AIP The Journal of Chemical Physics

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Citation: J. Chem. Phys. **20**, 574 (1952); doi: 10.1063/1.1700495 View online: http://dx.doi.org/10.1063/1.1700495 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v20/i4 Published by the AIP Publishing LLC.

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Kinetics of the Decomposition of Diethyl Peroxide*

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(Received December 17, 1951)

The kinetics of the gas-phase decomposition of diethyl peroxide have been studied in a flow system, using excess of toluene. The main reaction products were found to be ethane and formaldehyde, and there were smaller amounts of methane and dibenzyl. The frequency factor of the reaction is 2.1×1013, and the activation energy is 31.7 kcal per mole. The mechanism of the reaction is discussed, and it is shown that the measured rate must refer to the initial dissociation $C_2H_5OOC_2H_5 \rightarrow 2C_2H_5O$. With a new value of 47.8 kcal for the heat of formation of gaseous diethyl peroxide, the heat of formation of the C2H3O radical is calculated to be 8.1 kcal, which agrees satisfactorily with estimates from other kinetic data. Thermochemical values for other reactions involving this radical are calculated.

CTUDIES of the kinetics of the decompositions of S peroxides have a special interest in that they provide dissociation energies for O-O bonds in these compounds and enable heats of formation of the alkoxy radicals to be calculated. The main work of this type so far carried out has been on di-t-butyl peroxide^{1,2} for which dissociation energies of 39.1¹ and 36.0² kcal have been obtained. The decomposition of diethyl peroxide was studied in a static system by Harris and Egerton,³ and an activation energy of 31.5 kcal was obtained. These authors concluded the reaction to be a nonchain process at lower temperatures, and the present work substantiates this view. This conclusion was not entirely certain, however, particularly as the reaction became explosive at higher temperatures. A further reason for suspecting the conclusion that 31.5 kcal represented the dissociation energy of the O-O bond was that this assumption led to a heat of formation for the radical C₂H₅O that was inconsistent with other values; this latter difficulty we have, however, traced to an error in the value for the heat of formation of the peroxide itself.⁴ Walsh⁵ in particular has proposed that

TABLE I. Mass spectrographic analysis pattern of diethyl peroxide.

m/e	pattern	m/e	pattern
14	13.03	31	33.21
15	42.49	43	20.65
26	7.95	44	11.04
27	21.72	45	31.00
28	7.90	62	18.55
29	100.00	90	11.15
30	8.99		

* Abstracted from a dissertation presented by Richard E. Rebbert to the Graduate School of the Catholic University of America, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

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¹ Raley, Rust, and Vaughan, J. Am. Chem. Soc. **70**, 88 (1948); Rust, Seabold, and Vaughan, J. Am. Chem. Soc. **70**, 95 (1948). ² Muraski, Szwarc, and Roberts, J. Chem. Phys. **19**, 698 (1951).

⁸ E. J. Harris and A. C. Egerton, Proc. Roy. Soc. (London) A168, 1 (1938

⁴ E. C. Stathis and A. C. Egerton, Trans. Faraday Soc. 36, 606 (1940).

the O-O dissociation energy in diethyl peroxide is very much greater than 31.5 kcal; the present work, however, does not support this interpretation.

With a view to establishing with more certainty the heat of dissociation of the peroxide, we have made a study of its decomposition in a flow system with excess of toluene, using the method introduced by Szwarc.⁶

EXPERIMENTAL

Preparation of Diethyl Peroxide

Diethyl peroxide was prepared by the method of Baeyer and Villiger⁷ as modified by Harris and Egerton.³ The crude product was first vacuum distilled to remove all volatile products which were then distilled at atmospheric pressure and the fraction from 60-70°C was collected. This was washed with sodium hydroxide solution and dried with potassium carbonate. It was then redistilled and the fraction from 63-67°C was retained. It was washed again with sodium hydroxide and dried with potassium carbonate and redistilled, the final distillation range being 64.3-65.3°C.

To test the purity of the compound a mass spectrographic analysis was made.* The main peaks are shown in Table I; peaks which were less than 5 percent of the highest peak are omitted. The absolute purity of the sample could not be determined since there is no standard of diethyl peroxide with which to compare it. However, the lack of any appreciable peak at 17 m/eindicates the absence of any alcohol or hydroperoxide. Also, the lack of any appreciable peak at 74 m/e indicates the absence of diethyl ether. The index of refraction of the compound was taken at various temperatures and the results are given in Table II along with the results given in the literature.

The toluene used was from Mallinckrodt Chemical Works, analytical reagent grade (meets A.C.S. specifications).

⁵ A. D. Walsh, J. Chem. Soc., 331 (1948); Trans. Faraday Soc. 42, 264 (1946).
 ⁶ M. Szwarc, J. Chem. Phys. 16, 128 (1948); 17, 431 (1949).
 ⁷ A. von Baeyer and V. Villiger, Ber. deut. chem. Ges. B33, 3387

* Courtesy of the National Bureau of Standards.

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TABLE II. Index of refraction of diethyl peroxide.

Temperature	9.5°C	15°C	16.5°C	20°C
Observed	1.3752	1.3720	1.3718	1.3700
Literature	1.3758	1.3712	1.3715	1.3698

Kinetic Procedure

The apparatus, which is similar to that used by Szwarc,⁶ is shown in Fig. 1. Toluene was introduced through the capillary K_2 from flask V_1 which was maintained at constant temperature. Stopcocks S_1 and S_2 and the intervening tubing were heated to about 80°C with nichrome wire in order to prevent any condensation of toluene; Dow-Corning High Vacuum grease was used in this part of the system. The peroxide was introduced through capillary K_1 from flask V_2 which is also surrounded by a constant temperature bath. The gases were passed through a spiral R which was maintained at constant temperature in a thermostatically controlled furnace. The temperature of the furnace was measured using an iron-constantan thermocouple. The first trap after the furnace, T_1 , was surrounded with dry ice-acetone and condensed most of the toluene and undecomposed peroxide. The second trap T_2 was immersed in liquid nitrogen and retained the ethane and formaldehyde. The mercury diffusion pump P was capable of maintaining a steady pumping speed even when stopcock S_9 was closed and a small methane pressure built up in the vessel V_3 .

Before starting a run, flasks V_1 and V_2 were weighed. They were then inserted into the system and the contents repeatedly frozen in liquid nitrogen, evacuated, and melted. Every 15 minutes during a run the pressure was read on manometer M_1 using a traveling telescope and was usually constant to 0.2 mm. The toluene, peroxide, ethane, and formaldehyde were condensed in traps T_1 and T_2 , while the methane formed went into the storage vessel V_3 and its amount was determined at the end of the run. The storage vessel was then evacuated and a liquid nitrogen trap was placed around trap T_4 . Stopcock S_7 was opened and a liquid ethylene trap replaced the liquid nitrogen trap about T_2 . After about 15 minutes stopcock S_7 was closed and the liquid nitrogen was removed from trap T_4 . The temperature and pressure of ethane and formaldehyde were measured. Finally, flasks V_1 and V_2 were removed and reweighed in order to determine the amounts of toluene and peroxide that went through the furnace. The total volume of gas that went through the furnace could be calculated from the total number of moles of toluene and peroxide and the pressure and temperature of the furnace. The contact time was then determined from this total volume passed, the volume of the furnace, and the time in which it passed. From the contact time, the amount of peroxide passed, and the amount decomposed (see later), the specific rate at the temperature of the furnace was calculated using the first-order rate equation.

RESULTS

The main products of the reaction were found to be ethane and formaldehyde, and much smaller amounts of methane and dibenzyl were found. Some polymerization of the formaldehyde occurred in the traps; the polymer was a white solid which gave the Tollen and Fehling tests. The reaction rate was calculated from the amount of ethane formed plus one-half of the amount of methane; the justification for this is given in the next section. To determine the amount of ethane from the combined pressures of ethane and formaldehyde a correction had to be made for the amount of polymerization. It was estimated that 20 percent of the formaldehyde polymerized. The error in activation energy arising from inaccuracy in this figure is only slight; thus even taking the extreme cases of zero and 100 percent polymerization, the inaccuracy is only ± 2 kcal, and therefore is, in fact, very much smaller than this.

The results are summarized in Table III. The rate constants are shown plotted against 1/T in Fig. 2. The activation energy is found to be 31.7 ± 1 kcal, and the frequency factor is 2×10^{13} sec⁻¹. The latter value is consistent with the values found by Szwarc⁸ for reactions of this type, including the di-*t*-butyl peroxide reactions.² The activation energy is in excellent agreement with the value (31.5 kcal) given by Harris and Egerton³ for the over-all process in a static system.

DISCUSSION

Kinetic Mechanism

The products obtained for this reaction indicate that the main processes are

$$C_2H_5OOC_2H_5 \rightarrow 2C_2H_5O, \tag{1}$$

$$C_2H_5O \rightarrow CH_3 + CH_2O, \qquad (2)$$

$$2CH_3 \rightarrow C_2H_6.$$
 (3)



FIG. 1. Schematic diagram of apparatus. The stopcock S_9 is connected to the forepump, S_{10} to a McLeod gauge.

⁸ M. Szwarc, Chem. Revs. 47, 75 (1950).

T°C	Total pressure (mm)	Ratio toluene peroxide	Contact time (sec)	% decomp	k×10 ² (sec ^{−1})
239	12.15	68/1	0.863	31	42.4
245	12.62	74/1	0.850	42	64.3
234	12.51	76/1	0.858	26	35.0
234	12.05	73/1	0.857	28	38.6
218	11.91	73/1	0.894	10	14.7
213	10.91	74/1	0.893	6	6.63
210	11.13	78/1	0.888	7	8.30
206	11.99	91/1	0.900	6	6.41
242	12.01	84/1	0.832	24	57.4
226	12.04	89/1	0.856	17	22.3
241	11.48	78/1	0.850	39	57.6
200	11.39	79/1	0.914	3	3.58
210	11.53	77'/1	0.910	6	6.76

TABLE III. Summary of results.

In addition the reactions

$$CH_3 + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2 \tag{4}$$

$$2C_{6}H_{5}CH_{2} \rightarrow C_{6}H_{5}CH_{2}CH_{2}C_{6}H_{5}$$
(5)

must occur to a small extent to account for the fact that methane and dibenzyl are minor products. The fact that no ethyl alcohol is formed shows that reaction (2) is more rapid than the process $C_2H_5O+C_6H_5CH_3 \rightarrow$ $C_2H_5OH+C_6H_5CH_2$. The small amounts of dibenzyl formed are consistent with the result⁹ that the activation energy of (4) is 8.3 kcal higher than that of (3); dibenzyl will therefore only be formed in large amounts at higher reaction temperatures.

The reaction under our conditions is much simpler than as studied by Harris and Egerton³ who found appreciable amounts of acetaldehyde, ethyl alcohol, and carbon monoxide in addition to the products we obtained. These products are presumably formed by the following reactions:

$$C_{2}H_{b}O+C_{2}H_{b}OOC_{2}H_{b}\rightarrow C_{2}H_{b}OH+CH_{3}CHOOC_{2}H_{b}$$
(6)

$$CH_{3}CHOOC_{2}H_{5} \rightarrow CH_{3}CHO + C_{2}H_{5}O$$
(7)

$$CH_3CHO \rightarrow CH_4 + CO$$
 via chain processes. (8)

The absence of these complicating reactions in our investigation is to be attributed to the very low peroxide pressures employed, so that the bimolecular reactions occur slowly; reaction (3) is probably a surface reaction and therefore can occur readily at low pressures.

Kinetic Law

In terms of reactions (1)-(5) the rate of decomposition of peroxide is the rate of formation of ethane plus one-half the rate of formation of methane; this is so because every peroxide molecule gives rise to two methyl radicals, each of which may either dimerize to give $1/2C_2H_6$ or may react with toluene to give CH₄. The rates given in Table III are in fact determined in this way. Since diethyl peroxide only disappears by reaction (1), the over-all rate is

$$-\frac{d[C_2H_5OOC_2H_5]}{dt} = k_1[C_2H_5OOC_2H_5],$$

so that the over-all activation energy is applicable to reaction (1).

The O - O Dissociation Energy

The activation energy of 31.7 kcal for reaction (1) is almost certainly the energy of dissociation of the O-Obond in the peroxide, since the activation energy of the reverse reaction is probably zero. It is of interest to compare this value with that for other O-O bonds, the values for which are as follows:

D(HO-OH) = 54 kcal per mole $D(C_2H_5O-OC_2H_5) = 31.7$ kcal per mole $D(C_3H_7O-OC_3H_7) = 35$ kcal per mole $D((CH_3)_3CO-OC(CH_3)_3) = 36$, 39 kcal per mole.



FIG. 2. Plot of $\log_{10}k$ vs 1/T. The least squares activation energy is 31.7 kcal per mole.

Thermochemistry of the C₂H₅O Radical

Assuming the activation energy of 31.7 kcal to be the energy of dissociation of the O-O bond, the heat of formation of the C_2H_5O radical can be calculated provided that for the peroxide is known. Stathis and Egerton's value⁴ of 68.0 for the liquid peroxide gave rise to inconsistent results (see below), and we arranged for a redetermination of the heat of combustion to be carried out on our sample; this was very kindly done by Mr. F. A. Zihlman at the U. S. Naval Powder Factory at Indian Head, Maryland. His value (662.2 kcal per mole) leads to 55.6 kcal per mole for the heat of formation of the liquid peroxide, and a correction based on Trouton's rule gives 47.8 kcal for the gaseous substance. The heat of formation for C_2H_5O calculated from this value is 8.1 kcal per mole.

⁹ A. F. Trotman-Dickenson and E. W. R. Steacie, J. Chem. Phys. 19, 329 (1951).

Values for this quantity may also be calculated from other data. The activation energy of 37.7 kcal for the decomposition of ethyl nitrite¹⁰ is almost certainly the dissociation energy of the N-O bond in the molecule, and heats of formation are available for the nitrite and for nitric oxide. Two activation energies, 34.6 and 39.9 kcal, have been obtained for the decomposition of ethyl nitrate,^{11, 12} and these again almost certainly correspond to the dissociation energy of the bond. Unfortunately, the heat of formation of the nitrate is not certain since various values have been quoted.

In Table IV are presented a number of possible combinations of values for the peroxide, nitrite, and nitrate data; the value for the heat of formation of the C_2H_5O radical is given in each case. The value obtained on the basis of the Stathis-Egerton heat of formation of the peroxide is seen to be much higher than the remaining values. The value of 8.1 from the peroxide work agrees satisfactorily with that from the nitrite study. It also

TABLE IV. Data for reactions $C_2H_5OX \rightarrow C_2H_5O + X$.

-					
	X	$Q_f(C_2H_6OX)$	$Q_f(X)$	D	$Q_f(C_2H_bO)$
	C ₂ H ₅ O	47.8ª		31.7 ^b	8.1 ¹
	C_2H_5O	60.2°	• • •	31.7ь	14.3
	NO	25.9 ^b	21.6e	37.7 ⁴	9.8^{1}
	NO_2	33.4 ^d	-8.0^{g}	34.6 ^h	6.8
	NO_2	33.4 ^d	-8.0^{g}	39.9 ⁱ	1.5
	NO_2	34.9 ^j	-8.0^{g}	34.6 ^h	8.3 ¹
	NO_2	34.9i	- 8.0 ^g	39.9 ⁱ	3.0
	NO_2	35.8 ^k	8.0 ^g	34.6 ^h	9.2 ¹
	NO_2	35.8 ^k	-8.0^{g}	39.9 ⁱ	3.9

. F. A. Zihlman (private communication).

* F. A. Zihlman (private communication).
b Present investigation.
• E. C. Stathis and A. C. Egerton, Trans. Faraday Soc. 36, 606 (1940);
value corrected for the gaseous peroxide.
d J. Thomsen, Thermochemische Untersuchungen (Barth, Leipzig, 1882-6).
• M. P. E. Barthelot, Ann. chim. et phys. (5) 20, 255 (1880).
f E. W. R. Steacie and S. Katz, J. Chem. Phys. 5, 125 (1937).
• M. Randall, International Critical Tables, Vol. VII, p. 239.
b L. Phillips, Nature 160, 753 (1947).
• G. K. Adams and C. E. H. Bawn, Trans. Faraday Soc. 45, 494 (1949).
i E. Schmidt, Z. ges. Schiess-u. Sprengstoffw. 29, 262 (1934).
* Landolt-Bornstein, Physik. Chem. Tabellen, II. 1619.
¹ These values are mutually consistent within experimental error.

¹ These values are mutually consistent within experimental error.

agrees well with the results of the nitrate work, provided that Phillips's activation energy is used. The Adams and Bawn activation energy seems to be too high to give agreement using any of the heats of formation for the nitrate. The values marked with an asterisk in Table IV are the ones that appear to be most mutually consistent.

By assuming the heat of formation of C_2H_5O to be 8.1 kcal, other interesting heats of dissociation can be deduced. Those for C₂H₅O-H, CH₃CO-OC₂H₅, and

TABLE V. Derived heats of dissociation.

Dissociation	Heats of formation			Heats of dissociation kcal per
$AB \rightarrow A + B$	AB	A	В	mole
$\begin{array}{c} \hline \\ \hline $	57.0ª 59.6° 57.0ª 106.6° 8.1 ^b 8.1 ^b 8.1 ^b	8.1 ^b 8.1 ^b -26.0 ^d 6.6 ^d -31.0 ^d -26.0 ^d -51.9 ^a	-51.9ª -26.0d -10.0ª 8.1 ^b 28.7ª -59.2ª 44.0ª	100.8 77.5 93.0 91.9 10.4 93.3 16.0

* F. D. Rossini *et al.*, "Selected values of properties of hydrocarbons," Natl. Bur. Standards.

b Present investigation,
e F. Stohmann, J. prakt. Chem. (2) 35, 40, 136 (1887).
d E. Butler and M. Polanyi, Trans. Faraday Soc. 39, 19 (1943).
e E. Schjanberg, Z. physik. Chem. A172, 197 (1935).

 $CH_3 - CH_2O$, together with related dissociations, are given in Table V. The value of 10.4 for the reaction $C_2H_5O \rightarrow CH_3 + CH_2O$ clearly places a lower limit on the activation energy of this reaction which plays a part in many reaction mechanisms.

The low value of 77.5 kcal for the dissociation $C_2H_5OC_2H_5 \rightarrow C_2H_5O + C_2H_5$ is of special interest in that it suggests that this reaction will be the first step in the decomposition of the ether; the alternative process $C_2H_5OC_2H_5 \rightarrow CH_3 + CH_2OC_2H_5$ proposed by Rice and Herzfeld¹³ probably has a higher dissociation energy. The mechanism for the decomposition is thus probably

$$\begin{array}{c} C_2H_5OC_2H_5\longrightarrow C_2H_5O+C_2H_5\\ C_2H_5O\longrightarrow CH_2O+CH_3\\ C_2H_5+CH_3CH_2OC_2H_5\longrightarrow C_2H_6+CH_3CHOC_2H_5\\ CH_3+CH_3CH_2OC_2H_5\longrightarrow CH_4+CH_3CHOC_2H_5\\ CH_3CHOC_2H_5\longrightarrow CH_3CHO+C_2H_5.\\ \end{array}$$

If chain ending occurs mainly by recombination of CH₃ and C₂H₅ with CH₃CHOC₂H₅, the kinetics are first order in agreement with experiment.¹⁴ This scheme seems preferable to that of Rice and Herzfeld in avoiding the unlikely step

 $CH_3 + C_2H_5OC_2H_5 \rightarrow C_2H_6 + CH_2OC_2H_5$.

ACKNOWLEDGMENT

The authors are indebted to the Mass Spectroscopy Section of the National Bureau of Standards for their analysis of the diethyl peroxide. They are also grateful to Mr. F. A. Zihlman of the U. S. Naval Powder Factory, Indian Head, Maryland, for measuring the heat of combustion of the peroxide and for advice on various thermochemical matters.

¹⁰ E. W. R. Steacie and S. Katz, J. Chem. Phys. 5, 125 (1937).

¹¹ L. Phillips, Nature 160, 753 (1947). ¹² G. K. Adams and C. E. H. Bawn, Trans. Faraday Soc. 45, 494 (1949).

¹³ F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. 56, 284 (1934).

¹⁴ K. J. Laidler, Chemical Kinetics (McGraw-Hill Book Company, Inc., New York, 1950), pp. 269-270.