, but the mean chain length of D-ether is smaller than that of H-ether. Thus the chain part of the H-ether is more than twice as fast as the chain part of the D-ether. Since the primary process of the chain reaction depends upon the breaking of a carbon-carbon or a carbon-oxygen bond and is, therefore, unlikely to be much slower for the deuterium compound, the observed results probably means that the introduction of deuterium slows down some later stage in the chain process. This is consistent with the idea that one of the chain steps involves complete rupture of a carbon-hydrogen or carbon-deuterium bond.

Newitt and Vernon (62) studied ether decomposition around 490°C at pressures between 2.95 atm. and 13.8 atm.. Both HCHO and CH_3CHO were found to be present in the products in quantities depending upon the initial pressure of the ether and upon the stage of decomposition at which the reaction was arrested. In individual experiments aldehydes appeared in considerable quantities at a very early stage, increased to a maximum, and thereafter diminished slowly. The main gaseous products were CO, C_2H_4, C_2H_6 with small amounts of C_2H_4 and H_2. The velocity constants for different initial pressures followed a relation of a higher order than the first.

The higher pressure range was further extended by Steacie and others (63, 64) to as high as 280 atm.. The reaction was found homogeneous. The reaction rate as determined both by pressure change and analytical results still showed an increase with the initial pressure. The rate at 280 atm. was found to be far greater than the limiting rate extrapolated from the runs at normal pressures. It seems probable that an entirely different process of activation may be operative in such widely different pressure ranges. The products were mainly the same as in low pressure works, although certain condensation processes were favored by increase in pressure as indicated by a decrease in the percentage pressure increase at the end point.

Thermal Decomposition of Methyl Ethyl Ether

The reaction was first studied by Hinshelwood and Glass (65), and later by Steacie (66), by Ure and Young (67), and by Rice, Walters and Ruoff (68). The reaction rate obtained by Hinshelwood and Glass has been shown to be considerably faster than normal on account of the catalytic effect of a minute amount of iodine compound introduced during the preparation. Therefore only the later studies need to be considered.

Steacie measured the times for 25 % pressure increase at temperature range from 460 - 560°C under different initial pressures. This value t_{25} increases with decrease in initial pressure. By extrapolating the t_{25} - $1/p$ curve and by putting k_∞ equal to 0.30 times $(t_{25})_\infty$, obtained from the extrapolation, he obtained

$$k_\infty = 3.36 \cdot 10^{12} e^{-54500/RT} \text{ sec}^{-1}.$$

Some analytical work was done by Ure and Young. Their results on the composition of the products both at completion of reaction and at partial decomposition are listed in the following tables.

Products of the Thermal Decomposition of Methyl Ethyl Ether at Complete Reaction

Temp. °C	Ether sample	Percentage CO_2	Unsat. C_2H_4	O_2	CO	H_2	CH_4	C_2H_6
509	2	2.2	4.0	0	28.3	5.7	53.8	2.0
510*	3	0	0	1.0	33.3	1.1	55.7	4.7
456	4	0	4.0	0.8	30.8	4.0	55.6	4.7
457	5	0	5.1	0.8	33.1	8.4	45.2	6.6
487	5	2.9	0.7	0.7	31.8	9.8	52.7	4.4
509	5	0.2	1.8	0.5	32.0	9.4	50.5	5.6

* packed bulb

Products of the Partial Decomposition of Methyl Ethyl Ether

Temp. °C	Ether sample	Percentage CO_2	Unsat. C_2H_4	O_2	CO	H_2	CH_4	C_2H_6
400	5	0	6.8	1.0	32.2	5.1	37.9	11.6
486	5	0	1.7	0.6	31.2	7.5	52.5	7.9
507	5	0	4.5	1.2	38.7	8.3	41.2	32

Acetaldehyde and formaldehyde were both detected in the products. The amount of latter was always much smaller than that of the former. The following sheme was proposed for the over-all reaction.

$$CH_3OC_2H_5 = CH_3CHO + CH_4$$

$$CH_3CHO = CH_4 + CO$$

$$CH_3OC_2H_5 = HCHO + C_2H_6$$

$$C_2H_6 = C_2H_4 + H_2$$

$$HCHO = H_2 + CO$$

$$C_2H_4 + H_2 = C_2H_6$$

The first two steps constitute the major changes, the others being minor. Work with nitric oxide (53) gave result indicating that chains are involved in this decomposition. The mean chain length at 570°C is 7.5. The activation energy of the inhibited reaction is 62 kcal.

Rice, Walters and Ruoff (68) also found considerable amount of aldehydes in the decomposition product of this ether at 448°C and 473°C.

These authors, in addition, have studied the sensitized decomposition of methyl ethyl ether by methyl radicals from azomethane. The experiments were carried out at 300°C where normal decomposition of this ether is negligible. Their results are as follows:

Experiment 4

Temp. °C	Vol. ether c.c. N.T.P.	Vol. azomethane c.c. N.T.P.	% azomethane	Initial pressure mm.	% Pressure increase	Time min.
297	3351	19.1	0.57	473.5	10.4	92

Result of distillation, using Podbielniak column, and analysis of products c.c. at N.T.P.

CO	H_2	CH_4	C_2H_4	C_2H_6	$CH_3OC_2H_5$
124.7	44.3	34.7	10.2	94.4	2878

[a] Ether decomposed 3351 - 2878 = 473 cc. at N.T.P. .

[b] From the above data it was estimated that there were about 400 cc. (at NTP) of aldehyde and higher boiling compounds that were not decomposed.

Experiment 5

Temp. °C	Vol. ether c.c. NTP	Vol. azomethane c.c. NTP	% azomethane	Initial pressure mm.	% Pressure increase	Time min.
300	2884	102.3	3.43	426.0	55.8	280

Results of distillation and analysis of products cc. at NTP

CO	H_2	CH_4	C_2H_4	C_2H_6	$CH_3OC_2H_5$
630	132	1347	5.9	264	1553

[a] Ether decomposed 2884 - 1553 = 1331 cc. at NTP .

[b] From the above data, it was estimated that there were about 600 cc. (at NTP) of aldehydes and higher boiling point compounds that were not decomposed.

Both acetaldehyde and formaldehyde were found to be present. Assuming that each molecule of azomethane gives two methyl groups, the number of ether molecules decomposed by the addition of each radical in exp. 4 is 17 and in exp. 5 is 7. It may be mentioned that these experiments were performed by Rice, Walters and Ruoff chiefly to test the probability of the reaction

$$CH_3 + CH_3OC_2H_5 = CH_3OCH_3 + C_2H_5$$

i.e. the probability of a free radical attacking the bonded oxygen atom.

Actually, they found no break, even no trace of inflection, in the distillation curves at the boiling point (-24°C) of dimethyl ether. From the accuracy of this method as found from the blank runs, they concluded that not more than 5 % of the methyl ethyl ether decomposed in experiment 5 or 10 % in experiment 6 could have changed into dimethyl ether.

It is plainly seen that the chemical changes taking place in the sensitized decomposition are very much the same as these in the normal decomposition. Therefore, very probably same chain mechanism operates in the sensitized decomposition case and in the chain part of the normal decomposition.

Thermal Decomposition of Methyl n-Butyl Ether

A detailed study of decomposition of methyl n-butyl ether was made by Magram and Taylor (26). The reaction was found to be essentially homogeneous, 10 % of the reaction being, however, due to heterogeneity. It was approximately first order above 200 mm. pressure and 3/2 order in the range from 25 to about 100 mm. pressure. They made analysis of the gaseous products at different stages of reaction. The data recorded in the following table are part of their results.

p/p_i	T°C	% of total condensed at -80°C	% in KOH	Percentage in Gases					Remarks
				C_2H_4	CO	H_2	CH_4	C_2H_6	
1.18	480	81.1		32.8	7.1				
1.35	510	72.0		32.0	10.5	9.0	27.8	20.2	

p/p_i	T°C	% of total condensed at -80°C	% in KOH	Percentage in gases					Remarks
				C_2H_4	CO	H_2	CH_4	C_2H_6	
1.41	520	69.8	1.3	31.1	14.9	9.4	27.0	16.5	(287 mm ether 4.3 mm NO
1.70	509	53.0	0	29.3	10.4	7.0	30.0	23.5	
2.00	506	---	1.5	30.2	18.8				large surface
2.40	464	11.4	0.6	26.8	21.2	7.1	29.2	17.8	
2.40	520	----	0.7	25.3	22.6	6.7	29.5	14.0	(287 mm ether 2.3 mm NO
3.00	551	8.8	0.3	23.2	24.1	9.0	27.3	16.2	
335	501	---	0.7	8.0	26.0	3.5	26.0	36.0	30 hours

In the liquid part of the product, formaldehyde and butyraldehyde were found to be present, while negative results were obtained for tests of methyl alcohol, acetaldehyde and, in general, any compound containing CH_3CO- group.

Magram and Taylor suggested the following two simultaneous over-all changes to account for the products obtained

$$(1)\quad CH_3OC_4H_9 = HCHO + C_2H_4 + C_2H_6$$

$$HCHO = H_2 + CO$$

$$(2)\quad CH_3OC_4H_9 = CH_4 + C_3H_7CHO$$

$$C_3H_7CHO = C_2H_4 + CH_4 + CO$$

The amount of C_2H_4 is higher than this scheme can account for. It was proposed by them that the deviation may be caused by the 10 % heterogeneity.

Chain processes are involved in the decomposition since the reaction is inhibited by nitric oxide (26). The mean chain length at 536°C is 5.0. The following chain mechanisms were proposed.

$$R + CH_3OC_4H_9 = RH + CH_2OC_4H_9$$

$$CH_2OC_4H_9 = HCHO + C_4H_9$$

$$C_4H_9 = C_2H_4 + C_2H_5$$

$$R + C_4H_9OCH_3 = RH + CH_3CH_2CH_2CHOCH_3$$

$$CH_3CH_2CH_2CHOCH_3 = CH_3CH_2CH_2CHO + CH_3$$

$$R + C_3H_7CHO = RH + C_3H_7CO$$

$$C_3H_7CO = CO + C_3H_7$$

$$C_3H_7 = C_2H_4 + CH_3$$

The energy of activation calculated from rate constants of initial stage was found to be 56.6 kcal. from 10 to 100 mm. and 540 kcal. at pressures above about 200 mm..

Thermal Decomposition of Divinyl Ether

The thermal decomposition of divinyl ether has been studied by Taylor (69) at temperatures between 460° and 500°C, and at pressures from 30 to 1000 mm.. The reaction was shown to be very complex in nature. Increase in surface produced little effect at the highest pressures, but decreased the rate considerably in the lowest pressure range. Added nitrogen gave an interesting effect. For pressures of the ether around 100 to 200 mm. even twice that amount of nitrogen had relatively small effect. At higher ether pressures a considerably smaller amount of nitrogen caused a marked reduction in the initial decomposition rate.

The initial reaction rate decreased with the pressure. The log P - log k curve was concave upward in the lower pressure side and concave downward in the higher pressure side with a point of inflection between. The energy of activation calculated from initial rates increased with increased pressure. Around 30 mm. it was found to be 47000 cal.; at 100 mm. 50000 cal. while at 300 mm., 51000 cal..

Taylor concluded from these results that the reaction was a complex chain mechanism and suggested the chain carrier to be deactivated in the gas at high pressure but deactivated on the wall at low pressure.

A few analyses were also made. A small amount of liquid divinyl ether sealed in a small bomb and completely decomposed at 450°C. The resulting gases were then analyzed. The decomposition resulted in dark brown deposit in the bomb, but there were no signs of free carbon. A few drops of a colorless liquid were present which possessed an odor suggesting a paraffin hydrocarbon which volatilized around 70°C. A carbon-hydrogen balance from the gas analyses gave an end product with the formula $CH_{1.5}$. The data for the analyses are given in the table below. Included in the table are the analyses made in some dynamic experiments, the effluent gases from the furnace being bubbled through water to remove soluble products including unchanged ether, and the gas being collected over water. Ketene was found to be present in the effluent gas.

Decomposition Products of Divinyl Ether

	Complete decomposition (percentage)	Partial decomposition		
	450°C	450°C	475°C	500°C
CO	60.3	89.6	89.0	86.4
C_2H_2	1.6	1.5	1.4	1.6
C_2H_4	7.1	2.9	3.3	3.0
CH_4	17.1	3.8	4.0	5.0
C_2H_6	13.9	2.2	2.2	3.9

Decomposition of divinyl ether was found by Jahn to be sensitized by free radicals, as mentioned by Taylor in his paper, but no complete account of this work has yet been published.

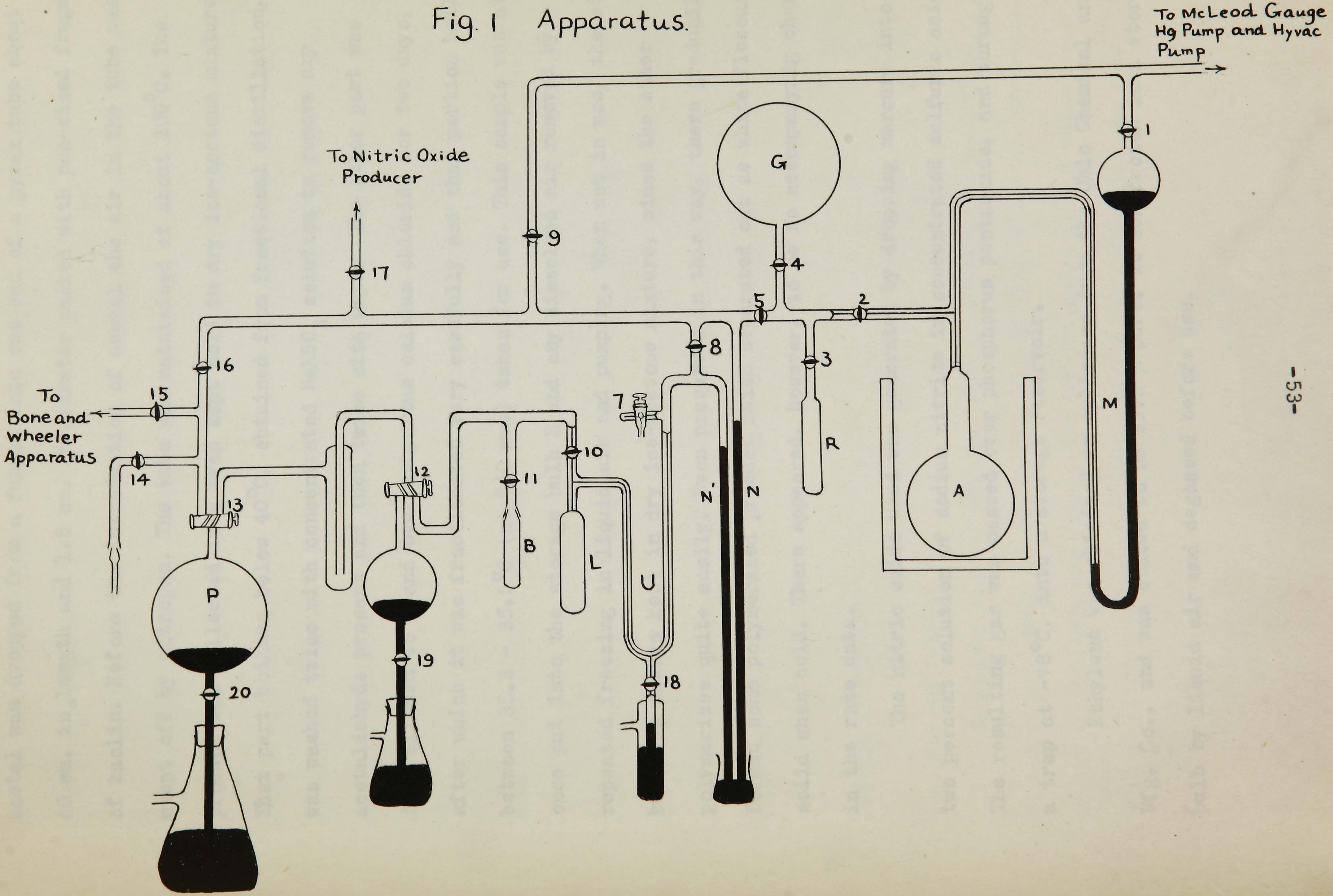
EXPERIMENTAL

The static method was used in this investigation, the reaction being followed by observation of the rate of pressure change and by analysis. The apparatus is shown diagrammatically in Fig. 1. The reaction vessel A was a pyrex vessel of about 500 cc. capacity. It was connected through cappillary tubing to a mercury manometer M and through stopcock 2 to a manifold to which were connected storage bulbs, Toepler pumps, liquid measuring apparatus, Bone and Wheeler gas analysis apparatus, nitric oxide producing apparatus, traps, McLeod gauge, mercury pump, etc.. The reaction vessel was heated by an electric furnace. The temperature of the reaction vessel was measured by a chromel-alumel thermocouple in contact with its outside wall together with a calibrated potentiometer. The temperature was controlled during a run to 0.5°C manually by varying a resistance in series with the furnace.

The mercury manometer M and stopcock 2, together with the capillary tubing between them, were kept at about 60°C by heating wire to prevent any possible condensation of product. When the desired temperature of the reaction vessel had been reached and kept for some time, the ether was introduced by expansion either directly from the vapor space of reservoir R or from gas bulb G. The initial pressure was obtained by extrapolation to zero time. If an analysis was to be made, the reaction mixture was expanded suddenly into the calibrated bulb P of the Toepler pump when the desired stage of reaction had been reached. The pressure was obtained as a difference between the readings on manometer N' and N. With room temperature known, the total amount of the sample in bulb P could be evaluated. This sample of mixture was then pushed back and forth between Toepler pumps P and P' through trap T cooled in a dry ice-acetone mixture for five complete cycles to condense out all condensable substances. That part of the gaseous portion contained in P at the end of this operation was then brought into the Bone and Wheeler gas analysis apparatus for analysis. The liquid part, on the other hand, was transferred to L, a calibrated tube. The pressure exerted by any gas here could be measured by introducing sufficient air over N' by operation of the three way stopcock 7 so as to keep mercury in the two limbs of U tube on the same level. The pressure of the gas was then equal to the difference between manometer readings of N and N', vacuum, of course, being kept over manometer N. In this way, the amount of residual gas present was measured by immersing L wholly in dry ice-acetone mixture, and the sum of liquid and gas by keeping L in a water bath at temperature enough high that all liquid was vaporized. Completeness of the vaporization was assured when two measurements at successive temperatures gave same value for the total amount of liquid and gas. The difference between the amount of liquid and gas and that of gas alone gave the amount of liquid in the sample taken.

For aldehyde analysis, the liquid was condensed into tube B into which 1 cc. of water had been introduced. The aqueous solution obtained was tested for its acidity, after which 1 cc. 0.5 N Na_2SO_3 was added and the solution let stand for 10 minutes. It was then titrated to faintest pink with 0.01 N hydrochloric acid, using phenolphthalein as indicator (70).

Fig. 1 Apparatus.



Vinyl ethyl ether was prepared by the pyrolysis of acetal (70, 71). Acetal was dropped from a funnel into one end of a pyrex tube about 60 cm. in length and 1.8 cm. in diameter packed with pea-sized fragments of kaolin. Before the introduction of acetal the air in the tube was swept off by nitrogen. The tube was maintained at about 200°C. The product was collected in a trap kept cold in dry ice-acetone mixture. That part boiling below 40°C, obtained from fractional distillation, was washed twice with concentrated $NaHSO_3$ solution to remove any acetaldehyde present and then twice with water. The ether part was then allowed to stand over anhydrous calcium chloride for two days, after which it was fractionated very carefully and that portion boiling between 35.3 - 35.5°C (at 760 mm.) taken for use. This sample was at once put into the storage bulb R and any dissolved air removed by repeated freezing in liquid air and pumping. When not in use, the ether bulb was always kept in dry ice-acetone mixture, since the ether polymerizes quite easily. Even preserved in this way, there gradually formed some polymerized product which separated out as white flocculent solid when cold. There appeared, however, to be no accompanying change in the rate data.

The nitric oxide used was generated by dropping mercury into a two percent solution of sodium nitrite in concentrated sulfuric acid. The resulting gas was passed over phosphorus pentaoxide, and through a trap at -78°C. into a storage reservoir.

Ethylene was obtained in cylinders from the Ohio Chemical and Mfg. Co., and was stated to be 99.5 % pure. It was frozen in a storage bulb by liquid air and degassed before use.

Acetaldehyde was prepared from recrystallized paraldehyde, and was put into storage bulb and degassed immediately after being obtained from fractionation .

In studying the rate of pressure change both in the cases of ether-acetaldehyde and ether-ethylene mixtures, the vapors were first mixed in the mixing bulb G, then admitted into the reaction vessel. Same is the case of most runs in the nitric oxide inhibition experiment, although in some of them the nitric oxide was first introduced into the reaction vessel with the subsequent addition of either vinyl ethyl ether or ether-acetaldehyde mixture.

Test of Homogeneity of the Reaction

Two runs with initial pressures around 10 cm. were made at 412°C using a packed bulb with surface-volume ratio about ten times that of the empty bulb. The rates were found to have no appreciable difference from the corresponding ones in the empty bulb case. Therefore, the reaction here investigated is essentially homogeneous.

Results of Analyses

Test for Hydrogen

Determinations of hydrogen were made using CuO combustion method in two runs, namely Run 32 and Run 41. In both cases, no appreciable amount of hydrogen was found. The effectiveness of CuO reagent was checked through blank experiments both before and after the runs.

Tests for Acetylene

Determinations of acetylene were made using alkaline potassium mercuric iodide solution as absorbing reagent (72) in two runs, namely, Runs 47 and 158 (412°C, p_0 10.0 cm. p/p_0 2.0). No appreciable amount of acetylene was found in both cases. This method was also checked by blank experiments.

Test for C_3 compounds

Sum of products from several runs at 412°C, withdrawn all at p/p_0 around 1.9, was distilled in a Podbielniak low temperature distillation apparatus. Not any C_3 hydrocarbon was detected.

Test for Ketene

In two runs at 412°C with p/p_0 equal to 2.0 and 1.7 respectively, the products collected in a gas pipette were shaken with water. In none of them, was any acidity found. Besides, in all the runs where the amounts of aldehyde was determined, the aqueous solutions were neutralized carefully before addition of Na_2SO_3 solution. In no case, was the solution appreciably acid.

In Tables I and II are listed all the analytical results obtained.

Table I

Gaseous Products of Decomposition of Vinyl Ethyl Ether

T 412°C

Run No.	Ether sample	P_o cm.	P/P_o	Percentage C_2H_4	CO	CH_4	C_2H_6	$CH_4 + C_2H_6$
64	III	10 ± 1 *	1.30	79.4	8.8	7.0	4.9	11.9
65	III	10 ± 2 △	1.42	73.8	12.7	---	---	13.5
42	II	13.4	1.55	66.9	17.4	10.2	5.5	15.7
44	II	11.1	1.58	68.4	16.2	9.6	5.8	15.4
40	II	15.4	1.62	65.0	14.9	15.0	5.1	20.1
39	II	6.6	1.71	63.1	17.4	13.6	5.9	19.5
43	II	10.6	1.76	57.4	22.8	13.2	6.6	19.8
41	II	13.5	1.78	57.2	21.9	15.6	5.3	20.9
37	II	8.6	1.92	52.8	23.5	----	---	23.7
59	III	9.9	1.93	49.1	26.9	----	---	24.0
48	III	10.5	1.94	51.8	24.2	15.1	8.9	24.0
47	III	9.4	2.42	25.6	33.6	29.3	11.5	40.8

* The total of four runs was analyzed.

△ The total of three runs was analyzed.

T 424°C

Run No.	Ether sample	P_o cm.	P/P_o	Percentage C_2H_4	CO	CH_4	C_2H_6	$CH_4 + C_2H_6$
32	II	10.5	1.95	43.4	27.5	---	----	29.1

Fig. 2

Composition of Gaseous Product (I)

T 412°C

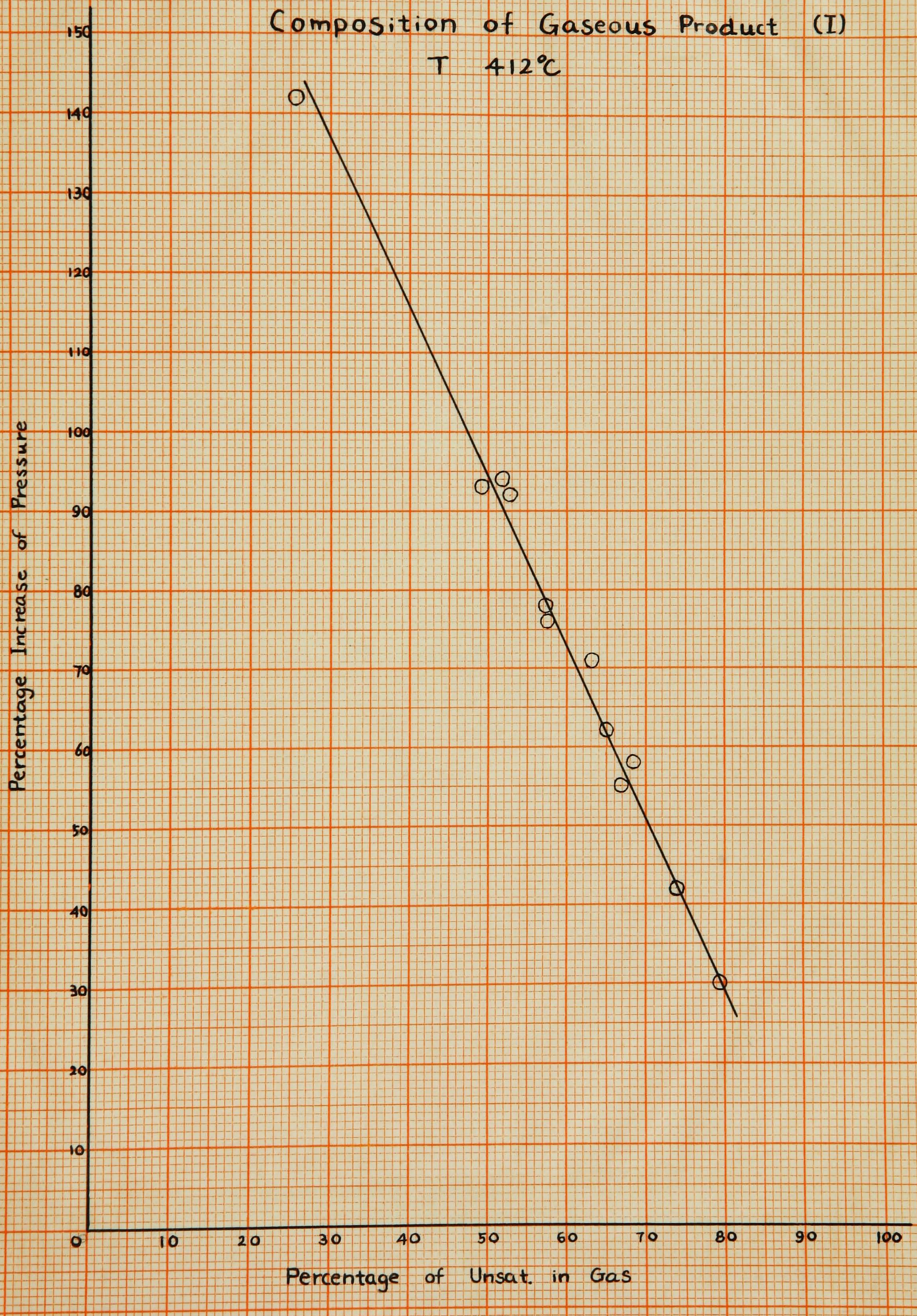


Fig. 3

Composition of Gaseous Product (II)

T 412°C

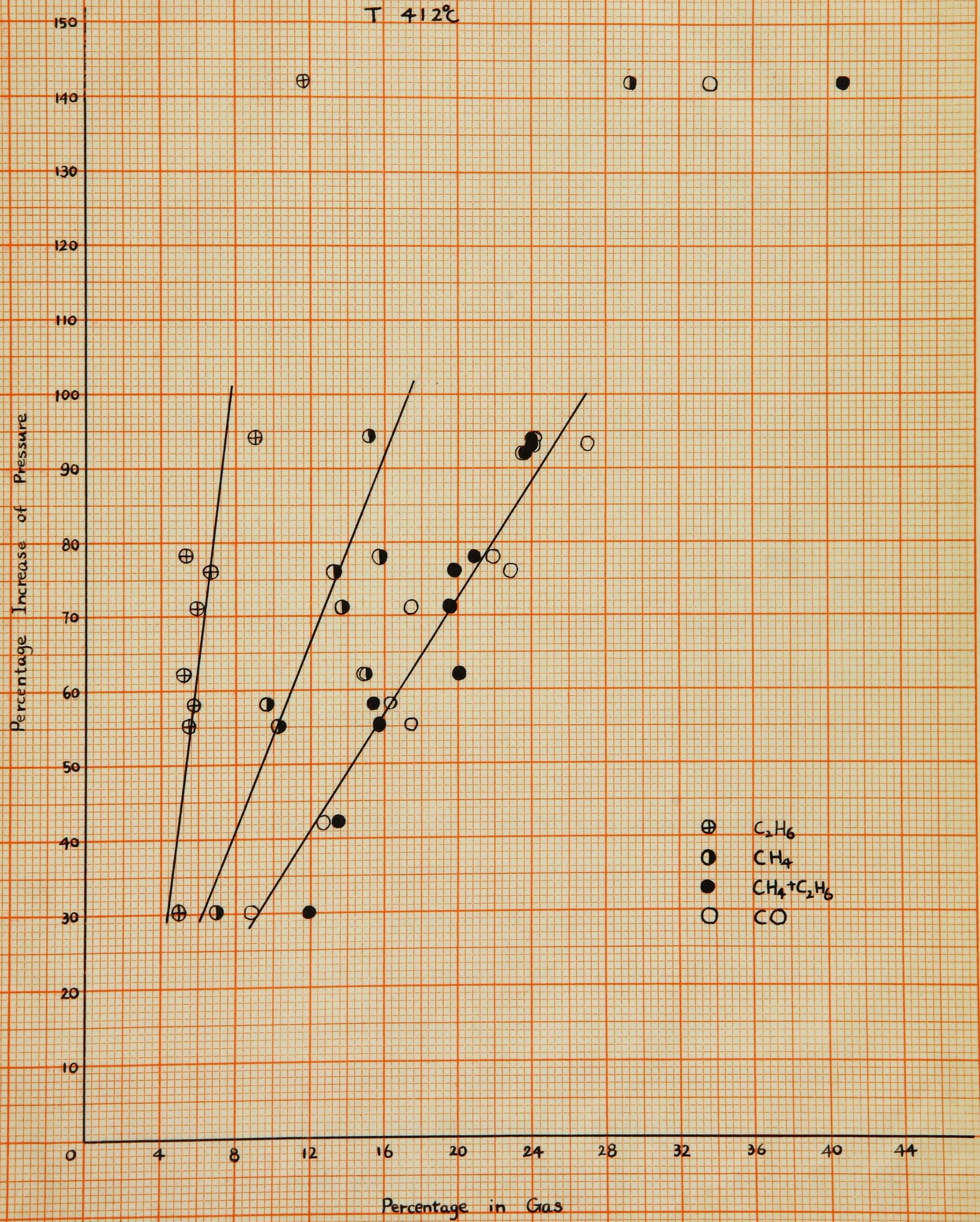


Table II

Products of Decomposition of Vinyl Ethyl Ether

T 412°C

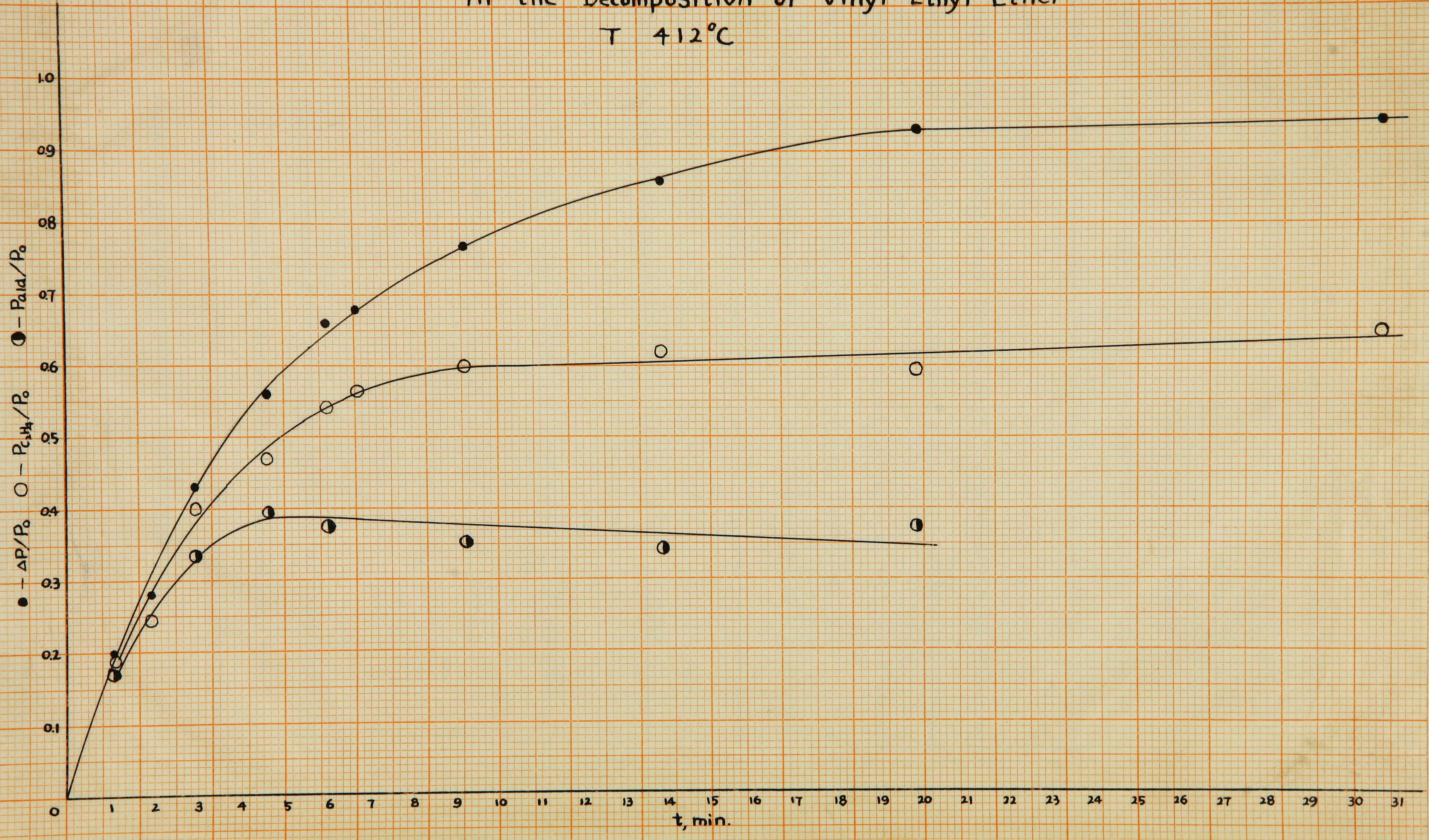
Run No.	Ether sample	Time	P_o cm.	P/P_o	P_l/P_o	P_g/P_o	P_{ald}/P_o	$P_{C_2H_4}/P_o$	P_{CO}/P_o
60	III	1' 6"	9.2	1.20	0.966	0.23	0.169	(0.19)	(0.013)
45	II	1' 57"	9.0	1.28	0.953	0.33	-----	0.243	(0.026)
58	III	2' 58"	9.2	1.43	0.900	0.53	0.333	(0.40)	(0.062)
55	III	4' 38"	10.0	1.56	0.885	0.67	0.394	(0.47)	(0.10)
62	III	6' 1"	9.9_6	1.66	0.836	0.82	0.374	(0.54)	(0.15)
49	III	6' 43"	10.3	1.68	0.811	0.87	----	(0.566)	(0.16)
54	III	6' 49"	9.9	1.66	----	---	0.339	-----	-----
57	III	9' 14"	11.9	1.77	0.769	1.00	0.353	(0.60)	(0.21)
43	II	10'	10.6	1.77	0.805	0.96	----	0.55	0.22
56	III	13' 52"	10.6	1.86	0.749	1.11	0.342	(0.62)	(0.25)
59	III	19' 50"	9.9	1.93	0.719	1.21	0.373	0.595	(0.30)
48	III	30' 33"	10.5	1.94	0.693	1.25	----	0.646	(0.31)
63	III	16 hrs	11.7	2.41	0.276	2.13	0.105	(0.59)	(0.68)

In the above table, P_o signifies the initial pressure of ether; P, P_l, P_g, P_{ald}, $P_{C_2H_4}$ and P_{CO} signify respectively the total pressure, the partial pressures of total liquid, total gas, aldehyde, ethylene and carbon monoxide in the reaction mixture at the time of drawing of the sample. The values in parentheses in the last two columns are not obtained as direct experimental results of these individual runs, but are estimated by the use of the experimentally established relations on the dependence of gaseous composition on the percentage pressure increase as shown in Fig. 2 and 3.

Fig. 4

Courses of Pressure Change and Formations of Ethylene and Aldehyde in the Decomposition of Vinyl Ethyl Ether

T 412°C



From the results of the gas analyses, it seems evident that, in the main, C_2H_4 is the primary product and CO, CH_4 and C_2H_6 are all secondary products, A tentative extrapolation of C_2H_4 curve to zero pressure increase suggests that in the primary process nearly 95 % of the gaseous product is ethylene. There might be, of course, an unimportant simultaneous process the existence of which is as difficult to disprove as to confirm.

This fact alone suggests the primary process to be the decomposition of ether to ethylene and acetaldehyde. This supposition is further supported by the merging together at initial period of the three curves $\Delta P/P_0$ - t, P_{ald}/P_0 - t and $P_{C_2H_4}/P_0$ - t, as seen from Fig. 4.

In the secondary gaseous products, the amount of CH_4 is always smaller than that of CO formed, while the sum of CH_4 and C_2H_6 is quite close to the amount of CO.

There are other regularities to be found in the results listed in Table II.

(I). P_{CO+ald}/P_0 values are almost the same as $P_{C_2H_4}/P_0$ values.

P/P_0	1.20	1.43	1.56	1.66	1.77	1.86	1.93	2.41
$P_{C_2H_4}/P_0$	0.19	0.40	0.47	0.54	0.60	0.62	0.59_5	0.59
P_{CO+ald}/P_0	0.18	0.40	0.49	0.52	0.56	0.59	0.67	0.80

This signifies that one molecule of aldehyde yields, on decomposition, one molecule of CO. The considerable departure in the latter stage may, in part, arise from the sensitized as well as normal polymerization of ethylene as shown to occur in separate experiments.

(II). $P_{C_2H_4+CO}/P_o$ values are practically equal to the corresponding values of $\Delta P/P_o$.

$\Delta P/P_o$	0.20	0.28	0.43	0.56	0.66	0.68	0.77	0.77	0.86	0.93	0.94
$P_{C_2H_4+CO}/P_o$	0.20	0.27	0.46	0.57	0.69	0.73	0.81	0.77	0.87	0.90	0.98

This signifies that the increase in pressure due to the decomposition of acetaldehyde is, in the main, equal to pressure of CO formed.

(III). $P_{CO + liq.}/P_o$ values are practically all equal to one.

P/P_o	1.20	1.28	1.43	1.56	1.66	1.68	1.77	1.77	1.86	1.93	1.94	2.41
P_{CO+liq}/P_o	0.98	0.98	0.96	0.99	0.99	0.97	0.98	1.03	1.00	1.02	1.00	0.98

This relation signifies that the liquid products are, essentially, all monooxy-compounds.

All these relations can be well accounted for by the following scheme of over-all changes:

(1). $C_2H_5OC_2H_5 = C_2H_4 + CH_3CHO$

(2). $CH_3CHO = CH_4 + CO$

(3). $2CH_3CHO = C_2H_6 + CO + HCHO$.

(1) is the primary change, (2) is the major secondary change, and (3) is the minor secondary change.

It should be emphasized here that the equations represent only the stoichiometric relations among reactant and the products. They have nothing whatsoever to do with the real mechanism through which these changes are accomplished. In fact, pure acetaldehyde decomposes at a negligible rate at this particular temperature as shown by blank experiments. Thus the second change alone suggests either that acetaldehyde formed from ether contains excess of energy which makes its decomposition rate higher than normal, or that the ether produced free radicals in its decomposition which sensitize the decomposition of acetaldehyde. The change represented in (3), however, can not be accounted for even by the assumption of activated acetaldehyde molecule. No such change has ever been observed in the normal acetaldehyde decomposition at elevated temperature.

Typical Experiments on Analyses

To illustrate the ways in which the values in Tables I and II are obtained, the detailed experimental results as well as the evaluations leading to the tabulated values of typical runs 43 and 62 are presented below:

Run 43

Ether sample II, Temperature of reaction vessel 412°C

Initial pressure of ether 10.6 cm. Time of reaction 9'55" - 10'5"

Percentage pressure increase 76.5

Total sample taken:

Volume of bulb	510 cc.
Room temperature	27.3°C = 300.4°K
Pressure of the mixture	5.13 cm.
PV/T of the sample	8.71 in cm. cc. degree unit

The liquid portion (condensable at -78°C) along with part of the gaseous portion was transferred to the calibrated bulb L. When L was wholly immersed in dry ice-acetone mixture, the following set of data was obtained:

Pressure of the mixture	1.3 cm.
Temperature	-78°C = 195°K
Volume of L	37.53 cc.
PV/T of the residual gaseous part present	0.25 in cm. cc. degree unit.

The dry ice-acetone bath was then replaced by a water bath. When water bath temperature was 49.1°C,

pressure reading	36.2 cm.
PV/T	4.22 in cm. cc. degree unit;

when water bath temperature was raised to 58.o°C,

pressure reading	37.3 cm.
PV/T	4.23 in cm. cc. degree unit.

The coincidence of these two PV/T values at two different temperatures indicated that the liquid portion was completely vaporized under these conditions. The PV/T of the liquid portion is then equal to

$$4.23 - 0.25 = 3.98$$ in cm. cc. degree unit.

Percentage of liquid in the reaction mixture is then

$$100 \cdot 3.98/8.71 = 45.6 \quad .$$

Percentage of gaseous part in the reaction mixture is

$$(100 - 45.6) = 54.4 \quad .$$

Gas analysis in the Bone and Wheeler type apparatus

	Vacuum reading v.r.	Pressure reading p.r.	Temp. °C	p.r.-v.r.	p.r.-v.r. corrected to 27.0°C	Difference	
Total gas	53.80	78.38	26.5	24.58	24.62		
After fuming H_2SO_4		64.29	27.0	10.49	10.49	14.13	unsat.
After ammon. Cu_2Cl_2	53.79	58.67	27.2	4.88	4.88	5.61 4.88	CO sat. H.C.
Oxygen	53.79	78.19	27.2	24.40	24.38		
Mixture after slow combustion	53.79	72.51	27.1	18.72	18.71		
After absorption by conc. KOH		66.00	27.0	12.21	12.21		

Total contraction $24.38 + 4.88 - 18.71 = 10.55$

Amount of CO_2 formed $18.71 - 12.21 = 6.50$.

Taking the hydrocarbon mixture as one of methane and ethane, from their total amount and CO_2 formed, we get

$P_{C_2H_6}$ $6.50 - 4.88 = 1.62$

P_{CH_4} $4.88 - 1.62 = 3.26$.

From this set of values, the calculated value of total contraction would be $2P_{CH_4} + 2\frac{1}{2}P_{C_2H_6}$,i.e. 10.57, which is in excellent agreement with the experimental value 10.55 .

From the gas analysis, we thus get the percentage composition of the gaseous part as follows:

unsat. (C_2H_4)	CO	CH_4	C_2H_6
57.4	22.8	13.2	6.6

From this gaseous composition and the previously determined relative proportion of gas and liquid in the reaction mixture, we have the percentage composition of the reaction mixture as follows:

unsat. (C_2H_4)	CO	CH_4	C_2H_6	liq.
31.2	12.4	7.2	3.6	45.6 .

On multiplying the percentages by P/P_0, e.i. 1.77, we get

$P_{C_2H_4}/P_0$	P_{CO}/P_0	P_{CH_4}/P_0	$P_{C_2H_6}/P_0$	P_1/P_0
0.55	0.22	0.12_7	0.06_3	0.805 .

Run 62

Ether sample III, Temperature of reaction vessel 412°C

Initial pressure of ether 9.96 cm. Time of reaction 5' 58" - 6' 6"

Percentage pressure increase 66

Total sample taken -- determined as in the above run

0.879 millimole

Liquid part of the sample -- determined as in the above run

0.443 millimole

The aqueous solution obtained from this liquid sample and 1 cc. of water was first tested for acidity. Using phenolphthalein as indicator, 0.05 cc. of 0.01 N NaOH was found to be more than enough to bring the solution to pink color. After 1 cc. of 0.5 N Na_2SO_3 solution was added, the solution was left to stand for 10 minutes. It was then titrated against 0.0102 N hydrochloric acid, and 21.1 cc of this acid was found to be needed for the neutralization. As blank experiment showed that 1.7 cc. of this acid was needed to bring the solution of Na_2SO_3 alone to the desired end point, the acid corresponding to the NaOH liberated by the aldehyde would be 21.1 - 1.7 or 19.4 cc., i.e. 0.198 millimole. This is also equal to the number of millimoles of aldehyde present in the sample taken. Therefore

percentage of aldehyde in the reaction mixture

$$= 22.5 \quad .$$

$$P_{ald}/P_o = 22.5\ \% \cdot 1.66 = 0.374 \quad .$$

Course of Pressure Change

The course of pressure change is partly illustrated in Fig. 4. A fast process of increase in pressure is followed by a slow one which lasts for hours. This behaviour is illustrated by Run 47 as listed in Table III.

The slow process is, as indicated by our analytical results listed in Table I, accompanied by the rise in percentages of CO and CH_4. It is therefore chiefly due to the slow decomposition of acetaldehyde. On the other hand, from the analytical results we also see that there is no clear cut dividing line between the primary decomposition of ether and the subsequent changes of acetaldehyde. For this reason, in the study of the kinetic aspects of ether decomposition, only the early stages of pressure change were investigated.

Table III

Pressure Change in the Decomposition of Vinyl Ethyl Ether

Run 47

Ether sample III Temperature of reaction 412°C

Initial pressure 9.4 cm.

Time	P/P_o
0	1.00
35"	1.10
1' 2"	1.17
1' 58"	1.30
2' 58"	1.42
4' 10"	1.52
5' 12"	1.60
6' 7"	1.65
7' 17"	1.70
9' 4"	1.77
13'	1.85
17'	1.89
25'	1.93
36'	1.96
52'	1.99
93'	2.04
140'	2.08
201'	2.13
256'	2.16
303'	2.19
359'	2.22
392'	2.23
960'	2.41

The Reaction Order of the Decomposition of Vinyl Ethyl Ether

The decomposition of vinyl ethyl ether is a first order reaction, since the time for definite percentage increase in pressure does not vary appreciably with the initial pressure as may be seen from the results tabulated below:

Table IV

Temp. 388.6°C

Run No.	Sample No.	Initial P. cm.	$t_{20\%}$ sec.	$t_{30\%}$ sec.	$t_{40\%}$ sec.
68	III	5.1	265	424	609
69	III	19.0	264	424	615
82	IV	8.8	268	445	660

Temp. 412.2°C

Run No.	Sample No.	Initial P. cm.	$t_{20\%}$ sec.	$t_{30\%}$ sec.	$t_{40\%}$ sec.
35	II	3.9	91	140	206
39	II	6.6	95	148	227
33	II	7.8	85	134	195
37	II	8.6	77	123	183
44	II	11.1	75	120	174
38	II	11.5	75	120	177
41	II	13.5	78	126	183
34	II	13.6	80	127	188
40	II	15.4	80	126	181

(to be continued)

Table IV (continued)

Temp. 412.2°C

Run No.	Sample No.	Initial P. cm.	$t_{20\%}$ sec.	$t_{30\%}$ sec.	$t_{40\%}$ sec.
73	III	4.4	73	119	174
47	III	9.4	75	118	169
54	III	9.9	76	124	178
55	III	10.0	73	121	170
49	III	10.3	74	116	167
56	III	10.6	77	122	176
57	III	11.9	74	116	168
76	III	12.9	76	119	169
85	IV	2.7	95	156	232
84	IV	3.7	98	156	229
77	IV	8.5	85	137	199
86	IV	19.3	83	136	198

Temp. 424°C

Run No.	Sample No.	Initial P cm.	$t_{20\%}$ sec.	$t_{30\%}$ sec.	$t_{40\%}$ sec.
31	II	3.9	53	82	118
32	II	10.5	44	72	104
30	II	11.3	43	70	101
74	III	6.5	47	73	105
75	III	15.3	46	72	103
78	IV	9.1	48	78	113

It appears that the rate begins to fall in the region of a few cm. pressure. However, this phase of the problem was not specifically examined.

Rate Expression

From the analytical results, it is apparent that only in the initial period of reaction does the percentage of pressure change correspond to the percentage of reaction of ether decomposition. By determining the rate expressions for 20 %, 30 % and 40 % pressure increase, it is possible to estimate the rate expression corresponding to the zero change, i.e. the rate expression for pure vinyl ethyl ether decomposition by extrapolation.

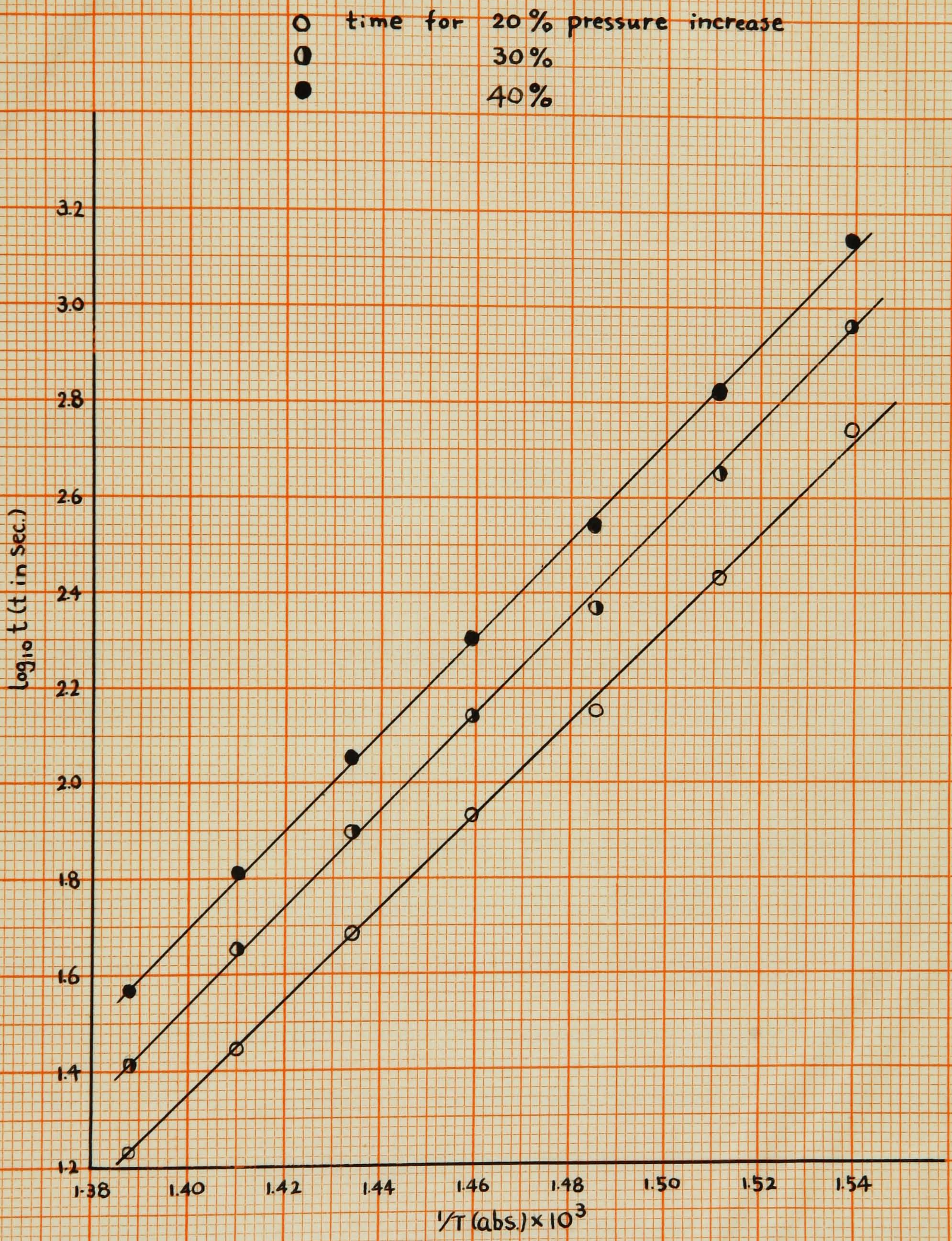
The data used in this calculation are listed in the following table.

Table V

Run No.	P_o	T^oC	$t_{20\%}$ sec.	$t_{30\%}$ sec.	$t_{40\%}$ sec.
81	8.7	376.8	554	912	1376
82	8.8	388,6	268	445	660
83	8.6	400.4	142	232	344
77	8.5	412.2	85	137	199
78	9.1	424.0	48	78	113
79	7.7	435.8	28	45	65
80	9.7	447.6	17	26	37

Fig. 5

Activation Energy Curves



From the straight lines obtained by plotting $\log_{10}t$ against $1/T_{abs.}$ as shown in Fig. 5, the following values for the activation energy E and frequency factor A are obtained:

percentage pressure increase	A	E calories
20	$4.6 \cdot 10^{11}$	44600
30	$5.1 \cdot 10^{11}$	44800
40	$9.1 \cdot 10^{11}$	45600

The rate expression for pure ether is estimated as

$$k = 4.0 \cdot 10^{11} e^{-44400/RT} \quad .$$

Sensitized Decomposition of Acetaldehyde by Vinyl Ethyl Ether

Rate of pressure changes of various mixtures of ether and acetaldehyde were determined. The results are listed in Table VI. On account of the complicating nature of the later stages, the percentageschanges of pressure relative to initial pressure of ether at the end of 90 seconds are used as a basis for comparison. The normal decomposition of acetaldehyde at 412°C, which is very slight, has been taken into account.

In Fig. 6 $(\Delta P/P_e)_{90''}$ values are plotted against P_a/P_e. It is seen that although there is some dependence of $(\Delta P/P_e)_{90''}$ on the value of pressure of the mixture, the general relation between these two quantities, nevertheless, is well represented by a linear expression, i.e.

$$\Delta P/P_e = (\Delta P/P_e)_o + C(P_a/P_e)$$

where $\Delta P / P_e$ and $(\Delta P / P_e)_o$ refer to the pressure increases relative to the initial pressures of ether at the end of 90 seconds for the mixture and for the ether in pure state, and C is a constant equal to about 0.05.

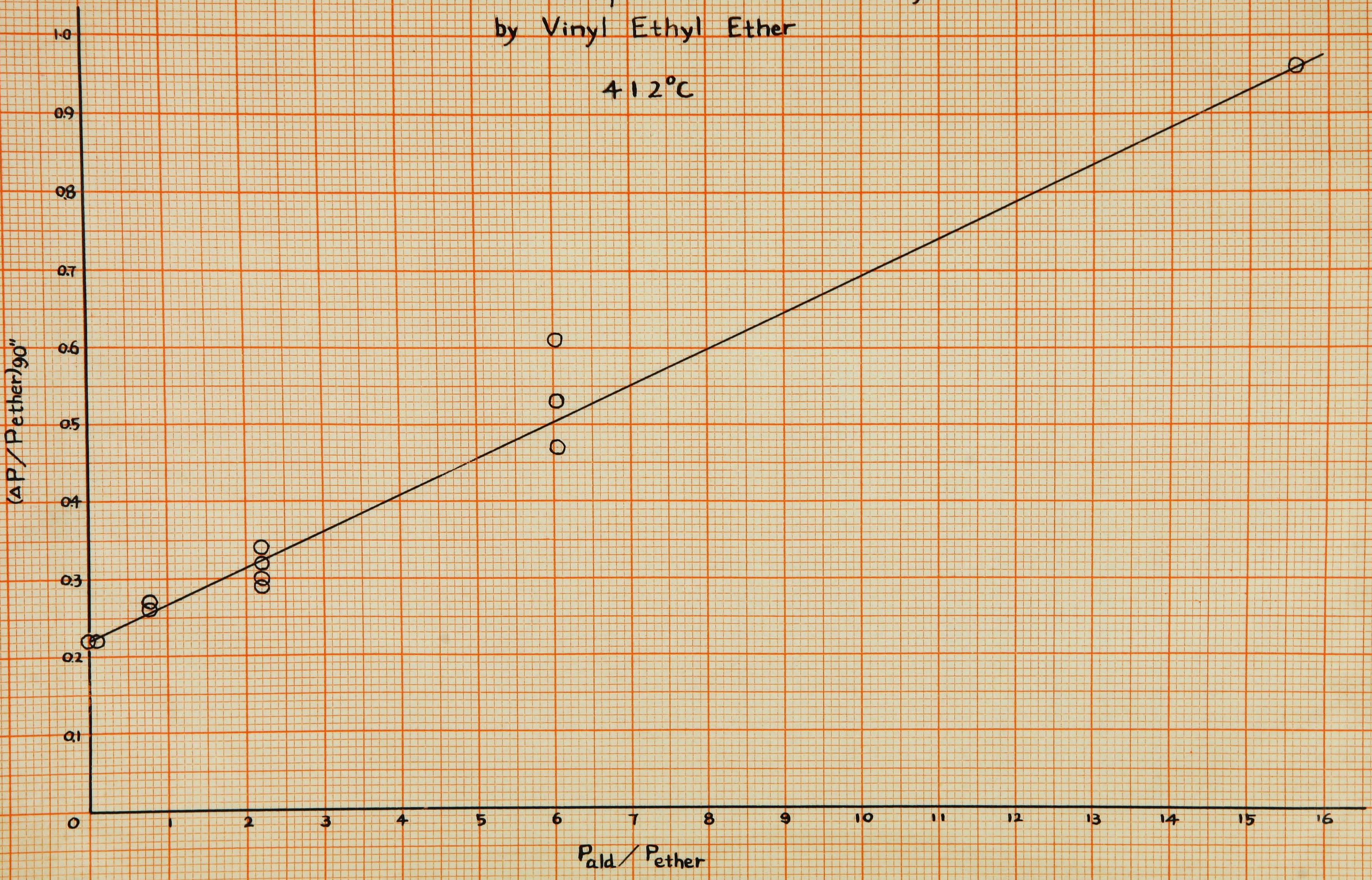
Table VI

Temp. 412°C

Run No.	$P_e(P_{ether})$ cm.	$P_a(P_{ald})$ cm.	P_a / P_e	$(\Delta P / P_e)_{90''}$
91	0.647	10.11	15.6	0.96
92	0.477	7.45	15.6	0.96
94	1.98	11.95	6.04	0.61
95	1.40	8.44	6.04	0.53
96	0.87	5.27	6.04	0.47
101	6.36	14.0	2.21	0.34
102	3.07	6.78	2.21	0.29
103	3.33	7.35	2.21	0.32
104	1.44	3.19	2.21	0.30
99	11.2	8.82	0.78	0.27
100	5.72	4.49	0.78	0.26
97	15.8	1.78	0.11	0.22
98	8.92	0.0	0.0	0.22

Fig. 6
Sensitized Decomposition of Acetaldehyde
by Vinyl Ethyl Ether

412°C



It is worth mentioning that the possibility of this increase in rate being due to activation of ether by acetaldehyde is definitely removed by consideration of total pressure changes taking place. In Run 91, for instance, at the end of thirty minutes $\Delta P / P_e$ is 4.1 after correction for the normal decomposition of acetaldehyde has been made. This is entirely inexplicable if the pressure increase is due to the decomposition of ether alone. This series of experiments appear to demonstrate quite conclusively that ether molecules produce free radicals during decomposition which, in turn, induce the decomposition of acetaldehyde.

In Table VII are listed the complete data of Run 91 which has been just referred to. In Fig. 7 are plotted the earlier parts of percentage pressure increase - time curves for several mixtures of different compositions.

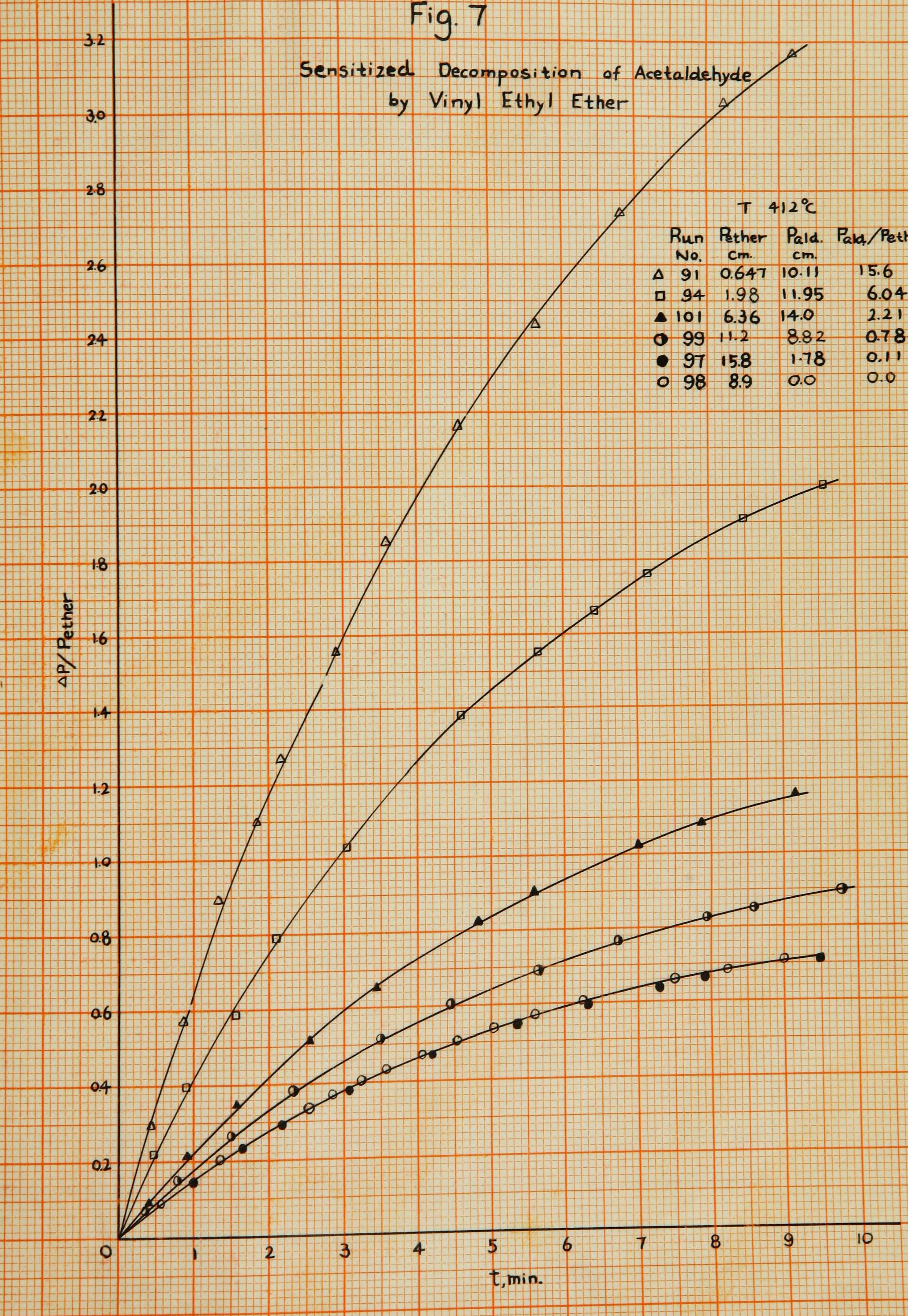


Fig. 7

Sensitized Decomposition of Acetaldehyde by Vinyl Ethyl Ether

Table VII

Run 91 Mixture of Acetaldehyde and Vinyl Ethyl Ether

Initial pressure of ether 0.647 cm.

Initial pressure of acetaldehyde 10.11 cm.

Temp. 412°C

Time	Pressure cm.	ΔP cm.	ΔP (corr.) cm.	ΔP (corr.) / P_e
0	10.76	0.0	0.0	0.0
26"	10.97	0.21	0.19	0.29_4
52"	11.16	0.40	0.37	0.57_2
1' 19"	11.38	0.62	0.58	0.89_5
2' 9"	11.63	0.87	0.82	1.27
2' 54"	11.83	1.07	1.01	1.56
3' 35"	12.03	1.27	1.20	1.85
4' 35"	12.23	1.47	1.40	2.16
5' 38"	12.43	1.67	1.58	2.44
6' 48"	12.63	1.87	1.77	2.74
8' 14"	12.83	2.07	1.96	3.03
10' 31"	13.05	2.29	2.16	3.34
12.'59"	13.23	2.47	2.32	3.58
17' 26"	13.43	2.67	2.49	3.85
22' 30"	13.52	2.76	2.57	3.97
28' 52"	13.59	2.83	2.62	4.05

ΔP (corr.) values are obtained by substracting from values of ΔP the changes expected from normal decomposition of acetaldehyde.

Effect of Ethylene on the Decomposition of Vinyl Ethyl Ether

The rates of pressure change for various mixtures of ether and ethylene have been studied. The initial rates as measured by the pressure increases relative to ether pressures at the end of 90 seconds are summarized in Table VIII.

Table VIII

Reaction temperature 412°C

Run No.	P_{ether} cm.	$P_{C_2H_4}$ cm.	$P_{C_2H_4}/P_{ether}$	$(\Delta P / P_{ether})_{90''}$
98	8.92	0.0	0.0	0.22
105	9.24	10.22	1.1	0.20
106	9.65	29.6	3.1	0.16
107	7.81	48.2	6.1	0.11
109	3.95	47.4	12.0	0.047
150	0.72	37.2	52	-0.06

The results are readily understood by postulating the production of free radicals in the decomposition of the ether. The induced polymerization of ethylene by free radicals would lead to a negative rate of pressure change. This tends to diminish the rate of pressure change to an extent increasing with the increase in the proportion of ethylene.

Nitric Oxide Inhibition Experiments

(I) Effect of Nitric Oxide on Normal Decomposition of Vinyl Ethyl Ether

Repeated experiments were made to study the effect of nitric oxide upon the decomposition of vinyl ethyl ether. The results all showed nitric oxide to have no effect, as may be seen from Table IX.

Table IX

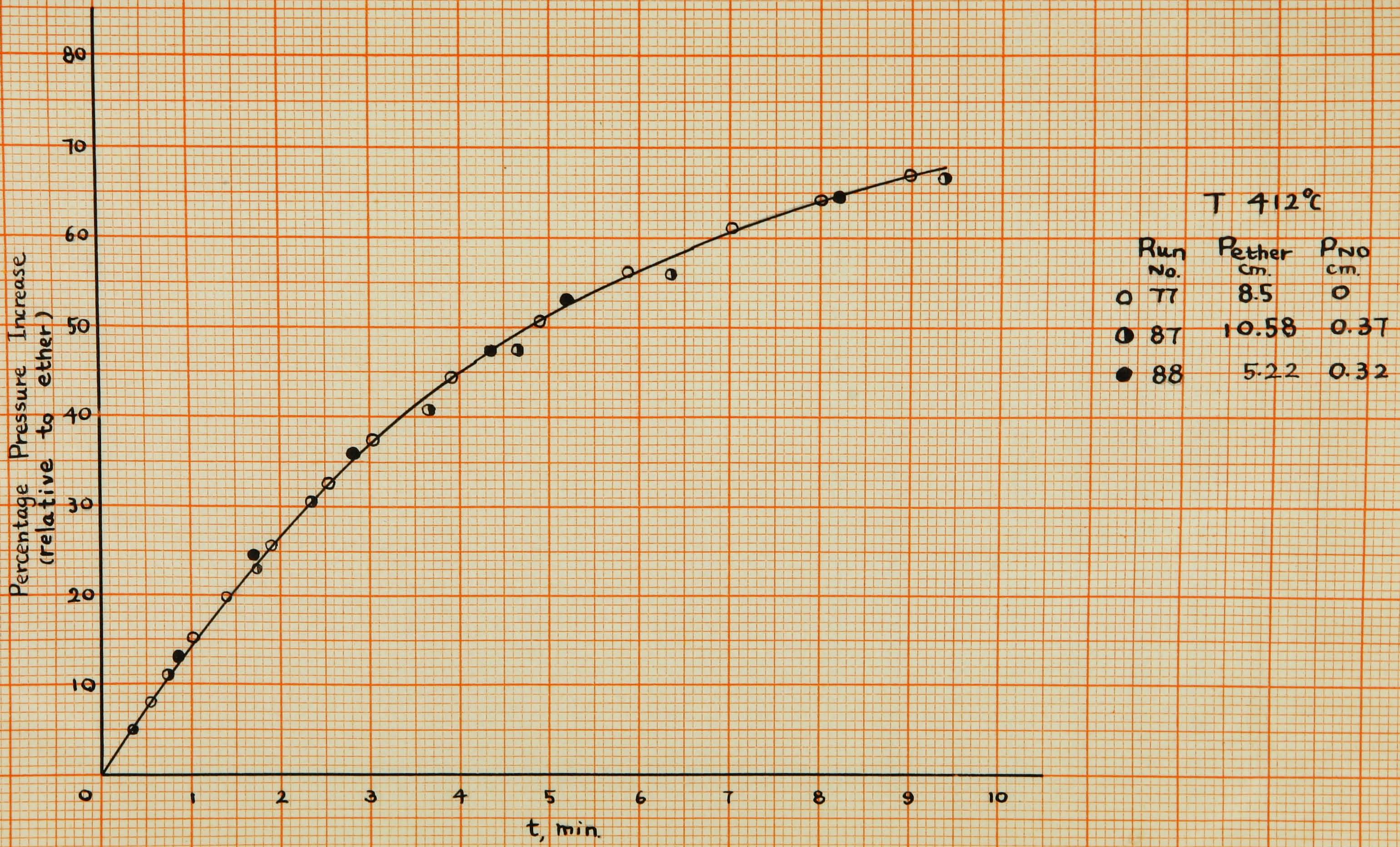
Run No.	Temp. °C	P_{ether} cm.	P_{NO} cm.	r
77	412	8.5	0	1.00
115	412	10.23	4.1	1.00
116	412	7.70	3.3	0.94
117	412	10.96	2.1	1.00
87	412	10.58	0.37	0.98
88	412	5.22	0.32	1.00
118	412	8.84	0.22	1.04
131	389	10.45	1.52	0.99

Here **r** designates (ΔP / P_{ether}) at the end of 90 seconds relative to the value of pure ether.

To further illustrate the ineffectiveness of nitric oxide, the percentage pressure increases with reference to the pressure of the ether in Runs 77, 87 and 88 are plotted together against time in Fig. 8. It is seen that these three runs are covered by a single curve.

Fig. 8

Effect of Nitric Oxide on Decomposition
Rate of Vinyl Ethyl Ether



(II) Effect of Nitric Oxide on Sensitized Decomposition of Acetaldehyde by Vinyl Ethyl Ether

In contrast to the previous case, a definite inhibiting effect of nitric oxide on the rate of pressure change of this sensitized process was observed. In comparing the different rates of change of different mixtures, the ratio between the percentage pressure increase of the mixture at the end of 90 seconds relative to the partial pressure of the ether to the percentage pressure increase of pure ether around 10 cm. pressure at the end of same period is used as reference. It is denoted by R in Table X.

Table X

Temp. 389°C

Run No.	P_{ether} cm.	$P_{ald.}$ cm.	P_{NO} cm.	$P_{ald.}/P_{ether}$	R
124	1.63	14.7	0	9.0	3.7
128	0.92	8.26	0	9.0	3.3
127	1.03	9.24	0.69	9.0	1.4
126	1.22	10.94	1.55	9.0	0.82
125	1.27	11.45	3.94	9.0	1.1

Temp. 400°C

Run No.	$P_{ether.}$ cm	$P_{ald.}$ cm.	P_{NO} cm.	$P_{ald.}/P_{ether}$	R
139	1.69	14.8	0	8.8	4.8
142	1.00	8.8	0.17	8.8	2.9
141	1.17	10.3	1.40	8.8	1.6
140	1.26	11.1	3.56	8.8	1.1

Table X (continued)

Temp. 412°C

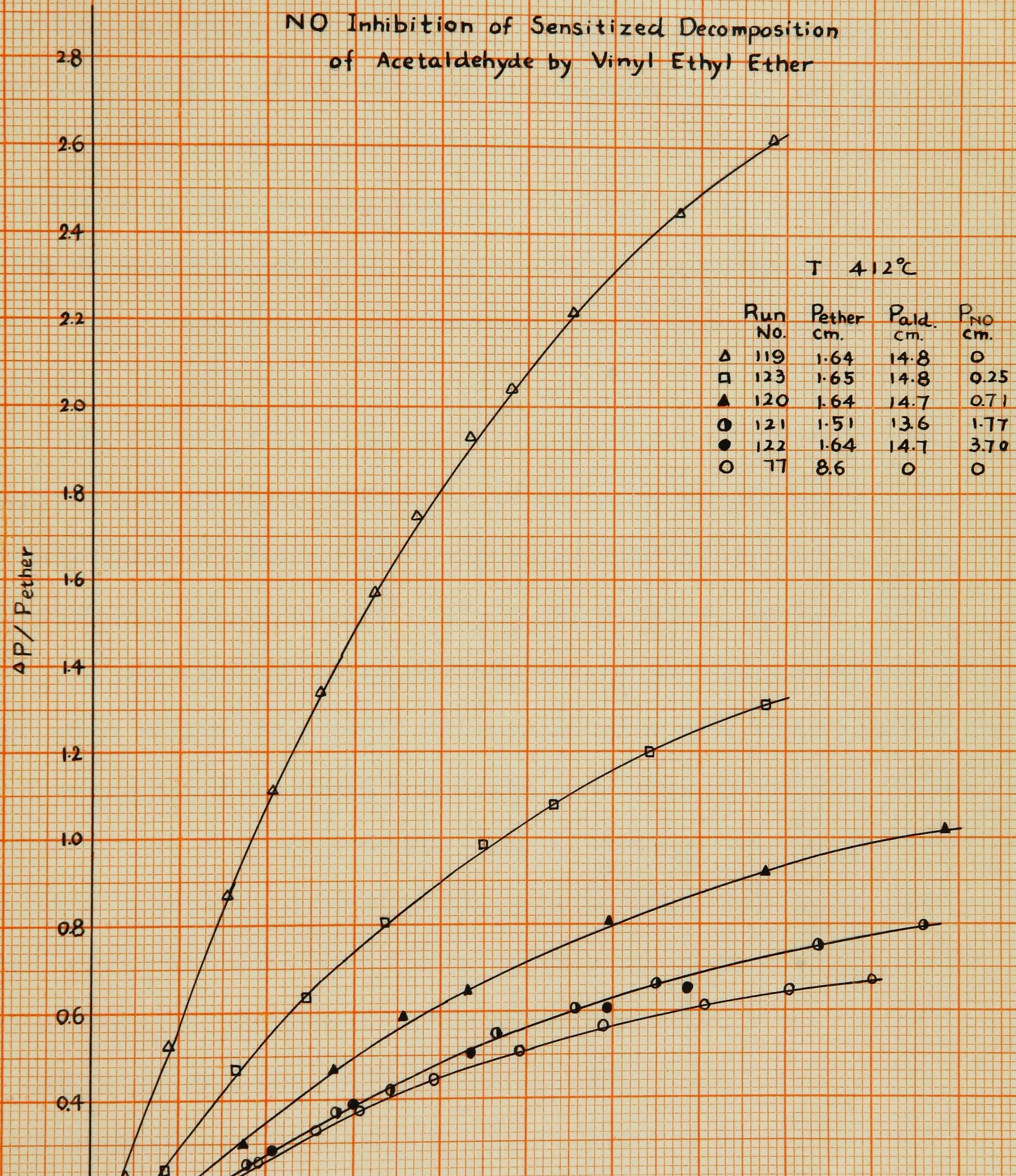
Run No.	P_{ether} cm.	$P_{ald.}$ cm.	P_{NO} cm.	$P_{ald.}/P_{ether}$	R
119	1.64	14.8	0	9.0	4.3
123	1.65	14.8	0.25	9.0	2.0
120	1.64	14.7	0.71	9.0	1.2
121	1.51	13.6	1.77	9.0	1.0
122	1.64	14.7	3.70	9.0	1.0

Temp. 424°C

Run No.	P_{ether} cm.	$P_{ald.}$ cm.	P_{NO} cm.	$P_{ald.}/P_{ether}$	R
134	1.57	13.8	0	8.8	3.9
138	1.66	14.6	0.19	8.8	2.2
137	1.69	14.8	0.70	8.8	1.7
136	1.97	17.3	1.77	8.8	1.1
135	1.86	16.4	4.05	8.8	0.9

It is obvious from this table that nitric oxide can bring down the rate of pressure increase of the mixture but a steady minimum seems to be reached when R is approximately equal to 1 in all these four temperatures studied. Fuller illustration is made in Fig. 9 where the dependence on the nitric oxide pressure of the curve representing change with time of the percentage pressure increase of the mixture relative to the partial pressure of ether is to be illustrated.

Fig. 9


NO Inhibition of Sensitized Decomposition of Acetaldehyde by Vinyl Ethyl Ether

Discussion

From the analytical results, it is apparent that vinyl ethyl ether decomposes first into ethylene and acetaldehyde. From the sensitizing effects of the ether on the decomposition of acetaldehyde and on the polymerization of ethylene, it is evident that free radicals are produced in the decomposition of this ether. On the other hand, nitric oxide exerts almost no effect on the decomposition rate of pure ether. Yet it does inhibit the decomposition of acetaldehyde sensitized by ether.

The first question that arises is whether free radicals play an important part in the decomposition of the ether itself. Quite aside from any arbitrary assumptions, some information of the free radical producing step can be inferred from the experimental results.

In the study of the sensitized decomposition of acetaldehyde by vinyl ethyl ether, the rate of pressure increase of a mixture containing 6 % ether at 412°C was found to be about 4.4 times that of pure ether. This means that the length of the chain produced by the free radical from the ether is greatly increased in the presence of acetaldehyde. The length of the chain in the mixture, nevertheless, must be smaller than that in the pure acetaldehyde. Mitchell and Hinshelwood (30), studying the photolysis of acetaldehyde, found that the quantum yield is 338 at 400°C and 589 at 450°C both at 100 mm. pressure. At 412°C it would probably be approximately 400. The length of the chain is greater than the value of quantum yield because part of the light absorption leads to the rearrangement process instead of a split into free radicals (73). In any case, we may put 400 as the upper limit of the chain length in the ether-acetaldehyde mixture containing 6 % ether. This being so, the rate of the free radical-producing process of the ether would be, at least, 3.4 / 400 or 0.8 % of the total rate of decomposition of the ether. Putting a $e^{-E/RT}$ as the rate expression of the free radical producing process, the mathematical expression of the above relation would be

$$\frac{4.0 \cdot 10^{11} e^{-44400/RT}}{A\ e^{-E/RT}} \leq \frac{100}{0.8}$$

i.e.

$$\frac{3.2 \cdot 10^{11}}{A} e^{(E - 44400)/RT} \leq 100$$

At 412°C a difference in activation energy of little more than 6 kcal. corresponds to one hundred fold difference in the exponential factor. If we assume, with Rice and Herzfeld (4), the frequency factor A to be of order 10^{14}, the activation energy E then can be, at most, 15 kcal. higher than 44 kcal., or 59 kcal.. This is quite a low value for the activation energy required to break a C-C or C-O bond.

There are three possible ways in which the ether may split into free radicals, namely,

(a) $C_2H_3OC_2H_5 = C_2H_3 + OC_2H_5$

(b) $C_2H_3OC_2H_5 = C_2H_3O + C_2H_5$

(c) $C_2H_3OC_2H_5 = C_2H_3OCH_2 + CH_3$

It is hardly possible to predict the relative probability of process (c) in preference to (a) or (b), because different kinds of bond splits are involved. For a C-C bond, a single bond in an α position to a double bond is, in general, stronger, and one in a β position weaker than a normal single bond. If we assume the behaviour of the C-O bond to be analogous to that of the C-C bond, reaction (b) should predominate largely over reaction (a). In (b) and (c) methyl and ethyl radicals are involved both of which have been shown to be capable of reacting with nitric oxide. If the free radicals do contribute an important part in the normal decomposition of the ether, we should expect that addition of nitric oxide would decrease the rate to an appreciable extent, since it would certainly combine with part of the methyl and ethyl radicals before they react further. However, in the present experiments, nitric oxide was found to exert negligible effect even when the ratio between nitric oxide pressure and ether pressure is as high as 0.4. This result is very difficult to understand if free radicals play an important part in normal ether decomposition.

Consider now the chain propagating step. In view of the analytical result, if the chain reaction does contribute an important part of the total, the chain propagating steps would presumably be:

$$R + CH_3CH_2OC_2H_3 = RH + CH_3CHOC_2H_3$$

$$CH_3CHOC_2H_3 = CH_3CHO + C_2H_3$$

$$C_2H_3 + CH_3CH_2OC_2H_3 = C_2H_4 + CH_3CHOC_2H_3 \quad .$$

To account for the absence of measureble nitric oxide inhibition, it would have to be assumed that the nitric oxide exerts no effect at all upon the vinyl and $CH_3CHOC_2H_3$ radicals, --- an assumption not, of course, impossible, but quite improbable.

The result for the sensitized decomposition of acetaldehyde and its inhibition by nitric oxide provides further evidence that free radicals do not play an important part in the normal decomposition of vinyl ethyl ether. Consider the mechanism of the sensitized decomposition first. Ether generates the free radicals which react either with ether or acetaldehyde molecules. Their respective chain mechanisms would presumably be as follows:

$$R + C_2H_3OC_2H_5 = RH + C_2H_3OC_2H_4$$

$$C_2H_3OC_2H_4 = CH_3CHO + C_2H_3$$

$$R + CH_3CHO = RH + CH_3CO$$

$$CH_3CO = CH_3 + CO$$

An individual chain propagating through the mixture would be a mixed sequence of these two different kinds of steps. The analytical results demand that if the chain part is important at all, the chains must be of appreciable length, otherwise a considerable portion of the products, arising from the chain ending process, should be something other than acetaldehyde and ethylene.

Even if we assume that nitric oxide has little or no effect on C_2H_3 and $C_2H_3OC_2H_5$ radicals, it should reduce the chain length in the mixture to not more than few steps as a result of its inhibiting action with methyl radicals. The minimum value of the nitric oxide inhibited rate of ether-acetaldehyde mixtures should then correspond to the rate of the rearrangement process in the pure ether case. The experimental results show that the fully inhibited rate is, in fact, very close to the rate of decomposition of ether alone in all cases studied. Hence, any chain mechanism must play a minor role, and the predominant part of the reaction proceed through a rearrangement mechanism.

Since the chain initiating processes are quite frequent (more than 0.8 % of the total rate), but the chain reaction does not play an important part, the chains must be very short. For the chains to be short, either the chain propagating steps involve very high activation energies or vinyl ethyl ether is itself very proficient in associating with free radicals to deactivate them. It is impossible to say anything definite about the chain propagating steps, On the other hand, it is by no means unexpected that this ether should inhibit chain propagation possibly as a result of its unsaturated linkage, as with ethylene (74), p ropylene (40) and azomethane (35).

Assuming that the chain mechanism plays only a small part, it is possible to account for the approximate quantitative relation found in sensitized decomposition of acetaldehyde at 412°C, namely,

$$(\Delta p / p_e) = (\Delta p / p_e)_o + C\ (p_a / p_e)$$

where $\Delta p / p_e$ and $(\Delta p / p_e)_0$ refer to the pressure increases relative to the initial pressures of ether at the end of 90 seconds for the mixture and for the ether in pure state, p_a is the partial pressure of acetaldehyde, and C is a constant equal to about 0.05. Comparing the cases with same partial pressure of ether and equating $\Delta p / \Delta t$ at the end of 90 seconds to the initial rates, we have the relation

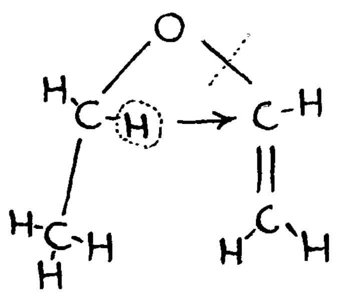
rate of pressure increase of mixture

= rate of pressure increase of pure ether + C'(pressure of aldehyde)

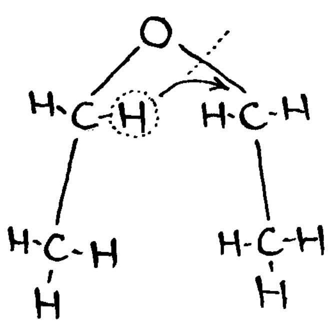
where C' is about $5 \cdot 10^{-4}$ sec^{-1}.

Assuming that rate of pressure increase for pure ether is equal to the rate of the rearrangement process, the rate of pressure increase for the mixture minus the rate of pressure increase for pure ether gives the rate of pressure increase due to the sensitized acetaldehyde decomposition. The rate of sensitized decomposition is then seen to be directly proportional to the aldehyde concentration. This relation is not difficult to understand. The chain length in pure acetaldehyde is much greater than in vinyl ethyl ether, as discussed previously. Therefore, for the mixture the effect of acetaldehyde on the chain ending process may be neglected. Moreover, since acetaldehyde does not start chains nor lead to any chain branching process, the introduction of acetaldehyde would not affect the concentration of free radicals to any large extent. Since cases with same vinyl ethyl ether partial pressure are being compared, this means that the concentrations of free radicals in all cases are practically the same. From this it follows at once that the rate of the sensitized decomposition, being proportional to the product of the acetaldehyde concentration and free radical concentration, would be proportional to the concentration of acetaldehyde or its partial pressure in the mixture.

The conclusion that the decomposition of vinyl ethyl ether occurs essentially by a rearrangement mechanism is not incompatible with the experimental value of the activation energy for the reaction. An estimate of the activation energy required for such a mechanism may be obtained by comparing the rearrangement processes for vinyl ethyl ether and diethyl ether. The actual processes may be depicted as in the following figure.



Vinyl ethyl ether



Diethyl ether

The essential difference between these two processes is that the hydrogen in diethyl ether has to attack a shielded carbon atom, while the hydrogen in vinyl ethyl ether attacks an essentially exposed carbon atom with a double bond. These two different cases are very similar to the two typesdiscussed by Rice and Teller (61), namely, reaction of free radicals with a shielded atom and reaction of free radicals with unsaturated linkages. These authors estimatedthe required energy to push the three hydrogen atoms of a methyl group into the same plane as the carbon atom to be around 40 kcal.. In diethyl ether it is, of course, unknown how far the hydrogen atoms must be pushed away from their normal positions shielding the carbon atom which is being attacked. With vinyl ethyl ether, interference of the one hydrogen shielding the carbon atom is probably responsible for a negligible contribution to the activation energy. On the contrary, the higher electron density ocassioned by the double bond should facilitate approach of the hydrogen atom being transferred. This effect might contribute a few kcal. towards the activation energy. The difference in activation energies of diethyl and vinyl ethyl ethers might therefore be estimated as of the order 10-20 kcal.. Taking 62 kcal., the activation energy for the inhibition reaction of diethyl ether (59), as the activation energy for its rearrangement process, the activation energy for rearrangement of vinyl ethyl ether would be of the order 40-50 kcal.. The experimental value of 44 kcal. for the activation energy therefore appears to be plausible for the rearrangement mechanism.

General Discussion of Decomposition of Ethers

With the addition of our results to the already extensively studied aliphatic ether series, it seems worth while to attempt a general discussion of kinetic behaviors of the ethers with a view to ascertaining to what extents change in structure affects their kinetic behaviour.

The four saturated ethers, namely, dimethyl, diethyl, methyl ethyl, and methyl butyl ethers, have been extensively studied, and their main chemical changes appears to be:

dimethyl ether $CH_3OCH_3 = CH_4 + HCHO$,

diethyl ether $C_2H_5OC_2H_5 = C_2H_6 + CH_3CHO$,

methyl ethyl ether
$CH_3OC_2H_5 = CH_4 + CH_3CHO$
$= C_2H_6 + HCHO$,

methyl butyl ether
$CH_3OC_4H_9 = HCHO + C_2H_4 + C_2H_6$
$= CH_4 + C_3H_7CHO$.

The activation energies of their decompositions are quite close together for both their normal reactions and thenitric oxide inhibited reactions. The mechanisms for their decompositions are predominantly of the chain type, yet there remain appreciable fractions accounted for by rearrangement mechanisms.

Table XI

Substance	Activation energy of normal reaction	Activation energy of inhibited reaction	Mean chain length
Dimethyl	58000	62000	17 (565°C)
Diethyl	58000	62000	3.7 (550°C)
Methyl Ethyl	54500	62000	7.5 (570°C)
Methyl butyl	56600	-----	5.0 (536°C)
Vinyl ethyl	44400	-----	1.0
Divinyl	50000	-----	----

The main propagating steps which have been proposed for the main chemical changes of these four saturated ethers are:

dimethyl ether

$$CH_3OCH_3 + R = R\,H + CH_3OCH_2$$

$$CH_3OCH_2 = CH_3 + HCHO \quad ,$$

diethyl ether

$$C_2H_5OC_2H_5 + R = R\,H + CH_3CHOCH_2CH_3$$

$$CH_3CHOCH_2CH_3 = CH_3CHO + C_2H_5 \quad ,$$

methyl ethyl ether

$$1, \; CH_3OCH_2CH_3 + R = CH_2OCH_2CH_3 + RH$$

$$CH_2OCH_2CH_3 = C_2H_5 + HCHO$$

$$2, \; CH_3OCH_2CH_3 + R = CH_3OCHCH_3 + R\,H$$

$$CH_3OCHCH_3 = CH_3CHO + CH_3 \quad ,$$

methyl butyl ether

$$1,\ CH_3OCH_2CH_2CH_2CH_3 + R = RH + H_2COCH_2CH_2CH_2CH_3$$
$$H_2COCH_2CH_2CH_2CH_3 = HCHO + C_4H_9$$
$$C_4H_9 = C_2H_4 + C_2H_5$$

$$2,\ CH_3OCH_2CH_2CH_2CH_3 + R = RH + CH_3OCHCH_2CH_2CH_3$$
$$CH_3OCHCH_2CH_2CH_3 = C_3H_7CHO + CH_3$$

These mechanisms are all similar in that the free radicals attack only the hydrogen atoms on either of the α carbon atoms. That these two modes of reaction are always observed in the unsymmetrical ethers shows that the lengthening of the hydrogen-carbon chain does not affect the activation energy of this type of process to any appreciable extent.

The total activation energy of a chain process depends not only upon the propagating steps but also the chain ending step. The fact that the activation energies for the normal decompositions of these four ethers are very close together indicates that their chain initiating as well as chain ending steps are quite similar to one another.

The same primary products can be obtained by a single type of rearrangement mechanism by which one hydrogen atom on either of the α carbon atoms finds its way to the other α carbon atom while the bond between this latter carbon atom and the oxygen atom breaks with the formation of an aldehyde and a hydrocarbon. The activation energy corresponding to such a process also changes very little with the length of the alkyl group as seen from the values of the activation energies for the nitric oxide inhibited reactions. Since with all these four ethers, the chain mechanism accounts for the major portion of the total reaction, it means that the activation energy involved in such rearrangement mechanism is higher than that of the chain mechanism.

The introduction of a α-β carbon-carbon double bond, however, changes the picture quite radically. The activation energy of the rearrangement mechanism becomes much lower than for the saturated ethers while it appears that either the chain propagating step is impeded or the chain ending process accelerated by the introduction of a double bond. The result is that the reaction apparently goes predominantly in a rearrangement manner. In passing, it may be pointed out that the process leading to the formation of ketene and ethane is entirely absent. This is perfectly obvious since such a process would undoubtedly require even higher activation energy than that for the saturated ethers, owing to the fact that a hydrogen atom is more firmly bound to a carbon atom with double bond than to one with single bonds only.

The thermal decomposition of divinyl ether has not been clarified, but one point is obvious. Since the activation energy is higher than that of vinyl ethyl ether, it may be concluded that a rearrangement process which would lead to ethylene and ketene must involve far greater activation energy than the rearrangement of vinyl ethyl ether into ethylene and acetaldehyde. This is in line with a higher strength of C-H bond in the vinyl than in ethyl group, although the stereo-relation may also play a part.

From the discussion presented in this thesis, it is apparent that although some minor features still await clarification, among the five ethers comparatively well studied the general behaviour can be brought together into a quite consistent picture. All the similarities as well as dissimilarities are compatible with the general physico-chemical behaviour of these molecules. Indeed, a hormonious interrelation among so many different studies on so many compounds is itself a strong indication that the explanations advanced are essentially correct.

SUMMARY AND CONTRIBUTION TO KNOWLEDGE

An investigation of various aspects of thermal decomposition of vinyl ethyl ether has been carried out.

From detailed analytical studies of products of the reaction at 412°C, it has been found that vinyl ethyl ether decomposes into ethylene and acetaldehyde, the latter of which undergoes further change although pure acetaldehyde decomposes at a negligibly slow rate at this temperature.

The decomposition of this ether has been found to be homogeneous, and essentially of first order in the pressure range from 3 cm. to 20 cm. and in the temperature range 380°- 450°C which were covered in this investigation.

The rate expression has been obtained by method of extrapolation to zero change as

$$k = 4.0 \cdot 10^{11} e^{-44400 / RT} .$$

Investigations have been made on the pressure changes of vinyl ethyl ether-ethylene mixture and vinyl ethyl ether-acetaldehyde mixture at 412°C. It was found that both the decomposition of acetaldehyde and polymerization of ethylene were accelerated in the presence of decomposing vinyl ethyl ether. This has been taken as the evidence of the production of free radicals during the decomposition of vinyl ethyl ether.

Nitric oxide has been found to exert practically no effect on the decomposition of vinyl ethyl ether alone, yet inhibit very pronouncedly the sensitized decomposition of acetaldehyde by vinyl ethyl ether.

An interpretation has been advanced for the decomposition of vinyl ethyl ether of which the essential points are as follows:

1). The most part of the decomposition proceeds through a rearrangement mechanism.

2). Although many free radicals are produced during the decomposition of the ether, the part played by the free radicals is inappreciable owing to the strong resistance of this ether to the propagation of chain.

It has been pointed out that an inhibiting action of vinyl ethyl ether toward the chain propagation is quite plausible owing to its unsaturated linkage, although it is not certain whether this is the true cause or not.

The experimental activation energy, 44400 cal, has been shown to be not unreasonable for a rearrangement mechanism of decomposition of vinyl ethyl ether.

A general comparative discussion of all the available knowledge about the thermal decompositions of aliphatic ethers has been made.

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