AIP | The Journal of Chemical Physics

The Thermal Decomposition of Divinyl Ether

H. Austin Taylor

Citation: The Journal of Chemical Physics **4**, 116 (1936); doi: 10.1063/1.1749797
View online: http://dx.doi.org/10.1063/1.1749797
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/4/2?ver=pdfcov
Published by the AIP Publishing

FEBRUARY, 1936 JOURNAL OF CHEMICAL PHYSICS VOLUME 4

The Thermal Decomposition of Divinyl Ether

H. AUSTIN TAYLOR, *New York University, University Heights*

(Received October 31, 1935)

The thermal decomposition of divinyl ether has been studied at temperatures between 460° and 500°C, and at pressures from 30 to 1000 mm. That the reaction has a chain mechanism, chains being broken on the walls at low pressure and in the gas phase at high pressure, is concluded from the effects of (a) increased surface, (b) added nitrogen (c) varying temperature coefficient with pressure and (d) induced decomposition with azomethane. The over-all order at high pressure is three-halves judged both from the individual velocity constants during a run and from the variation of velocity constant with pressure.

THE thermal decomposition of numerous relatively complex organic compounds has been shown to proceed with an over-all first order rate. This has been satisfactorily accounted for by the free radical chain theory in many instances for which experimental data are available; a treatment confirmed by a specific rate enhancement upon introduction of free radicals either thermally or photochemically. The theoretical treatment of certain reactions however from this point of view is not without difficulty and rival theories must not be overlooked. The ethers constitute a series, the decompositions of which seem undoubtedly to follow a chain mechanism, and analysis of the chain steps has furnished indirect evaluations of the activation energies of various radical-molecule reactions. Divinyl ether being unsaturated might be expected to furnish additional evidence for or against the free radical mechanism as a general scheme for ether decompositions. This choice would seem particularly interesting since from the point of view of a direct decomposition into product molecules the reaction would appear to be very simple. The prevalent view of ether decomposition prior to the chain mechanism suggestion, considered the possibility of a hydrogen transfer across the oxygen in the ether molecule followed by rupture to yield a hydrocarbon and an unstable residue which subsequently decomposed. Thus for methyl ether the hydrogen transfer would yield methane and formaldehyde. The parallel for divinyl ether would suggest the formation of ethylene and ketene, the latter in turn yielding ethylene and carbon monoxide. If the reaction were to proceed at temperatures below which ethylene polymerizes and decomposes, the products expected would be very simple and the reaction kinetics therefore easier of interpretation even than those of the saturated ether. Such a procedure, however, is not found. On the contrary the complexity appears to be even greater. Evidence is presented that the reaction has a chain mechanism and from a theoretical point of view at least will be equally as complex as diethyl ether in the contingency of multiple interacting chains with possibly doubtful establishment of a steady state.

EXPERIMENTAL

The divinyl ether employed was a Merck product obtained through the courtesy of Dr. Major to whom thanks are due. It was furnished containing one-hundredth of a percent of an oxidation inhibitor and for the first series of experiments was distilled from this. The boiling point was 28.3°C in agreement with that found by Miles and Menzies.[1] Subsequent experiments were performed with the sample direct without further purification with no change in the decomposition rates. This is to be expected in view of the nonvolatility of the inhibitor present. It may be well to remark at this stage that polymerization of the liquid ether was observed on a few occasions but in all such cases oxygen may have been present. The liquid under its own vapor pressure alone showed no tendency to polymerize and the vapor maintained for long periods of time at temperatures where decomposition was just too slow to measure showed no volume decrease.

---

[1] Miles and Menzies, J. Phys. Chem. **37**, 425 (1933).

The experimental procedure was similar to that previously reported for static studies from this laboratory. The reaction vessel of Pyrex glass was about 250 cc capacity. During an attempt to find a limiting rate at high pressure condensation of some product of the reaction in the capillaries outside the furnace necessitated an auxiliary heating of these to about 80°C. In the lower pressure range this was not found necessary.

To investigate the products of decomposition several dynamic experiments were made. The ether vapor was forced through a small capillary under constant pressure, thence through a furnace, by varying the temperature of which the products corresponding to more or less reaction as desired could be found.

RESULTS AND DISCUSSION

The results of a typical static experiment in the early stages are given in Table I.

TABLE I. *Initial Pressure 339 mm; temperature 500°C.*

TIME (min.)	PRESSURE CHANGE	k_{uni} (sec.$^{-1}$)	k_{bi} (sec.$^{-1}$)
1	48	2.54×10^{-3}	8.11×10^{-6}
2	87	2.47	8.49
3	119	2.40	8.86
4	147	2.37	9.41
5	169	2.30	9.78
6	187	2.23	10.1
7	201	2.14	10.2
8	216	2.11	10.8
10	237	2.00	11.4
12	252	1.89	11.9

The endpoint of the reaction appeared to be somewhat erratic varying between 1.05 and 1.24 for the ratio of pressure change to initial pressure. No systematic variation with temperature was found though the higher the initial pressure the greater in general was the endpoint ratio. In Table I, are included the values of the unimolecular and bimolecular velocity constants calculated in the usual way but assuming an endpoint ratio of unity; the time unit is the second, the concentration unit in k_{bi} being the pressure directly observed in mm mercury. Since only the relative variation is required this is satisfactory. It will be observed that k_{uni} decreases whilst k_{bi} increases, the latter somewhat more rapidly than the former. The over-all order during a run is thus between one and two. For comparison of results at different pressures and temperatures use has therefore been made of the extrapolated first order constant obtained graphically from the pressure-time ratios in the early stages. This at least may be expected to give a more nearly true initial decomposition rate of the pure substance even when the products of reaction do affect the rate, than any other simple method.

Table II contains these data for the various pressures and temperatures studied. Numerous other experiments were made at lower pressures down to about one mm. In all these cases, however, a marked induction period was ob-

TABLE II.

INITIAL PRESSURE (mm)	$k\times10^4$ (sec.$^{-1}$)	INITIAL PRESSURE (mm)	$k\times10^4$ (sec.$^{-1}$)
460°C		480°C	
18	1.48	33	4.04
26.5	1.57	60	4.86
45	1.85	98	6.30
65	2.10	126	7.94
77	2.16	167	7.98
83	2.41	199	8.79
103	2.90	353	10.9
170	3.49	377	11.5
210	3.77	475	13.0
302	4.14	561	13.7
417	4.40	691	14.7
520	4.81	817	15.3
702	5.22	977	17.1
891	5.61		
1008	5.95	490°C	
1050	6.03	19	5.25
470°C		35	6.21
19	2.19	60	8.05
27	2.47	101	9.57
54.5	3.06	112	11.2
94	3.52	183	13.7
143	4.65	260	16.0
198	5.89	358	18.2
327	6.63	401	18.7
421	7.52	738	22.6
551	7.86	871	23.9
637	8.63	942	26.5
760	9.21		
1056	10.1		
500°C		470°C	
22	7.58	added surface	
30	8.33		
57	11.7	39	1.92
102	15.4	89	2.53
110	16.1	133	3.01
204	20.4	288	5.06
339	26.1	474	6.74
439	28.3		
491	28.5		
587	31.5		
762	36.1		
928	39.9		

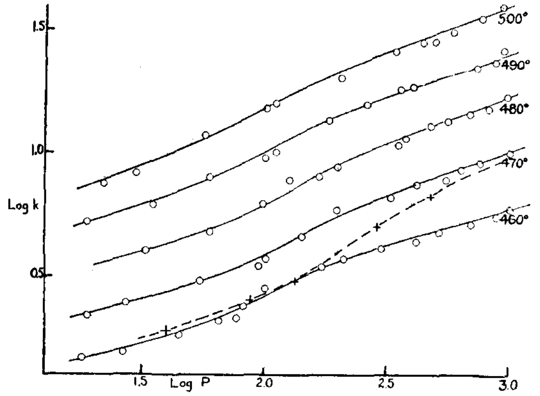

FIG. 1. Curves showing the variation of initial reaction rate with pressure at 460°, 470°, 480°, 490° and 500°C.

servable, greater at lower temperatures. The data are not included even though the slope of the pressure-time curve after the induction period would seem to fall well on the log $k-\log p$ plot. Experience with several reactions with induction periods has shown that such agreement is frequently fortuitous and always misleading.

The above data are plotted in the figure, the resulting curves being reminiscent of the type found in diethyl ether and propylamine[2] but not at all like those to be expected for a simple unimolecular reaction which would be concave downwards. There does seem to be evidence that the curves are becoming concave downwards at the highest pressures measured though the rate of approach to a limit is too slow to justify any extrapolation. At the lowest pressures studied too, there does not appear to be any indication of a limiting value. The average slope of the curves is about 1/3 corresponding to a 4/3 order and at the highest pressures the slope is 1/2, that is the reaction is 3/2 order.

The effect of added surface is shown in Fig. 1 by the dotted curve. The reaction vessel was filled with short lengths of 5-mm tubing, the ends being fire-polished, whereby the calculated surface to volume ratio was increased 3.5 times. At the highest pressures the effect is very small but in the lowest pressure range the rate is decreased to an extent approximately equivalent to a decrease of ten degrees in temperature. This fact alone is suggestive of a chain mechanism for the reaction.

Table III contains the data obtained in a study of the effect of various gases added to the system. The gas labeled products was simply the residue after some divinyl ether had completely decomposed. An examination of these data shows that the effect of added gases is in general to reduce the rate of reaction. With the exception of hydrogen there is no reason to suspect from the results that specific chemical action was occurring in any case. With hydrogen, although the initial rate was the same as that for the ether alone the pressure-time curve reached its endpoint sooner yielding a value 0.9 as compared with 1.1 to 1.2 as previously mentioned. It seems likely that this reduction of the endpoint ratio, is due to hydrogenation of unsaturated bodies shown later to be present. This does not absolutely preclude of course the possibility that chemical action might have occurred for example with the products even though the endpoint is apparently unchanged. Thus the ratio for 100 mm ether alone at 500°C was 1.12 and for 112 mm ether in presence of 112 mm of product was also 1.12. The point is mentioned because the effect of products in reducing the initial rate of decomposition seems considerably greater in the lower ether pressure range than is found for example with the more probably inert gas nitrogen. Since ethylene and carbon monoxide are among the products their effects were tested separately but showed no such marked reduction of the rate as did the products. When a sufficiently large excess of ethylene was used a

TABLE III.

ETHER PRESSURE (mm)	ADDED GAS PRESSURE (mm)	T°C	$k\times10^4$ (sec.$^{-1}$)
110	None	500	16.1
112	Products, 112	500	12.7
116	Products, 240	500	10.1
103	Products, 350	500	8.15
100	Nitrogen, 100	500	16.3
200	None	470	5.50
200	Nitrogen, 204	470	5.42
344	None	470	6.92
344	Nitrogen, 153	470	6.05
464	None	470	7.76
464	Nitrogen, 100	470	6.83
111	Hydrogen, 99	500	16.1*
102	Ethylene, 96	500	16.3
109	Ethylene, 202	500	15.0
103	Carbon Monoxide, 104	500	16.2

* Endpoint reduced to 0.9.

---

[2] O. K. Rice and D. V. Sickman, J. Am. Chem. Soc. **56**, 1444 (1934); **57**, 22 (1935).

relatively small rate reduction was observed. The results for nitrogen are particularly illuminating. For pressures of the ether around 100 to 200 mm even twice that amount of nitrogen has a relatively small effect. At higher ether pressures a considerably smaller amount of nitrogen causes a marked reduction in the initial decomposition rate. Now it is precisely in this higher range of ether pressures that the effect of surface is least, hence that the reaction is a chain reaction, chains being broken on the walls at lower pressures and in the gas phase at higher pressures would seem a possible explanation. It would thus appear possible that the curves shown in the figure are complex, the one showing the variation with pressure of the over-all rate of reaction heterogeneously terminated, the other homogeneously. The apparent inflection should then correspond to a pressure at which the homogeneous and heterogeneous effects become approximately equal. It would be interesting to study the reaction in presence of very extensive surfaces at considerably higher pressure and also in large volume with a correspondingly small surface at lower pressure, to give an idea of the variation of the heterogeneous and homogeneous effects over a larger pressure range. The indication herein is that the $\log k - \log p$ plot is concave upwards for the heterogeneous effect and the reverse for the homogeneous. The former is explicable on the basis of increasing saturation of the surface for deactivation or chain breaking; the latter since the over-all order is less than two whereas deactivating or chain-breaking collisions are presumably bimolecular.

An examination of the figure shows that the $\log k - \log p$ plots for the different temperatures are not parallel but approach each other in the low pressure range and diverge from each other at higher pressures. This is tantamount to saying that the energy of activation increases with increasing pressure. Thus it is found that around 30 mm pressure the mean energy of activation, calculated from the curves for the different temperatures at constant pressure, is 47,000 calories; at 100 mm it is 50,000 whilst at 300 mm, 51,000 calories. Such a variation is outside the limits of experimental error, which should not be more than 1000 calories, and would be inexplicable for a simple reaction. In a chain of reactions with the possibility of more than one chain carrier such a variation is at least explicable if not in fact to be expected.

In an effort to determine the products of the reaction a small amount of the liquid divinyl ether was sealed in a small bomb and completely decomposed at 450°C. The resulting gases were then analyzed. The bomb after the decomposition was dark brown in color but showed 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 C—H balance from the gas analyses gave an end product with the formula $CH_{1.5}$. The data for the analyses are given in Table IV. Included in the table are the analyses made in the dynamic experiments by the method outlined above. The effluent gases from the furnace were bubbled through water to remove soluble products including unchanged ether, the gases in the above analyses being collected over water. The presence of ketene in the effluent gas was demonstrated by treatment with alkali and subsequent identification of acetic acid. The multiplicity of products renders a complete systematization of mechanism extremely difficult. However even a cursory review of the possibilities of chain reactions in this decomposition will indicate the complexities to be expected.

TABLE IV.

	COMPLETE DECOMPOSITION (Percent)	PARTIAL DECOMPOSITION 450	475	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

There is very little evidence to indicate definitely what types of disruptions may be expected in a molecule as unsaturated as divinyl ether. The only apparent rule relative to unsaturated compounds[3] is that with a doubly bound carbon atom, the alpha-bonds are stronger than normal whereas the beta-bonds are weaker. Actually in divinyl ether there are no beta-bonds

---

[3] F. O. Rice and K. K. Rice, *Aliphatic Free Radicals* (Johns Hopkins Press, 1935).

unless the C−O bonds may be considered as beta to the farther double bond. It would seem probable though that the ether linkages would be slightly weaker in this case than for the saturated ethers and hence the primary break would certainly occur there. Beyond that there is little precedent to indicate the relative strengths of the remaining bonds. The following equations summarize the majority of the more obvious possibilities.

$$\begin{gathered}
\mathrm{CH_2:CH{-}O{-}CH:CH_2 \rightarrow CH_2:CHO+CH_2:CH} \\
\mathrm{CH_2:CH+CH_2:CH{-}O{-}CH:CH_2 \rightarrow CH_2:CH_2+CH_2:COCH:CH_2} \\
\mathrm{CH_2:CH+CH_2:CH{-}O{-}CH:CH_2 \rightarrow CH_2:CH_2+CH:CH{-}O{-}CH:CH_2} \\
\mathrm{CH_2:COCH:CH_2 \rightarrow CH_2:CO+CH_2:CH} \\
\mathrm{CH:CH{-}O{-}CH:CH_2 \rightarrow CH \vdots CH+CH_2:CHO} \\
\mathrm{CH_2CHO \rightarrow CH_3+CO} \\
\mathrm{CH_3+CH_2:CH{-}O{-}CH:CH_2 \rightarrow CH_4+CH_2:COCH:CH_2} \\
\mathrm{CH_3+CH_2:CH{-}O{-}CH:CH_2 \rightarrow CH_4+CH:CH{-}O{-}CH:CH_2} \\
\mathrm{2CH_2:CH \rightarrow C_4H_6} \\
\mathrm{2CH_3 \rightarrow C_2H_6} \\
\mathrm{CH_3+CH_2:CH \rightarrow CH_4+CH \vdots CH}
\end{gathered}$$

There is therefore a high probability of at least two distinct chain carriers with the possibility of two alternative modes of reaction of each, one of which regenerates itself whilst the other regenerates the second carrier. The two schemes are therefore considerably interlocked and judicious assumptions could easily account at least qualitatively for a variation of reaction order and a variation of energy of activation with pressure. Furthermore, as numerous efforts, which find no place here, have shown, judicious choice from among the above can give a three-halves order reaction rate which in most cases corresponds to an over-all activation energy around 50,000 calories as observed. It seems useless to be more specific at the present time until further evidence is forthcoming.

It should be remarked in passing that the presence in quantity of acetylene and butadiene in the final products should not be expected since decomposition of the former sets in markedly around 500°C, of the latter below 400°C, whilst polymerization of acetylene could account for the presence of condensable products observed in the high pressure runs. Moreover it should not be overlooked that addition reactions as well as polymerizations are possible in a system as unsaturated as that of vinyl ether and its products, though it is doubtful if they are likely to any appreciable extent under the temperature conditions used herein.

The most hopeful indication of further evidence seems to be forthcoming from work now in progress in this laboratory by F. P. Jahn on the decomposition of divinyl ether induced thermally by azomethane. The reaction proceeds quite rapidly at 330°C with less than ten percent of azomethane. The over-all order is about three-halves though a resolution of this into the separate orders relative to the ether and azomethane alone has not yet been made. It is not certain that the induced reaction is identical with the decomposition here studied; a lower endpoint signifies a difference. Such a difference may however actually afford a means of distinguishing between the many possible chains suggested.