Studies on Organic Peroxides. VI. Thermal Analysis of the Decomposition of Benzoyl Peroxide by Ferrous Ion*

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In the previous paper[1], the analytical method was applied to follow the rate of the decomposition of benzoyl peroxide catalyzed by ferrous ion and it was found that the apparent decomposition rate was of the first order with respect to the concentration of benzoyl peroxide and that the activation energy of the decomposition was about 14 kcal./mol. This was much less than that of the spontaneous decomposition. In this report, similar reactions were carried out in methanol, ethanol, *n*-propanol and *n*-butanol and the reaction was followed by means of the method of thermal analysis[2].

Experimental

Reagents.—Benzoyl peroxide and ferrous chloride were prepared by the methods reported earlier[3]. Other chemicals used were of reagent grade and repeatedly distilled.

Apparatus and Procedure.—The reaction was carried out in a glass calorimeter shown in Fig. 1. In this figure, A is a Dewar vessel, the capacity of which is about 200 cc., B a glass stirrer sealed by mercury, C a Beckmann thermometer, D a platinum wire heater, E a glass vessel of about 30 cc. and F and F' glass tubes.

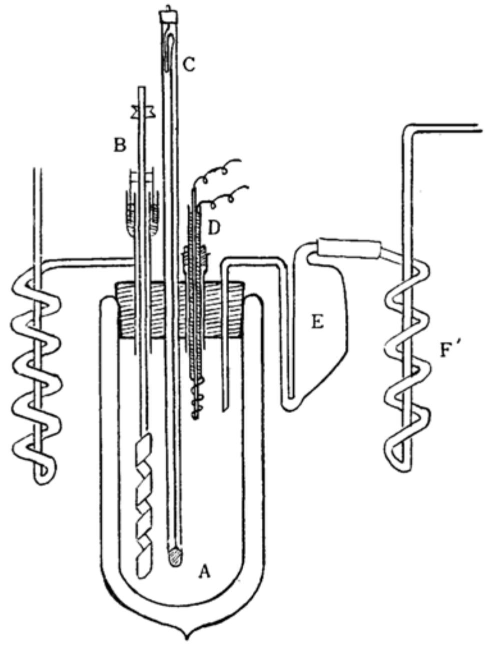

Fig. 1. Reaction vessel.

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* Presented in part at the Chugoku-Shikoku and Kinki Local Meeting of the Chemical Society of Japan, Tokushima, August 29 (1958).

[1] S. Hasegawa and N. Nishimura, This Bulletin, 33, 775 (1960).

[2] S. Horiba and T. Ichikawa, *Rev. Phys. Chem. Japan*, 1, 145 (1927); Ichikawa, *Z. Physik. Chem.*, (B) 10, 299 (1930).

[3] S. Hasegawa et al., This Bulletin, 31, 696 (1958).

The atomosphere of the vessel was previously substituted by carbon dioxide. Oxygen-free benzoyl peroxide and ferrous chloride solutions were introduced into A and E, respectively. The calorimeter was held in a thermostat. The temperature in A was adjusted to that of the thermostat by the heater D. After thermal equilibrium was attained, the ferrous chloride solution in E was siphoned into A. As soon as they were mixed, the reaction started and the rise of the temperature was recorded as the time passed.

The initial concentration of benzoyl peroxide was 0.01 mol./l. for all runs.

The Method of Thermal Analysis.—The fundamental equation of thermal analysis is given by Eq. 1[2,4],

$$\frac{dT}{dt}+K\Delta T=\frac{Q}{W}\cdot\frac{dx}{dt} \tag{1}$$

where dT/dt is the velocity of temperature change in solution, and $K\Delta T$ is a correction term for Newtonian cooling due to the temperature difference ΔT between the system and its surroundings and hence the rise in the temperature of reaction solution, K being the cooling constant. Q and W denote the heat of the reaction and the water equivalent of the reaction vessel, respectively, and dx/dt the rate of the reaction.

The cooling constant K can easily be determined by plotting the temperature difference between the reaction vessel and the thermostat against time.

When a reaction is of the first order, the rate of the reaction may be expressed as:

$$dx/dt=ka\mathrm{e}^{-kt} \tag{2}$$

where k is the specific reaction rate and a is the initial concentration of the reactant. From Eqs. 1 and 2, it follows,

$$\log(dT/dt+K\Delta T)=\log\frac{Q}{W}\cdot ka-\frac{kt}{2.303} \tag{3}$$

Accordingly, the plot of the left hand side of Eq. 3 against time t will give a straight line, the slope of which is $k/2.303$.

Results

The ferrous ion catalyzed decomposition of benzoyl peroxide is a exothermal reaction and an example is shown in Fig. 2 in which curves I and II show the dependence of ΔT upon

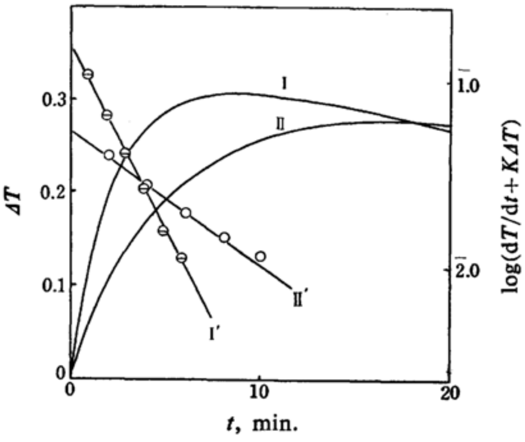

Fig. 2. Curves I and II: ΔT vs. t; curves I' and II': $\log(dT/dt+K\Delta T)$ vs. t in ethanol at 15°C; $[FeCl_2]_0$: 0.0038 mol./l. for I and 0.0012 mol./l. for II, respectively; $[BPO]_0$: 0.01 mol./l.

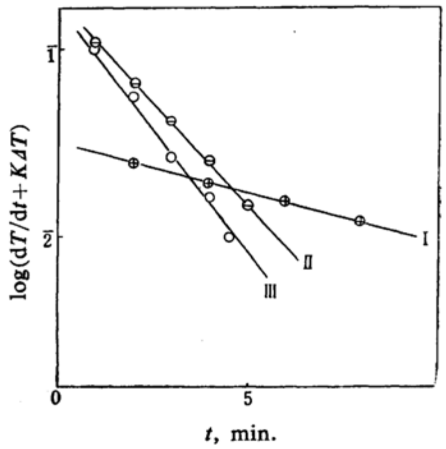

Fig. 3. $\log(dT/dt+K\Delta T)$ against t.
I: methanol, 40°C, $[FeCl_2]_0$: 0.0050 mol./l.
II: butanol, 15°C, $[FeCl_2]_0$: 0.0030 mol./l.
III: propanol, 15°C, $[FeCl_2]_0$: 0.0030 mol./l.
$[BPO]_0$: 0.01 mol./l.

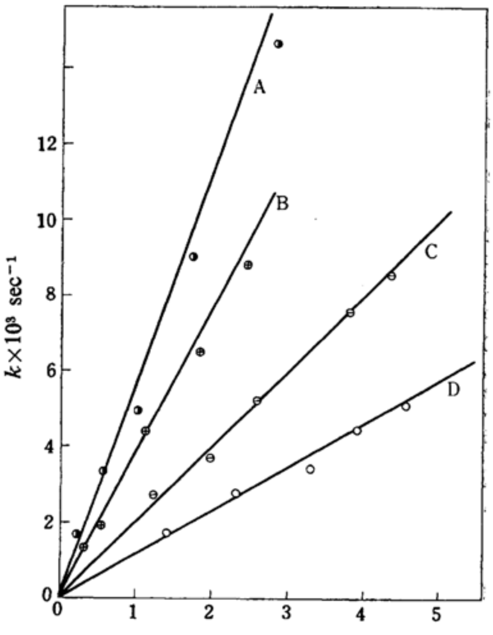

Fig. 4. Dependence of k upon $[FeCl_2]_0$ in ethanol at various temperatures: A, 30; B, 25; C, 15; D, 10°C, respectively; $[BPO]_0$: 0.01 mol./l.

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[4] E. Suito, *Rev. Phys. Chem. Japan*, **13**, 74 (1939).

TABLE I. THE RATE CONSTANTS FOR THE DECOMPOSITION OF BENZOYL PEROXIDE BY FERROUS ION

Temp. °C	$[FeCl_2]_0$ $\times 10^3$ mol. l^{-1}	$k \times 10^3$ sec^{-1}	k' l. mol^{-1} sec^{-1}	k'_{av}
		Methanol		
25	2.00	0.18	0.09	0.10 ± 0.00^{3}
	3.00	0.29	0.10	
	4.00	0.43	0.11	
	5.00	0.48	0.10	
30	1.90	0.54	0.28	0.23 ± 0.01^{4}
	3.00	0.69	0.23	
	4.66	0.92	0.20	
	4.90	0.92	0.19	
35	1.50	0.48	0.32	0.29 ± 0.02
	2.50	0.84	0.34	
	3.50	0.98	0.28	
	4.50	1.04	0.23	
40	1.50	1.00	0.67	0.54 ± 0.03
	2.74	1.38	0.50	
	3.50	1.80	0.51	
	5.00	2.34	0.47	
		Ethanol		
10	1.38	1.77	1.28	1.16 ± 0.03
	2.31	2.80	1.21	
	3.30	3.45	1.05	
	3.92	4.49	1.15	
	4.54	5.14	1.13	
15	1.22	2.76	2.26	2.03 ± 0.04
	1.99	3.76	1.89	
	2.59	5.26	2.03	
	3.81	7.60	1.99	
	4.35	8.56	1.97	
25	0.29	1.34	4.62	3.87 ± 0.13
	0.53	1.92	3.62	
	1.11	4.41	3.97	
	1.83	6.52	3.56	
	2.45	8.83	3.60	
30	0.23	1.65	7.08	5.70 ± 0.27
	0.55	3.34	6.07	
	1.00	4.91	4.91	
	1.71	8.98	5.25	
	2.82	14.66	5.20	

Temp. °C	$[FeCl_2]_0$ $\times 10^3$ mol. l^{-1}	$k \times 10^3$ sec.	k' l. mol^{-1} sec^{-1}	k'_{av}
		n-Propanol		
5	0.96	1.42	1.48	1.34 ± 0.05
	2.39	3.30	1.38	
	3.08	3.65	1.18	
	3.82	5.76	1.51	
	5.00	5.83	1.17	
10	1.28	3.22	2.52	2.44 ± 0.04
	2.17	5.37	2.48	
	2.92	6.72	2.30	
	4.00	10.48	2.62	
	5.04	11.55	2.29	
15	1.00	3.84	3.84	3.44 ± 0.10
	2.00	7.22	3.61	
	3.00	10.36	3.45	
	4.00	13.43	3.36	
	5.00	14.58	2.92	
		n-Butanol		
5	1.04	1.80	1.73	1.38 ± 0.06
	2.10	2.92	1.39	
	3.08	3.88	1.26	
	3.98	5.07	1.27	
	5.20	6.49	1.25	
10	1.00	2.23	2.23	2.02 ± 0.05
	2.00	3.84	1.92	
	3.00	5.53	1.84	
	4.00	7.98	2.00	
	5.00	10.75	2.15	
15	1.00	2.92	2.92	3.01 ± 0.08
	2.00	6.64	3.32	
	3.00	8.83	2.94	
	3.52	10.94	3.13	
	4.00	12.47	3.11	
	5.00	13.05	2.61	

time t in ethanol at 15°C. The slope dT/dt of the curve at any time t can be obtained from the figure. Curves I′ and II′ which are obtained by plotting the left hand side term in Eq. 3 against time give straight lines, therefore, it may be concluded that this reaction is apparently of the first order. Reactions in methyl, *n*-propyl and *n*-butyl alcohols were also the case, as shown in Fig. 3.

It was also found that the slope of the $\log(dT/dt+K\Delta T)$ vs. t curve was independent of the initial concentration of benzoyl peroxide.

According to Eq. 3, the slope of the line should give $k/2.303$. However, the specific rate constant k thus obtained in this reaction can not be considered as the true rate constants, because the ferrous ion may be considered to take part in the reaction. The discussion will be undertaken shortly.

The initial concentrations of the ferrous ion, alcohols and the values of k at various temperatures are listed in Table I. From the table, it may be concluded that the values of k seem directly proportional to the initial concentration of the ferrous ion. For example, k vs. $[FeCl_2]_0$ was plotted at temperatures between 10 and 30°C in ethanolic solution as shown in Fig. 4. It seems that each of the values falls on a straight line and converges to the origin. If this conclusion is correct, it follows:

$$k=k'[FeCl_2]_0 \qquad (4)$$

where k' is a constant. In the fourth and fifth columns in Table I are listed the values of k' calculated from Eq. 4. The slopes in Fig. 4 represent the average values of k' for each temperature.

It may be seen that the differences in the reaction rates among ethanol, *n*-propanol and

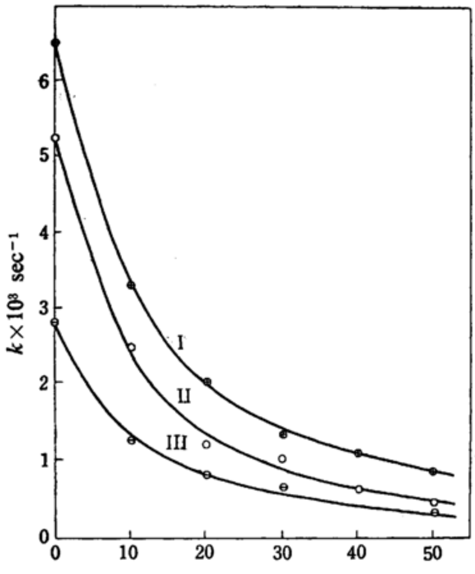

Fig. 5. Values of k for methanol-ethanol mixture: I, 20; II, 15; III, 10°C; $[BPO]_0$: 0.01 mol./l., $[FeCl_2]_0$: 0.0025 mol./l.

n-butanol are not particularly appreciable, but in methanol, the rate is appreciably smaller than in the three other alcohols. In the mixture of methanol and ethanol, k values were rapidly decreased by increasing the proportion of methanol as seen in Fig. 5. Above 50% of methanol, the reaction rates became too small to determine over the experimental temperature range.

Reaction Mechanism

As suggested in the previous paper[1], the overall reactions in this system will take place as follows:

First of all, reaction between benzoyl peroxide and ferrous ion will occur:

$$Fe^{2+}+P \xrightarrow{k_1} RCOO\cdot+RCOO^-+Fe^{3+} \qquad (5)$$

The benzoxy radical thus produced will attack a solvent molecule and abstract a hydrogen atom on α-carbon atom.

$$RCOO\cdot+R'CH_2OH \xrightarrow{k_2} RCOOH+R'\underset{\cdot}{C}HOH \qquad (6)$$

In addition, the reduction of ferrous to ferric ion is assumed:

$$R'\underset{\cdot}{C}HOH+Fe^{3+} \xrightarrow{k_3} RCHO+Fe^{2+}+H^+ \qquad (7)$$

Therefore, the heat evolved in this reaction may be the sum of the contribution from these reactions. Hence, the apparent rate constant k may be considered to include some specific rate constants.

In the previous paper, it was also mentioned that the rate of the decomposition of benzoyl peroxide might well be expressed as

$$-d[P]/dt=k_1[P][Fe^{2+}] \qquad (8)$$

In addition, the apparent overall decomposition rate was approximately of the first order, that is

$$-d[P]/dt=k_0[P] \qquad (9)$$

where k_0 is a constant. Therefore, the ferrous ion concentration should be constant during the reactions, if Eqs. 8 and 9 are not inconsistent with each other. From Eqs. 8 and 9, it follows,

$$k_0=k_1[Fe^{2+}] \qquad (10)$$

As was assumed, if the rate of reduction of ferric to ferrous ions are equal or almost equal to that of oxidation, the equilibrium between ferrous and ferric ions would be attained. Then, ferrous ion concentration may be expressed in terms of its initial concentration and the equilibrium constant K_0, i.e.,

$$[Fe^{2+}]=\frac{K_0}{1+K_0}[Fe^{2+}]_0 \qquad (11)$$

Inserting this value into Eq. 10, it follows,

$$k_0=k_1\cdot\frac{K_0}{1+K_0}\cdot[Fe^{2+}]_0 \qquad (12)$$

Thus, as was suggested, in the previous paper, k_0 should be a linear function of $[Fe^{2+}]_0$. Eq. 9 shows that k_0 can be obtained from the slope of the log[P] vs. t curve. If Eq. 12 is compared with Eq. 4, the conclusion that the rate constant k obtained from the thermal analysis is a linear function of the initial ferrous ion concentration, agrees formally with the conclusion that the apparent first order rate constant k_0 obtained from the analytical data, would be a linear function of the initial ferrous concentration. Each value of k and k' could, therefore, be referred as a measure of k_0 and k_1, respectively. Thus, it may be concluded that though the data from the thermal analysis in this reaction do not offer true rate constants, they still offer a means for studying the mechanism of this reaction in alcohols.

Solvent Effect

Since k' corresponds to the true rate constant k_1 as mentioned above, it is of interest to calculate the apparent activation energy by plotting log k' against $1/T$. The Arrhenius plots may be seen in Fig. 6. By applying the least squares method, the activation energies and the frequency factors for each alcohol were calculated and listed in Table II.

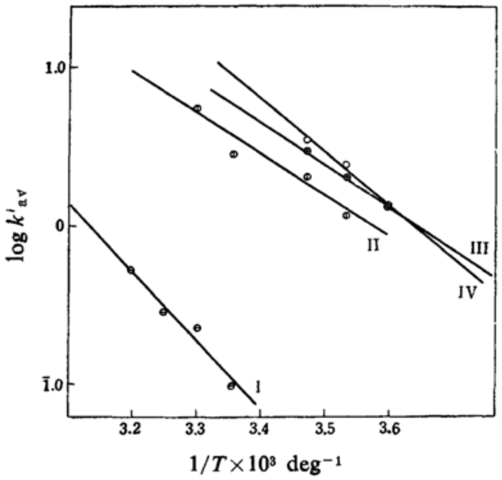

Fig. 6. Plots of log k'_{av} against $1/T$, solvent, I, methanol; II, ethanol; III, *n*-propanol; IV, *n*-butanol.

TABLE II. ACTIVATION ENERGIES AND FREQUENCY FACTORS

Solvent	E(kcal./mol.)	A	$S^{\neq}$(e. u.) 300°K
Methanol	19.8	3.3×10^{13}	1.3
Ethanol	12.0	2.3×10^{9}	−17.7
n-Propanol	15.0	8.7×10^{11}	−5.9
n-Butanol	12.4	7.5×10^{9}	−15.3
Methanol (10%)-Ethanol (90%)	15.2	3.2×10^{11}	−7.9
Methanol (20%)-Ethanol (80%)	16.7	2.3×10^{12}	−4.0

The influence of the solvent on chemical reaction rate would be partly due to its physical properties such as dielectric constant or molecular size. In reactions between ions and molecules, the solvent will play an important role and the increase in the dielectric constant of the solvent will cause a decrease in the free energy of the system, and hence will result in a decrease in their reaction rates. Since ferrous ions in alcohol are solvated, the reaction rates between ferrous ion and benzoyl peroxide will depend partly on the dielectric constants of the solvents. The dielectric constants of methanol, ethanol, *n*-propanol at 20°C and *n*-butanol at 25°C are 33.7, 25.7, 21.8 and 17.8, respectively[5].

It may be seen from the table that the k' values are increased in the order of methanol, ethanol, *n*-butanol and *n*-propanol, in agreement with the order of decreasing dielectric constants except that the order of *n*-propanol and *n*-butanol is reversed. But the difference in the rates between these alcohols is not so appreciable.

It was pointed out[6] that abstraction of the hydrogen atom from the alcohol molecule took place on the α-carbon atom exclusively.

In reaction 6, methylenic hydrogen atoms will exclusively be abstracted in ethanol, *n*-propanol and *n*-butanol, whereas methyl hydrogen atoms will be abstracted in methanol. This will suggest the exceptionally slow reaction rates in methanol.

Enthalpy-Entropy Relationship

Mention may be made about the relation between activation energy and frequency factor.

There are cases when a linear relationship between $\Delta S^{\neq}$ and E can be observed. Especially, it was pointed out that in a series of reactions, log A was a linear function of E when the Hammett equation held[7].

According to the theory of the absolute reaction rates[8], the specific rate constant k of a reaction is related to the standard free energy of activation $\Delta F^{\neq}$ by Eq. 13:

$$k=\kappa\frac{\boldsymbol{k}T}{\boldsymbol{h}}\exp\left(-\frac{\Delta F^{\neq}}{RT}\right) \qquad (13)$$

The free energy of activation may be a function of the intensity factors such as steric, resonance, or solvent effects. In a series of reactions, all such intensity factors are assumed to remain constant except that there is a change in one of these intensity factors, and $\Delta F^{\neq}$ is assumed to be linearly related to it.

Any reaction in the series may be chosen as standard and its specific rate constant may be denoted by k_0. If the difference in the intensity factor between any reaction and the standard one is expressed by $\Delta\chi$, then from the assumption mentioned above, the specific rate constant k can be derived from Eq. 13:

$$\begin{aligned}\ln k/k_0 &= -\frac{\Delta\Delta F^{\neq}}{RT} = -\frac{1}{RT}\left(\frac{\partial\Delta F^{\neq}}{\partial\chi}\right)_T\Delta\chi\\ &= -\frac{1}{RT}\left\{\left(\frac{\partial\Delta H^{\neq}}{\partial\chi}\right)_T - T\left(\frac{\partial\Delta S^{\neq}}{\partial\chi}\right)_T\right\}\Delta\chi \qquad (14)\end{aligned}$$

where $\Delta\Delta F^{\neq}$ represents the difference in the standard free energy of activation between the reaction and the standard one; $\Delta H^{\neq}$ and $\Delta S^{\neq}$ denote the standard activation enthalpy and entropy, respectively.

In a case when the intensity factor χ represents a substituent effect, the reaction constant

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[5] International Critical Table, VI, p. 83.

[6] M. S. Kharasch, J. L. Rowe and W. H. Urry, *J. Org. Chem.*, **16**, 905 (1951).

[7] J. E. Leffler and Shih-Kung Liu, *J. Am. Chem. Soc.*, **78**, 1949 (1956); I. Meloche and K. J. Laidler, ibid., **73**, 1712 (1951); D. A. Brown and R. F. Hudson, *J. Chem. Soc.*, **1953**, 883.

[8] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York (1941), p. 195.

ρ in the Hammett equation[9] may be expressed as

$$-\frac{1}{RT}\left\{\left(\frac{\partial \Delta H^{\neq}}{\partial \chi}\right)_T - T\left(\frac{\partial \Delta S^{\neq}}{\partial \chi}\right)_T\right\} = \rho \times \text{const} \quad (15)$$

Jaffé[10] has pointed out, quoting many examples, that in a series of reactions where the Hammett equation held, ρ was linearly related to $1/T$. This fact can successfully be explained by Eq. 15 if $(\partial \Delta H^{\neq}/\partial \chi)_T$ and $(\partial \Delta S^{\neq}/\partial \chi)_T$ are both independent of temperature.

In a series of related reactions, changes in polarity of a substituted group may be associated with the change in the electrostatic field strength at the reaction center.

Hence it may be reasonable to expect that the greater the enthalpy of activation, the greater will become the entropy of activation, because formation of a more rigid activated complex will need fewer entropy and enthalpy changes and vice versa.

In case of solvent changes, the linear relationship between enthalpy and entropy of activation is also observed[11,12]. If reactants are solvated, solvation will cause the decrease in the potential energy and entropy of the system, and hence both the enthalpy and entropy of activation will be increased. Thus, it may be reasonable to assume that the sign of $(\partial \Delta H^{\neq}/\partial \chi)_T$ is the same as that of $(\partial \Delta S^{\neq}/\partial \chi)_T$ and that neither of them is zero. Then, there must be a temperature, denoted by β, at which the left hand side of Eq. 14 becomes zero and it must be characteristic in the reaction series. From the discussion mentioned above, it is concluded that at the temperature β, which has been called "isokinetic temperature"[12], all the reaction rates should become identical.

From Eq. 14, it follows:

$$\left(\frac{\partial \Delta H^{\neq}}{\partial \chi}\right)_T \Delta\chi = \beta\left(\frac{\partial \Delta S^{\neq}}{\partial \chi}\right)_T \Delta\chi \quad (16)$$

or

$$\Delta\Delta H^{\neq} = \beta \Delta\Delta S^{\neq} \quad (17)$$

where $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ denote the difference in the activation enthalpy and entropy between a reaction and the standard one, respectively. Hence, $\Delta\Delta H^{\neq}$ is a linear function of $\Delta\Delta S^{\neq}$, in agreement with experimental facts.

In this study, the apparent activation energy E was also proportional to the activation entropy. In Fig, 7, the reaction in ethanol was chosen as standard, and the differences in activation energies were plotted against the differences in the activation entropies. A straight line was obtained as shown in the figure. From the slope, the isokinetic temperature was calculated to be 400°K.

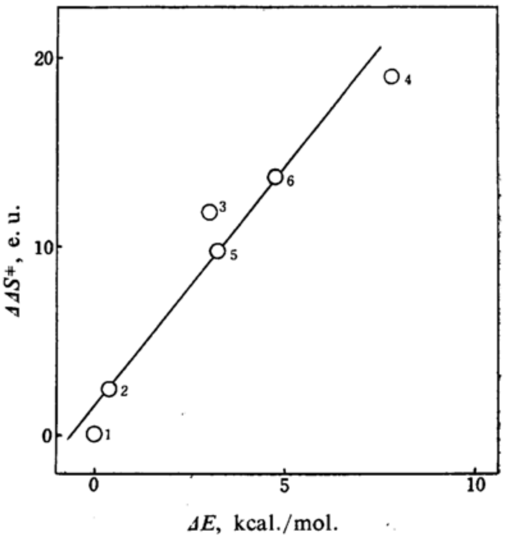

Fig. 7. Relationship between ΔE and $\Delta\Delta S^{\neq}$. 1, ethanol; 2, butanol; 3 propanol; 4, methanol; 5, methanol (10%)-ethanol (90%); 6, methanol (20%)-ethanol (80%).

Summary

The thermal analysis method was applied to follow the rate of the decomposition of benzoyl peroxide catalysed by ferrous ion in methanol, ethanol, *n*-propanol and *n*-butanol.

The apparent rates were of the first order and no fundamental difference in the reaction mechanism was observed among these alcohols. However, the reaction rates in methanol were much slower than in three other alcohols. Solvent effects on the reaction rate were discussed.

Linear enthalpy-entropy relationship was deduced, assuming that the free energy of activation is the linear function of an intensity factor in a series of reactions. This was found to be true in our case.

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[9] L. P. Hammett, *J. Am. Chem. Soc.*, 59, 96 (1937).

[10] H. H. Jaffé, *Chem. Revs.*, 53, 191 (1953).

[11] E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution", Second Ed., Oxford Univ. Press (1947), p. 278.

[12] J. E. Leffler, *J. Org. Chem.*, 20, 1202 (1955).