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THERMAL DECOMPOSITION OF DIETHYL PEROXIDE.

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I. Introduction.

It is known that organic peroxides are produced as intermediate compounds in the combustion of hydrocarbons. It is interesting to examine chemical properties of a known organic peroxide. Thus the thermal decomposition of diethyl peroxide has been investigated. Diethyl peroxide decomposes slowly below a certain temperature and pressure, and explosively above them. According to Harris and Egerton⁽¹⁾, the slow decomposition is a monomolecular reaction and the explosion is a thermal one. On the contrary, Neumann⁽²⁾ says that the slow and explosive decompositions are completely a chain reaction. Both of their experimental results, however, are not enough to decide the mechanism of these decompositions. The results obtained in this investigation, especially the influences of various gases on the decomposition did not completely agree with their results, but proved to be interesting.

II. Experimental Methods.

The experimental apparatus is shown in Fig. 1. A is a reaction vessel which lies in an electric furnace F. S_1, S_2, and S_3 are spring manometers made of glass, the needles of which are enlarged by the optical levers. M_1, M_2, and M_3 are mercury manometers. C is a reservoir of diethyl peroxide, and G is one of the

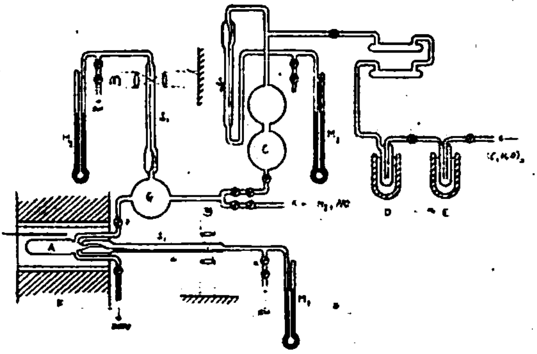

Fig. 1.

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1) *Proc. Roy. Soc.*, **A198**, 1 (1938); *ibid.*, **A175**, 254 (1940).

2) *Z. physik. Chem.*, **B33**, 33 (1936); *Acta. phys. Chim. U. R. S. S.*, **9**, 861 (1938); *ibid.*, **10**, 273 (1939); *ibid.*, **14**, 201 (1941).

mixtures of other gases and diethyl peroxide. The temperatures of the reaction vessel were measured by means of a mercury thermometer. D and E are traps, and a and b cocks.

Diethyl peroxide was introduced into the heated reaction vessel from the reservoir G and then the pressure increase caused by its decomposition was measured with a time by means of the spring manometer S_1 of which sensibility is about 1/50 m.m. Hg. The zero point method was generally used, but when the pressure change was too fast to measure, the method could not be used and the motion of the needle in the spring manometer was projected on a section paper by an optical lever and calibrated by known pressures. When diethyl peroxide decomposed explosively, this method was used. The time required to introduce the gas into the reaction vessel was always within 1 second. Therefore, the induction period which was within 1 second could not be observed in this procedure. The pressure kept for 10 minutes after any pressure change had not been observed was the final. The reaction vessel was heated and pumped out to a degree of $10^{-3} \sim 10^{-4}$ m.m. Hg before every experiment.

Diethyl peroxide was prepared and purified by Baeyer and Villiger's method³⁾, where the index of refraction $n_D^{18} = 1.37278$ and the specific gravity $d_{17} = 0.8226$. These values agreed with Rieche's results. The gas was fractionally distilled by liquid air and dried on pottasium carbonate.

Hydrogen and oxygen, which were commercial electrolysed hydrogen and oxygen, were purified through Pt-asbestos heated at a temperature of 360°C and dried over phosphor pentaoxide.

Commercial tetramethyl lead was solidified by liquid air in a trap and evacuated, and then it was evaporated at room temperature and mixed with diethyl peroxide.

Nitric oxide was prepared by Winkler's method⁴⁾, and then it was solidified by liquid air and evacuated to remove oxygen and nitrogen. This was fractionally distilled by liquid air in vacuum and evaporated into a reservoir.

III. Experimental Results.

a) The slow decomposition.

The slow decomposition velocities of diethyl peroxide were measured in the temperature range from 160 to 204°C and in the pressure range from 1 to 40 m.m. Hg in the cylindrical reaction vessel (diameter of 3.4 cm.).

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3) *Ber. deutsch. chem. Ges.*, **B33**, 3387 (1900).
4) *Ber. deutsch. chem. Ges.*, **B34**, 1408 (1901).

Fig. 2 showed the pressure-time curves of the slow decomposition, in which the initial pressures were 6.7, 10.7, 14.9, and 28.9 m.m. Hg at temperature of 179.5°C. These results showed that the final time of each decomposition was equal regardless of the initial pressures.

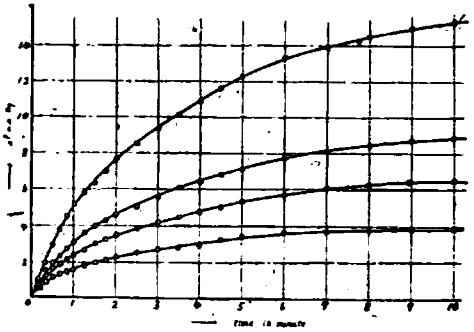

Fig. 2.

The pressure increases ΔP at the temperatures of 193, 185, 179.5, and 175°C were constant and about 9 m.m. Hg. The ratio of the final pressure to the initial pressure was always 160.7% without any influence of the initial pressures and temperatures.

If $t_{1/2}$ and $t_{3/4}$ were the time that the decomposition pressure increase by 50 and 75% respectively, the ratio of $t_{3/4}/t_{1/2}$ was nearly equal to 2. Thus the order of the reaction was the first.

Now assuming that the ratio of the concentration of the diethyl peroxide which decomposed during the time t to that of the decomposed products was equal to the ratio of the final pressure to the initial pressure, the constant of the reaction velocity k was calculated by the following equation, as the reaction was the first order,

$$k=\frac{2.3}{t_2-t_1}\log\frac{P_f-P_1}{P_f-P_2}$$

where P_f was the final perssure, P_1 and P_2 the pressure increases at the time t_1 and t_2. An example of the calculated velocity constants is shown in Table 1.

The influence of temperature on the reaction velocity is shown in Fig. 3. Using Arrhenius's equation, the energy of activation was calculated from the inclination of the straight line and its value was 29.9 k. cal.

Now, when a spherical reaction vessel (diameter of 7.5 cm.) was used, the velocity constants obtained were not different from those in the cylindrical reaction vessel (diameter of 3.4 cm.), but the ratio of the final pressure to the initial pressure was 210%.

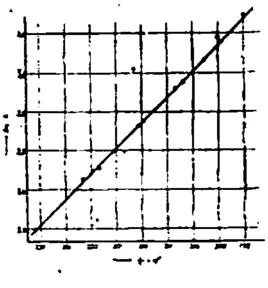

Fig. 3

The addition of 5 and 8% of oxygen in the experiments carried out at a temperature of 185°C and under the initial pressures of 20 and 15 m.m. Hg, retarded

Table 1. $T=175°C$, $P_1=28.9$ m.m. Hg.

time t sec.	P m.m. Hg	$\log \frac{P_f-P_1}{P_f-P_2}$	k sec.$^{-1}$
0	0		
30	1.55	0.0474	0.0033
60	2.83	0.0897	0.0032
90	3.95	0.1327	0.0032
120	5.00	0.1761	0.0029
150	5.83	0.2123	0.0032
180	6.40	0.2416	0.0027
210	7.01	0.2730	0.0030
240	7.73	0.3128	0.0026
270	8.25	0.3468	0.0029
300	8.82	0.3837	0.0028
390	9.73	0.4519	0.0026
420	10.41	0.5133	0.0029
480	11.00	0.5740	0.0031
540	11.52	0.6383	0.0028
	15.00		means 0.0030

Table 2.

Temperature °C	Per cent of hydrogen %	Initial pressures m.m.Hg	k sec.$^{-1}$	k sec^{-1} Diethyl peroxide
185	10	24.0	0.00561	
	10	15.0	0.00589	
	30	50.3	0.00637	
	30	37.7	0.00652	
	30	24.5	0.00620	
	50	39.23	0.00599	
	50	26.77	0.00621	
	80	63.0	0.00635	
	80	40.7	0.00617	0.00620
			means 0.00620	
200	10	19.5	0.0202	
	10	13.0	0.0203	
	30	33.3	0.0195	
	30	20.0	0.0202	
	50	34.77	0.0198	
	50	20.93	0.0195	
	80	62.13	0.6208	
	80	40.0	0.0204	
			means 0.0200	0.0200
217	10	27.0	0.6489	
	50	29.5	0.0483	
	50	18.4	0.0484	
			means 0.0486	0.0544

the slow decomposition, but the velocity constants were not influenced by the initial pressures. The reaction rate was the first order.

By the addition of 10, 30, 50, and 80% of hydrogen by volume per cent the decomposition was not influenced, and the rate was the first order. In Table 2 the velocity constants are given. The ratio of the final pressure to the initial pressure was 220%.

By the addition of 6.36 and 2.7% of tetramethyl lead the reaction rate was not influenced, being the first order. In consequence of the temperature the energy of activation was 28.5 k. cal.

As shown in Fig. 4, the addition of nitric oxide not only retarded the decomposition of diethyl peroxide, but some induction periods were observed, and in the addition of 50% of nitric oxide no decomposition was found. After the induction period the reaction rate was the first order.

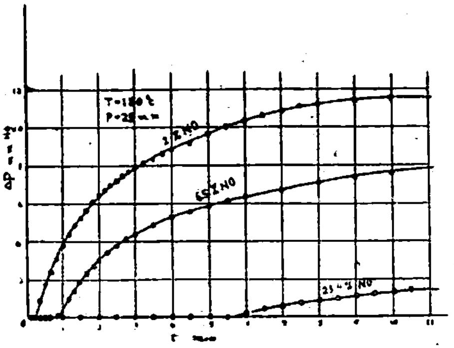

Fig. 4.

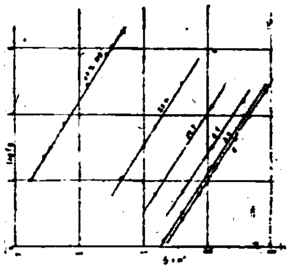

Fig. 5.

If $t_{1/2}$ is the time of 50% pressure increase and the reciprocal of the absolute temperature $1/T$, the relation between $\log t_{1/2}$ and $1/T$ was a straight line regardless of the concentration of nitric oxide, as shown in Fig. 5. Thus the energy of activation was about 30 k. cal.

The ratio of the final pressure to the initial pressure was 142% regardless of the initial pressure, temperature and the concentration of nitric oxide.

b) The explosive decomposition.

The pressure limits of explosion are shown in Fig. 6 in the temperature range from 170 to 260°C. The ratio of the final pressure to the initial pressure was always about 310%, and the decomposition was complete.

The relation between the pressure limit P and the temperature T did not obey Semenoff's formula, but the following empirical formula,

$$\log 1/(T-T_k)=AP+B,$$

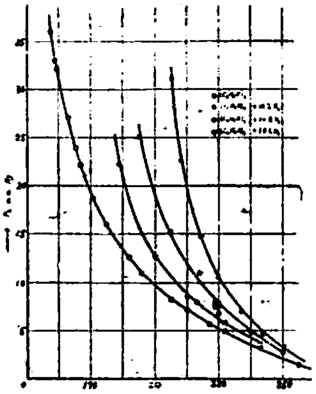

Fig. 6.

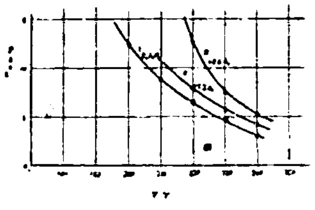

Fig. 7.

where T is the explosion temperature, T_k the lowest temperature where no explosion occurs under any pressure of diethyl peroxide, P the pressure limit, A and B constants.

In the case of a spherical vessel (diameter of 7.5 cm.) above 204°C the explosion occurs more easily than in the cylindrical vessel (diameter of 3.4 cm.) and below the temperature harder.

The addition of hydrogen retarded the explosive decomposition, as shown in Fig. 6 and 7. The rise of the pressure limits was proportional to the concentration of added hydrogen. In the case of hydrogen the pressure and temperature curves converged to the curve of diethyl peroxide at a temperature of 260°C, but in the case of oxygen they did not. In the former, the ratio of the final pressure to the initial pressure was 230% and in the latter it was nearly equal to that of diethyl peroxide.

The pressure limit and temperature curves in the addition of tetramethyl lead

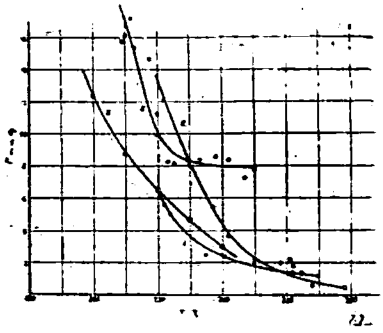

Fig. 8.

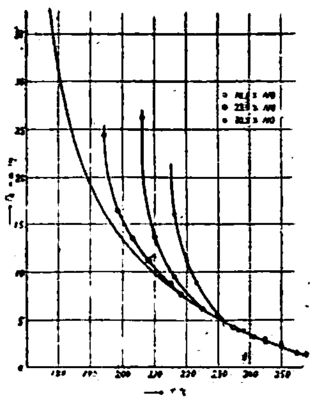

Fig. 9.

are shown in Fig. 8. As seen in these curves, tetramethyl lead retarded the explosions, but as in curve II obtained after many experiments, the explosions were more difficult to occur owing to the after-effect of tetramethyl lead.

The addition of nitric oxide influenced remarkably the explosive decomposition of diethyl peroxide, but in the addition of 1～3% no influence was observed. The effect of nitric oxide is shown in Fig. 9. Thus the pressure limits of explosion rose as the concentration of nitric oxide increased, and at 230°C they gave the same values as those of pure diethyl peroxide. The ratio of the final pressure increased as the concentration of added nitric oxide increased: in the case of the addition of 20 and 30% nitric oxide, the ratios were 1.84 and 2.25 respectively.

c) Induction period.

When hydrogen, oxygen and tetramethyl lead were added to diethyl peroxide, any induction period was not observed in the decomposition of the mixtures. On the contrary, the addition of nitric oxide caused some induction period in the slow and explosive decomposition. But during the induction period of the slow decomposition the pressure decreased at most to 2 m.m. Hg.

The induction period of the slow decomposition obeyed the following expression, as shown in Figs. 10 and 11,

$$\tau P^n e^{-\gamma/T} = \text{const.}$$

where τ is the induction period, P the initial pressure, T the temperature, and n and γ constants. γ is a function of the concentration of nitric oxide and the following has been obtained experimentally,

$$e^{\gamma} = (1/\mathrm{NO})^m,$$

where m is a constant.

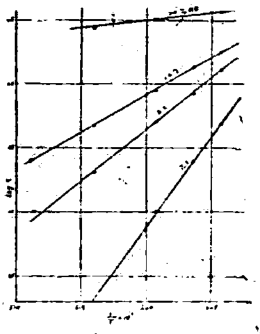

Fig. 10.

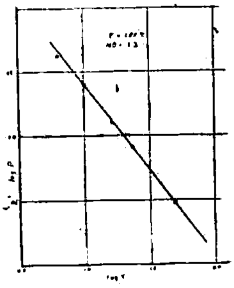

Fig. 11.

The induction period in the explosion was observed, but the relation between log τ and $1/T$ did not show a straight line.

IV. Consideration.

It is difficult to determine from the results above obtained whether the decomposition of diethyl peroxide is a monomolecular reaction or a chain reaction. In this decomposition the characteristics of a monomolecular reaction appears in the slow reaction, in which the rate is the first order, being independent from the initial pressure, and the diameter of the reaction vessel and the addition of hydrogen. But the induction period observed in the addition of nitric oxide in the slow reaction obeys Semenoff's formula, which is generally established when reactions have chains. In the explosive decomposition the addition of hydrogen and oxygen exerts remarkable influences on the explosion limits of pressures. As Harris says, if the explosion limits rise owing to the large thermal conductivity of hydrogen, the addition of oxygen, of which thermal conductivity is 1/10 of hydrogen, should make the rise of the explosion limits more difficult. However, the effect of hydrogen and oxygen is of the same order, and the explosion limits are influenced by the diameters of the reaction vessel. But in the case when nitric oxide is added to diethyl peroxide, the induction period does not obey Semenoff's formula. But it was difficult to measure accurately the induction period of the explosion by means of this apparatus. The difference of the ratio of the final pressure to the initial pressure in the slow and explosive decomposition seems to be such an evidence that the reaction products are not the same.

According to Neumann, nitrogen accelerates the rate of the decomposition and widens the range of explosions, and the values of the induction period are much larger than the theoretical values in thermal explosion, and the number of collision Z in a monomolecular reaction should be equal to the internal vibration of the molecule and of the order of $10^{-12} \sim 10^{-13}$, according to Eyring's theory of activated complex, but Z calculated from 23 k. cal. of the energy of activation obtained in the decomposition of diethyl peroxide gave the order of 10^{-9}. Therefore, he concluded that the decomposition of diethyl peroxide would be chain reactions. Neumann, however, did not investigate the decomposition at lower pressures, and the energy of activation obtained in this investigation was 29.9 k. cal., from which the numerical value of Z gave 10^{-13}. Thus, it is considered that the decomposition of diethyl peroxide has characteristics of a monomolecular and chain reaction. In fact, a few examples are found which develop from a monomolecular reaction to a chain reaction.[5]

Now the part in the least bond energy of diethyl peroxide is o–o bond, of which energy is about 40 k. cal.[6] Therefore, diethyl peroxide will at first decompose as follows:

$$C_2H_5OOC_2H_5 \rightarrow C_2H_5O + C_2H_5O \qquad (1)$$

In fact, C_2H_5O radical was confirmed in the photo-decomposition of diethyl peroxide by Barak and Style[7]. It will be decided by the form of the decomposition of C_2H_5O radical whether the diethyl peroxide decomposes slowly or explosively. For the decomposition of C_2H_5O, the following two schemes are considered:

$$C_2H_5O \rightarrow CH_3 + HCHO \qquad (2)$$
$$C_2H_5O \rightarrow H + CH_3CHO \qquad (3)$$

If it is assumed that (2) predominates at higher temperatures or in higher concentration of diethyl peroxide, the explosion probably occurs, according to the following:

$$C_2H_5OOC_2H_5 + CH_3 \rightarrow C_2H_5OH + CH_2OC_2H_5 \qquad (4)$$
$$CH_2OC_2H_5 \rightarrow CH_3 + CH_3CHO \qquad (5)$$
$$CH_3CHO \rightarrow CH_3CHO^* \qquad (6)$$
$$C_2H_5OOC_2H_5 + CH_3CHO^* \rightarrow C_2H_5O + C_2H_5O + CH_3CHO \qquad (7)$$

It is known that acetaldehyde is easily activated by thermal energy in the oxidation and forms a peroxide with oxygen[8]. Diethyl peroxide is oxygen rich and will be decomposed in collision with acetaldehyde. The existence of $CH_2OC_2H_5$ radical in the decomposition of ether has been proposed by Hinshelwood[9]. At lower temperatures or in lower concentrations of diethyl peroxide (3) is assumed to predominate, where H atom and acetaldehyde are not so much activated. Thus the following schemes are proposed

$$CH_3CHO \rightarrow CH_4 + CO \qquad (8)$$
$$C_2H_5O + H \rightarrow C_2H_5OH \qquad (9)$$

Thus, in this case diethyl peroxide decomposes slowly.

In the explosion hydrogen exerts as a chain breaking molecule, but in the slow decomposition it will be inert. On the contrary, since diethyl peroxide is

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[5] Hinshelwood, *Kinetics of Chemical Change*, Oxford Press, 127 (1940).

[6] Lewis and von Elbe, *Combustion, Flames, and Explosions of Gases*, Cambridge Press, 386 (1938).

[7] *Nature*, 135, 307 (1935).

[8] Jost, *Explosions- und Verbrennungsvorgänge in Gasen*, 375 (1939).

[9] Hinshelwood, *Kinetics of Chemical Change*, Oxford Press, 130 (1940).

oxygen rich, oxygen may retard the slow and explosive decomposition. Tetramethyl read decomposes above a temperature of 200°C. Therefore, it is considered that tetramethyl lead retards the explosion only.

Now with the addition of nitric oxide the induction period appeared, during which the pressure decrease was observed. As Hinselwood says, if nitric oxide combinates with a free radical, the pressure decrease should not be observed. Therefore, in this case it is considered that after nitric oxide combinates with diethyl peroxide and is completely consumed up, the reaction complex will be decomposed. But the mechanisms on the decomposition of this complex will be investigated in future.

I wish to express my appreciations to Prof. S. Horiba for his guidance throughout this work.

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