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Studies of Organic Peroxides. X. The Reaction of Benzoyl Peroxide with Secondary Amines*[1]

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The reaction of benzoyl peroxide with secondary amines, namely diphenylamine, diethylamine, piperidine and pyrrolidine was studied in benzene. The rates of reactions were followed by the thermal analysis and the titration method. The rates of reactions of these amines increase in the order diethylamine < diphenylamine < piperidine < pyrrolidine. The effect of the p, p'-substituents of benzoyl peroxide on the reaction rate was examined. The Hammett relationship with respect to p, p'-substituents held for all amines with positive ρ values. It was concluded that the reactions involve nucleophilic attack by the amines on the peroxide. Stoichiometry of the reaction was also examined by the method of thermal analysis. Diethylamine reacts with the peroxide in the 2 : 1 amine-peroxide ratio, while piperidine about 1.3 : 1 and diphenylamine 0.6 : 1, respectively. ESR spectra showed that diphenylamine and diethylamine produce fairly stable free radicals in low yields, while piperidine and pyrrolidine do not yield detectable free radicals.

In the previous paper,[1] the reaction of benzoyl peroxide with 5, 5'-indigo-disulfonic acid was studied. It was found that the reaction is promoted by either electron-attracting substituents or electron-releasing substituents of the peroxide, and multicenter mechanism was postulated for the reaction. However, the general applicability of this mechanism to the reaction between benzoyl peroxide and secondary amines are remained in question, since the type of the reaction products differs from those of usual secondary amines.

In this report, the reaction of more typical secondary amines was studied and the effect of substituents on the para position of benzoyl peroxide on the reaction rate was investigated. The reaction rates were followed by means of thermal analysis and/or titration method. The ESR study was made as an auxiliary means.

Experimental

Materials. Benzoyl peroxide and substituted benzoyl peroxides were prepared by the method reported previously.[2]

Diphenylamine, diethylamine, pyrrolidine and piperidine were commercially available GR grade reagents. All except diphenylamine were used without further purification. Diphenylamine was recrystallized from 95% ethanol.

Benzene was dried over metallic sodium and distilled.

Measurements of Reaction Rate. Reactions were carried out at temperatures between 15 and 30°C.

The apparatus and procedure of the thermal analysis were similar to those already reported.[3] In the present work, however, a thermistor was used in place of a Beckmann thermometer and the change in temperature of the reaction system was automatically recorded. In the thermal analysis the concentration of one reactant was taken to be larger than that of the other by a factor of about ten to forty.

For volumetric analysis, the method which was recommended by Nozaki[4] was used: A definite amount of peroxide was dissolved in benzene (100 ml) in a three-necked flask attached by a condenser, and the reaction was initiated by the addition of benzene solution (100 ml) of amine. Nitrogen gas was bubbled through the reaction mixture for the purpose of stirring the solution. At specified times after the beginning of the reaction, 10 ml of the reaction mixture were pipetted out from the flask into a conical flask containing 10 ml of acetic anhydride and 1 g of sodium iodide. The mixture was allowed to stand for about 10 min at room temperature, and 100 ml of water was then added to the mixture. Liberated iodine was titrated with 0.01 N sodium thiosulfate solution adding 1% starch solution towards the end. In this case, the concentration of the amines was taken to be larger than that of the peroxide by a factor of about two to ten. Reactions were followed to about 40—80% completion.

Measurements of the ESR Spectra. Equal amounts (5 ml) of benzene solutions (0.2 M) of benzoyl peroxide and amine were charged in a H-shaped glass tube separately and frozen, followed by evacuation. After sealing, the solutions were mixed. The ESR spectra were obtained by using a Japan Electron Optics

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1) S. Kashino, N. Nishimura, K. Ino and S. Hasegawa, This Bulletin, **40**, 33 (1967).

2) S. Hasegawa, N. Nishimura, S. Mitsumoto and K. Yokoyama, *ibid.*, **36**, 522 (1963).

3) S. Hasegawa, N. Nishimura and K. Miura, *ibid.*, **33**, 1323 (1960).

4) K. Nozaki, *Ind. Eng. Chem., Anal. Ed.*, **19**, 872 (1947).

Lab. Co., Ltd. Type JES 3BS spectrometer at room temperature.

Results and Discussion

It is already known that the reaction of benzoyl peroxide and secondary amine is of the first order with respect to each reactant.[1,5,6] Chaltykyan *et al.*[5] have pointed out that the reaction of benzoyl peroxide with aliphatic amines is retarded by the addition of benzoic acid, and the acid resulting from the reaction would form non-reacting salts with amines. In such a case, it is expected that the plot of $\log[b(a-2x)/a(b-x)]$ against t is more favourable than that of $\log[b(a-x)/a(b-x)]$ against t, where a and b denote the initial concentrations of amine and peroxide respectively, and x is an amount (per unit volume) of the peroxide that has reacted at time t. In practice, however, it is difficult to decide the stoichiometry by the titration method alone. It can be shown that under the condition in which a is larger than b by a factor of 2.5 to 12, if the plot of $\log[b(a-x)/a(b-x)]$ against t is linear, same linearity in the plot of $\log[b(a-2x)/a(b-x)]$ against t is resulted unless the reaction is followed to 60% or more completion. Even if slight deviation from linearity may occur, it is difficult to distinguish it from experimental error.

To avoid this difficulty, the method of thermal analysis was applied. The fundamental equation of thermal analysis is given by[7,8]

$$\frac{\mathrm{d}T}{\mathrm{d}t} + K\Delta T = \frac{Q}{W}\frac{\mathrm{d}x}{\mathrm{d}t} \tag{1}$$

where $\mathrm{d}T/\mathrm{d}t$ is the rate of temperature change in the solution, $K\Delta T$ is a Newtonian correction term for cooling; Q and W denote the heat of reaction and the heat capacity of the reaction system, respectively.

If amine (A) and benzoyl peroxide (B) react to form benzoic acid (C) and other products (D+⋯), and benzoic acid further reacts rapidly with amine to form acid-base adducts (C·A, C_2·A,⋯C_n·A), the reaction may be represented as follows:

$$\begin{aligned} &\mathrm{A} + \mathrm{B} \xrightarrow{\text{slow}} \mathrm{C} + \mathrm{D} + \cdots \\ &\mathrm{C} + \mathrm{A} \xrightarrow{\text{fast}} \mathrm{C\cdot A} \\ &\mathrm{C} + \mathrm{C\cdot A} \xrightarrow{\text{fast}} \mathrm{C_2\cdot A} \\ &\qquad\vdots \\ &\mathrm{C} + \mathrm{C}_{n-1}\cdot\mathrm{A} \xrightarrow{\text{fast}} \mathrm{C}_n\cdot\mathrm{A} \end{aligned}$$

Then the rate equation may be expressed as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a-\alpha x)(b-x) \tag{2}$$

where $\alpha=(n+1)/n$, depending on stoichiometry. When $a \gg b$,

$$\frac{\mathrm{d}x}{\mathrm{d}t} \cong ka(b-x) = kab\exp(-kat) \tag{3}$$

From Eqs (1) and (3), it follows,

$$\log\left(\frac{\mathrm{d}T}{\mathrm{d}t} + K\Delta T\right) = \log\left(\frac{Q}{W}kab\right) - \frac{ka}{2.303}t \tag{4}$$

When $b \gg a$, similar treatment gives

$$\log\left(\frac{\mathrm{d}T}{\mathrm{d}t} + K\Delta T\right) = \log\left(\frac{Q}{W}kab\right) - \frac{\alpha kb}{2.303}t \tag{5}$$

Therefore, if the left hand sides of Eqs. (4) and (5) are plotted against time t, straight lines may be given. The values of k and α can be calculated from the slope of these lines.

The result for diethylamine is listed in Table 1. α is about 2 and the values of k from thermal analysis and k' from the titration method agree within experimental errors. This result supports the proposition of Chaltykyan *et al.*[5]

The stoichiometries for other amines are somewhat interesting. The results for piperidine and

TABLE 1. RATE CONSTANT FOR BENZOYL PEROXIDE-DIETHYLAMINE REACTION IN BENZENE AT 25°C

Thermal analysis method

a mM	b mM	$k\times10^3$ $\mathrm{sec^{-1}\,M^{-1}}$	$\alpha k\times10^3$ $\mathrm{sec^{-1}\,M^{-1}}$
329	8.04	3.85	—
316	8.60	4.02	—
329	8.37	3.71	—
132	7.72	3.44	—
132	7.72	3.47	—
6.58	110	—	7.90
6.58	110	—	7.85
Average		3.70	7.88
	$\alpha=2.1$		

Titration method

a mM	b mM	$k'\times10^3$ $\mathrm{sec^{-1}\,M^{-1}}$
18.9	8.03	3.71
18.9	6.06	3.73
128	5.94	3.73
42.8	6.87	3.77
Average		3.74

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5) O. A. Chaltykyan, E. N. Atanasyan, A. A. Sarksyan and D. S. Gaibakyan, *Zhur. Fiz. Khim.*, **32**, 2601 (1958).

6) O. A. Chaltykyan, E. N. Atanasyan, N. M. Beieryan and G. A. Marmaryan, *ibid.*, **33**, 36 (1959).

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

8) E. Suito, *Rev. Phys. Chem. Japan*, **13**, 74 (1939).

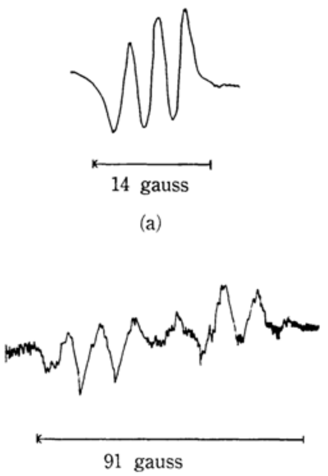
TABLE 2. RATE CONSTANTS FOR BENZOYL PEROXIDE-SECONDARY AMINES REACTIONS BY THE THERMAL ANALYSIS METHOD AT 25°C

Piperidine

a mM	*b* mM	$k\times10^2$ sec^{-1} M^{-1}	$\alpha k\times10^2$ sec^{-1} M^{-1}
159	9.44	4.46	—
159	9.44	4.61	—
159	9.44	4.56	—
7.95	110	—	6.15
7.95	110	—	6.32
7.95	110	—	5.85
Average		4.54	6.11
	$\alpha=1.34$		

Diphenylamine

a mM	*b* mM	$k\times10^2$ sec^{-1} M^{-1}	$\alpha k\times10^2$ sec^{-1} M^{-1}
77.4	9.44	2.24	—
96.5	9.44	2.14	—
2.90	90.0	—	1.28
9.65	110	—	1.12
9.65	90.0	—	1.28
Average		2.19	1.23
	$\alpha=0.56$		



(a)

(b)

Fig. 1. The ESR spectra of secondary amine-benzoyl peroxide reaction mixture.
(a) Diphenylamine (b) Diethylamine

diphenylamine are shown in Table 2. For piperidine, α is about 1.3. Bruckenstein and Saito9) studied equilibria between carboxylic acids and amines in benzene. They found that some of these substances (*e. g.*, trichloroacetic acid and *N, N*-dimethylbenzylamine) form not only 1 : 1 salts but 2 : 1 or 3 : 1 adducts in the acid-base ratio. Concerning to benzoic acid and piperidine they identified the 1 : 1 and 2 : 1 acid-base adducts in benzene by infrared study. The present authors isolated the 2 : 1 adduct as crystals (mp 97—98°C). Main factor which decreases the value of α from 2 may be ascribed to the formation of such an acid-base adduct.

For diphenylamine, α was about 0.6. This indicates that some of the reaction products or intermediates further react with benzoyl peroxide.

The reaction mixture of diphenylamine and benzoyl peroxide exhibited an ESR spectrum. As is seen in Fig. 1(a), the spectrum shows isotropic three lines with equal intensities, the coupling constant being 3.65 gauss. Although decisive assignment of the hyperfine splittings could not be made, the coupling with ^{14}N may be responsible to the spectra. Abnormally small coupling constant, compared with that of nitric oxides (8—17 gauss10)), suggests that the spin density on ^{14}N atom is very low and therefore an electron-attracting group such as carbonyl is attached to the nitrogen. It is certain, therefore, this radical is not diphenyl nitrogen radical which was postulated6) to be formed in main process of this reaction. Ashkinazi *et al.*11) reported that diphenyl nitrogen radical has electronic absorption at 460 mμ, while in the present experiment, no characteristic absorption was observed at the neighbor of 460 mμ.

The ESR spectra were also examined for other amines. The reaction of diethylamine and benzoyl peroxide gives an ESR spectrum as shown in Fig. 1(b). The spectrum differs from that of $R_2NO\cdot$ type radical which is formed in the reaction betwen secondary aliphatic amines and *t*-butyl hydroperoxide.12) If the radical is of $R_2NO\cdot$ or $R_2N\cdot$ type, isotropic three lines should be observed. However, it is not the case. The ESR spectrum in Fig. 1(b) may be divided in two parts consisting of four lines with the intensity ratio 1 : 2 : 2 : 1. Central part of the spectrum is not clear because of poor resolutions. However, it may be considered that $-\dot{C}H-NH-R$ type radical is responsible to the spectrum. The radical was fairly stable, but its concentration was low. Probably this radical came from side reaction.

Piperidine and pyrrolidine did not form detectable free radicals at room temperature.

The substituent effects were investigated for the reaction of diethylamine, pyrrolidine and diphenylamine. In Table 3, the values of the reaction constants *k* are listed. Using the data in Table 3, the values of the enthalpy and entropy of activation were estimated and are listed in Table

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9) S. Bruckenstein and A. Saito, *J. Am. Chem. Soc.*, **87**, 698 (1965).

10) J. C. Baird and J. R. Thomas, *J. Chem. Phys*, **35**, 1507 (1961).

11) M. S. Ashkinazi, V. E. Karpitskaya and B. Ya. Dain, *Zhur. Fiz. Khim.*, **38**, 2889 (1964).

12) H. E. De la Mare, *J. Org. Chem.*, **25**, 2114 (1960).

TABLE 3. RATE CONSTANTS[a] FOR SYMMETRICALLY PARA-SUBSTITUTED BENZOYL PEROXIDE-SECONDARY AMINE REACTIONS IN BENZENE

Diethylamine[b]				
Substituent	15°C	20°C	25°C	30°C
CH_3O	6.26×10^{-4}	9.66×10^{-4}	1.70×10^{-3}	2.58×10^{-3}
CH_3	8.99×10^{-4}	1.16×10^{-3}	2.07×10^{-3}	3.04×10^{-3}
H	1.61×10^{-3}	2.43×10^{-3}	3.70×10^{-3}	5.33×10^{-3}
Cl	5.66×10^{-3}	7.68×10^{-3}	1.27×10^{-2}	1.61×10^{-2}
Diphenylamine[c]	15°C	23°C	30°C	
CH_3O	2.17×10^{-3}	4.98×10^{-3}	7.86×10^{-3}	
CH_3	3.44×10^{-3}	6.99×10^{-3}	1.19×10^{-2}	
H	7.34×10^{-3}	1.38×10^{-2}	2.31×10^{-2}	
Cl	2.86×10^{-2}	5.11×10^{-2}	8.50×10^{-2}	
NO_2	3.56×10^{-1}	4.64×10^{-1}	5.76×10^{-1}	
Pyrrolidine[c]	15°C	20°C	25°C	30°C
CH_3O	1.19×10^{-2}	1.59×10^{-2}	2.50×10^{-2}	3.11×10^{-2}
CH_3	3.01×10^{-2}	3.75×10^{-2}	4.29×10^{-2}	5.51×10^{-2}
H	6.55×10^{-2}	8.33×10^{-2}	1.04×10^{-1}	1.16×10^{-1}
Cl	1.64×10^{-1}	2.08×10^{-1}	2.38×10^{-1}	2.61×10^{-1}
NO_2	1.00	1.09	1.18	1.34
Piperidine[b]	15°C	20°C	25°C	30°C
H	2.69×10^{-2}	3.57×10^{-2}	4.61×10^{-2}	6.02×10^{-2}

a) Average value in $l\,mol^{-1}\,sec^{-1}$.
b) Data from thermal analysis method.
c) Data from titration method.

TABLE 4. ENTHALPY AND ENTROPY OF ACTIVATION FOR THE REACTION OF PARA-SUBSTITUTED BENZOYL PEROXIDES WITH SECONDARY AMINES AT 30°C, kcal/mol or cal/deg mol

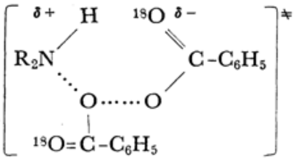
Substituent	σ	Diethylamine		Diphenylamine		Pyrrolidine		Piperidine	
		$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$
CH_3O	−0.268	15.5	−19.3	14.5	−20.3	11.3	−28.0	—	—
CH_3	−0.170	14.3	−22.9	13.9	−21.8	6.8	−41.0	—	—
H	0	13.3	−25.1	12.7	−24.2	6.4	−41.6	8.6	−35.8
Cl	0.227	11.3	−29.5	12.1	−23.5	4.6	−45.9	—	—
NO_2	0.778	—	—	5.3	−42.2	2.5	−49.6	—	—

4, together with the values of Hammett's substituent constant σ.[13]

In Fig. 2, the enthalpy of activation, $\Delta H^{\neq}$, is plotted against the entropy of activation, $\Delta S^{\neq}$. It may be seen that the isokinetic relationship hold for all reactions. The isokinetic temperatures of these reaction series are about 440, 420 and 400°K for diethylamine, pyrrolidine and diphenylamine respectively, well above experimental temperatures.

In Fig. 3, $\log k$ at 30°C is plotted against σ. Hammett's relationship also gives straight lines for all amines. From the slopes the values of the Hammett reaction constant ρ are evaluated to be about 0.9, 0.8 and 1.0 for diethylamine, pyrrolidine and diphenylamine, respectively. From the fact that the values of ρ obtained below the isokinetic temperature are positive, it may be concluded that the reaction of benzoyl peroxide with these amines involves nucleophilic attack by the amines on the peroxide.

Denney and Denney[14] studied the reaction of dibenzylamine with benzoyl peroxide, labeled with oxygen-18 in the carbonyl positions, and proposed that the mechanism for the reaction involves the following transition state.



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

[14] D. B. Denney and D. Z. Denney, *J. Am. Chem. Soc.*, **82**, 1389 (1960).

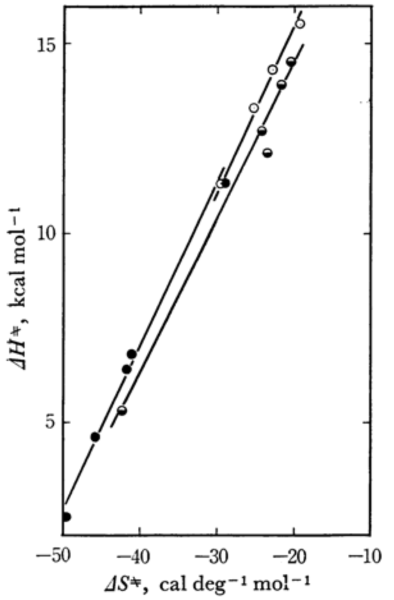


Fig. 2. Relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$.
● Pyrrolidine ○ Diethylamine
◒ Diphenylamine

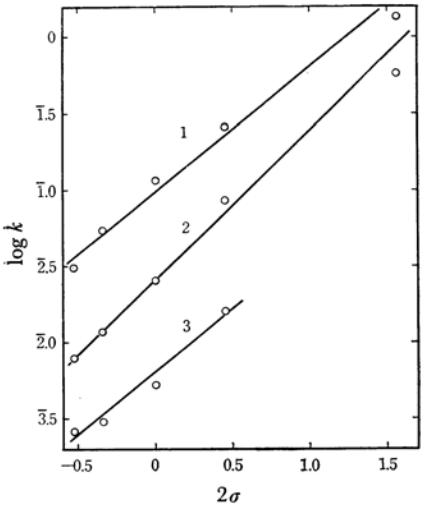


Fig. 3. Hammett's relationship.
1, Pyrrolidine 2, Diphenylamine 3, Diethylamine

It is considered that such an activated complex is probably a prototype of the activated complex of the reaction of benzoyl peroxide with these amines.

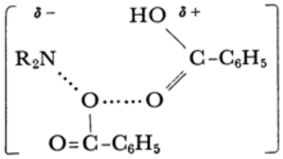
In contrast with the reaction of 5, 5′-indigodisulfonic acid,1) the electropositive substituents of benzoyl peroxide did not promote the reaction in the case where usual secondary amines were employed. Therefore, in this case a multicenter mechanism can not be applied. The activated complex must be formed by the nucleophilic attack of the nitrogen atom of amine on the peroxide oxygen, even if the electropositive substituents are on the peroxide.

The rates of reactions of these amines increases in the order diethylamine < diphenylamine < piperidine < pyrrolidine. It is noted that the cyclic aliphatic amines have larger reaction velocity and lower activation enthalpy and entropy than the other amines.

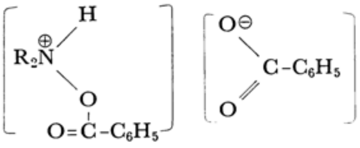
Chaltykyan *et al.*5) pointed out that the reactivity of aliphatic amines depend on the basicity of the amines. From the point of basicity, it may be explained qualitatively that cyclic aliphatic amines are more reactive than diethylamine, according to the mechanism presented above. However, the minor steric hindrance in addition to the strong basicity of the cyclic amines would cause great diminution of the activation enthalpy and entropy.

Diphenylamine has rather higher reactivity in spite of its lower basicity. Chaltykyan *et al.*5,6) have shown that basic aliphatic amines react more rapidly in acetone (the dielectric constant $\varepsilon^{20^\circ\mathrm{C}}=21.3$15)) than in ethyl ether ($\varepsilon^{20^\circ\mathrm{C}}=4.335$15)), while diphenylamine has almost the same reactivity in these solvent.

From the solvent effect, it is considered that in case of diphenylamine proton transfer in the activated complex of type I forms less-ionic intermediate II, whereas in case of basic aliphatic amines ionic scission of –O–O– linkage in the activated complex forms ion pair III, and II and III decompose in different way respectively.



II



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This explains the fact that diphenylamine reacts more rapidly than expected from its basicity alone.

The authors wish to express their thanks to Dr. Norio Nishimura for his helpful discussions and ESR technique, and to Mr. Iwao Nabeshima, Mr. Shoji Oka and Mr. Hiroshi Yamashita for their experimental aid.

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15) National Research Council of U. S. A., "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," Vol. VI, McGraw-Hill, New York (1929), p. 82.