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# Studies of Organic Peroxides. XI. The Reaction of Benzoyl Peroxide with Secondary Amines in Binary Mixed Solvents

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The rate constants of the reaction of benzoyl peroxide with some typical secondary amines, namely, diphenylamine, *N*-methylaniline, and piperidine, were measured in benzene-nitrobenzene binary mixed solvents. The reaction rates of diphenylamine and *N*-methylaniline are little influenced by the compositions of the solvents, while the reaction of piperidine proceeds more rapidly in nitrobenzene than in benzene. The isokinetic relationship holds for the reaction of piperidine in the binary mixed solvents. The isokinetic temperature is calculated to be 265°K. The analysis of the behavior of these reactions in the mixed solvents leads to the conclusion that, in the cases of diphenylamine and *N*-methylaniline, there are no specific interactions between the activated complexes and solvent molecules, whereas in the case of piperidine the activated complex is weakly solvated with the polar nitrobenzene. The reaction of benzoyl peroxide with *N*-methylaniline and *N*-*n*-butylaniline was also studied in benzene. These amines have a higher reactivity than would be expected from their basicity. This higher reactivity is probably due to the resonance stabilization of the activated complex besides the formation of a less-ionic activated complex.

In a previous work,1) the reaction of benzoyl peroxide with some typical secondary amines was studied in benzene. It was ascertained that the reaction involves a nucleophilic attack by the amines on the peroxide, and it was noted that diphenylamine has rather a higher reactivity in spite of its lower basicity. This higher reactivity of diphenylamine was explained by the formation of a less-ionic activated complex. The explanation, however, was not conclusive.

In the present investigation, in order to obtain more clear-cut information on the activated complex, the reaction of benzoyl peroxide with *N*-methylaniline and *N*-*n*-butylaniline was studied in benzene, further, the rate constants of the reaction of benzoyl peroxide with diphenylamine, *N*-methylaniline, and piperidine were measured in benzene - nitrobenzene binary mixed solvents.

## Experimental

The benzoyl peroxide, diphenylamine, piperidine, and benzene were the same as those described in the previous paper.1) *N*-Methylaniline and *N*-*n*-butylaniline were commercially-available GR-grade reagents. The nitrobenzene was dried with anhydrous sodium sulfate and fractionated at reduced pressure.

The reaction rates were followed by means of the thermal-analysis method at temperatures between 20 and 35°C. The apparatus and procedure were also the same as those described in the previous paper.1)

## Results and Discussion

The reactions of benzoyl peroxide with amines were of the first order with respect to each reactant for all amines examined. It was reported previously1) that diphenylamine and piperidine reacted with the peroxide in amine-peroxide ratios of 1.3 : 1 and 0.6 : 1 respectively. In the reaction of *N*-methylaniline and *N*-*n*-butylaniline, however, the stoichiometry was found to be 1 : 1.

The values of the second-order rate constants, $k$, for the reactions of *N*-methylaniline and *N*-*n*-butylaniline in benzene are shown in Table 1, together with those for the other amines studied previously;1) the values of the enthalpy and entropy of activation are listed in Table 2.

Table 1. Rate constant $k \times 10^3$ ($l$ mol$^{-1}$ sec$^{-1}$) for benzoyl peroxide-secondary amine reactions in benzene

| | 15°C | 20°C | 23°C | 25°C | 30°C | 35°C |
|---|---|---|---|---|---|---|
| *N*-Methylaniline | | 14.5 | | 20.2 | 26.9 | 33.6 |
| *N*-*n*-Butylaniline | | 15.0 | | 21.5 | 27.0 | 34.8 |
| Diethylamine a) | 1.61 | 2.43 | | 3.70 | 5.33 | |
| Piperidine a) | 26.9 | 35.7 | | 46.1 | 60.2 | |
| Diphenylamine a) | 7.34 | | 13.8 | | 23.1 | |

a) Data from Ref. 1.

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1) S. Kashino, Y. Mugino, and S. Hasegawa, This Bulletin, **40**, 2004 (1967).

TABLE 2. ENTHALPY AND ENTROPY OF ACTIVATION FOR THE REACTION OF BENZOYL PEROXIDE WITH SECONDARY AMINES IN BENZENE AT 25°C, kcal mol$^{-1}$ or cal deg$^{-1}$ mol$^{-1}$

| | $\Delta H^{\neq}$ | $\Delta S^{\neq}$ |
|---|---|---|
| *N*-Methylaniline | 7.9 | −40.0 |
| *N*-*n*-butylaniline | 7.5 | −41.4 |
| Diethylamine[a] | 13.3 | −25.1 |
| Piperidine[a] | 8.6 | −35.8 |
| Diphenylamine[a] | 12.7 | −24.2 |

a) Data from Ref. 1. $\Delta S^{\neq}$ is calculated from the rate constant at 30°C.

As may be seen in Tables 1 and 2, the alkylanilines have a slightly higher reactivity than diphenylamine. This can be explained by a mechanism which involves a nucleophilic attack by the amines on the peroxide,[1,2] because an inductive effect of the alkyl group would cause the increase in the electron density on the nitrogen atom of the amines, thus reducing the activation enthalpy and increasing the rate of the reaction.

The reactivities of both *N*-methylaniline and *N*-*n*-butylaniline are almost comparable to that of highly-basic piperidine, and are obviously higher than that of diethylamine. It can be said that the alkylanilines as well as diphenylamine have a rather higher reactivity than would be expected from the basicity. This suggests that the aromatic amines, that is, the alkylanilines and diphenylamine, form activated complexes somewhat different from those of the aliphatic amines.

TABLE 3. RATE CONSTANTS FOR BENZOYL PEROXIDE-SECONDARY AMINE REACTIONS IN BENZENE-NITROBENZENE MIXED SOLVENTS

| Molar fraction of nitro-benzene *x* | Rate constant $k\times 10^3$ ($l$ mol$^{-1}$ sec$^{-1}$) Diphenyl-amine | | *N*-Methyl-aniline | Piperidine | | |
|---|---|---|---|---|---|---|
| | 25°C | 30°C | 25°C | 20°C | 25°C | 30°C |
| 0.000 | 17.6 | 29.6 | 20.2 | 35.7 | 46.1 | 60.2 |
| 0.224 | 19.7 | 28.2 | 21.8 | 46.5 | 65.7 | 76.1 |
| 0.306 | 20.8 | 28.5 | 21.2 | 48.8 | 67.9 | 88.8 |
| 0.500 | 17.3 | 26.7 | 23.4 | 58.2 | 79.1 | 104.5 |
| 0.635 | — | — | 22.0 | 58.6 | 83.6 | 111.9 |
| 0.673 | 17.6 | 28.5 | — | — | — | — |
| 0.725 | 16.7 | 27.5 | 22.0 | 70.5 | 82.1 | 116.4 |
| 1.000 | 16.0 | 27.5 | 22.4 | 64.9 | 97.8 | 129.9 |

In order to clarify this difference, the solvent effect was examined. The experimental results are listed in Table 3 and are plotted in Fig. 1. It may be seen that, in the cases of *N*-methylaniline and diphenylamine, the compositions of the solvents have little influence on the rates of reactions, while in piperidine the rates obviously increase with the increase in the molar fraction of nitrobenzene.

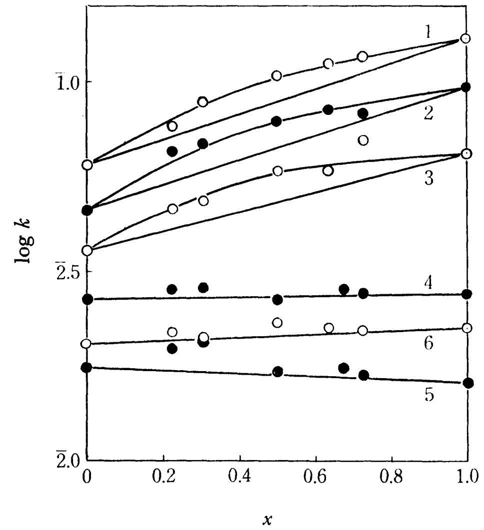

Fig. 1. Plot of log $k$ *vs.* mole fraction of nitrobenzene, $x$, for the reaction of benzoyl peroxide with secondary amines in benzene-nitrobenzene mixed solvents.
1: piperidine, 30°C, 2: piperidine, 25°C, 3: piperidine, 20°C, 4: diphenylamine, 30°C, 5: diphenylamine, 25°C, 6: *N*-methylaniline, 25°C

These results are in line with the solvent effects observed by Chaltykyan *et al.*[3,4] They have shown that basic aliphatic amines react more rapidly in acetone than in ethyl ether, while diphenylamine has almost the same reactivity in these solvents.

For the reaction of piperidine in the binary mixed solvents, the values of the enthalpy and the entropy

TABLE 4. ENTHALPY AND ENTROPY OF ACTIVATION FOR THE REACTION OF PIPERIDINE WITH BENZOYL PEROXIDE IN BENZENE-NITROBENZENE MIXED SOLVENTS AT 25°C, kcal mol$^{-1}$ or cal deg$^{-1}$ mol$^{-1}$

| Molar fraction of nitrobenzene | $\Delta H^{\neq}$ | $\Delta S^{\neq}$ |
|---|---|---|
| 0.000 | 8.6 | −35.7 |
| 0.224 | 8.7 | −34.8 |
| 0.306 | 9.8 | −31.0 |
| 0.500 | 10.0 | −30.0 |
| 0.635 | 9.9 | −30.3 |
| 0.725 | 10.8 | −27.1 |
| 1.000 | 11.7 | −23.9 |

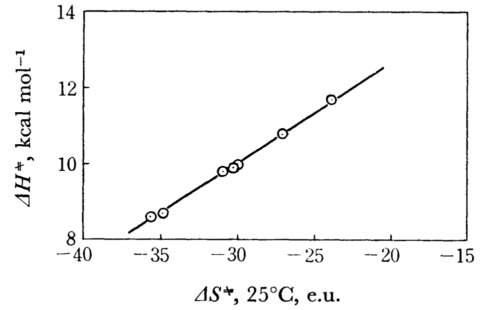

Fig. 2. Plot of $\Delta H^{\neq}$ *vs.* $\Delta S^{\neq}$ for the reaction of piperidine with benzoyl peroxide in benzene-nitrobenzene mixed solvents.

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

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

[4] O. A. Chaltykyan, E. N. Atanasyan, N. M. Beileryan, and G. A. Marmaryan, *ibid.*, **33**, 36 (1959).

of activation are listed in Table 4. It may be noted that, in this reaction series, a higher enthalpy of activation does mean a higher rate; this is in contrast to the majority of reactions. The enthalpy of activation, $\Delta H^{\ast}$, is plotted against the entropy of activation, $\Delta S^{\ast}$, in Fig. 2. It may be seen that the isokinetic relationship holds for this reaction. The isokinetic temperature is calculated to be 265°K, below the experimental temperature. Pearson[5] has pointed out that the reactions in which ionic products are formed from neutral molecules frequently have an isokinetic temperature lower than the experimental temperature. Thus, it may be said that the reaction of piperidine with benzoyl peroxide has the same character as many ionic reactions.

Recently, Kondo and Tokura[6] have shown that, in the reactions in which the activated complexes have polar structures and are solvated in such polar solvents as nitrobenzene, the plot of log $k$ *vs.* the composition of the mixed solvent deviates upward. Further, they have derived[7] theoretical expressions for the rate constants in binary mixed solvents on the basis of the theory of the non-electrolyte solution. An application of this theory was made in analyzing the reaction behavior of benzoyl peroxide with secondary amines.

According to Kondo and Tokura,[7] for the system in which all the solutes yield regular solutions the theoretical expression for the rate constant in a binary mixed solvent, $k_{mix}$, is given by:

$$\ln k_{mix} = x_1 \ln k_1 + x_4 \ln k_4 - \alpha_{14} x_1 x_4 \qquad (1)$$

where $k_i$ and $x_i$ stand for the rate constant in a pure solvent, $i$, and the mole fraction of the $i$ solvent, respectively, and where $\alpha_{14}$ is a parameter expressing the deviation from the ideal-solution behavior of the solvent system.[8]

For the system in which there are specific interactions between the activated complex and the polar solvent, the expression for the rate constant can be given by:

$$\ln k_{mix} = x_1 \ln k_1 + x_4 \ln k_4 - \{x_1 \ln (K+1) - \ln(x_1 K + 1) + x_1 x_4 \alpha_{14}\} \qquad (2)$$

where $K$ is an equilibrium constant, defined in terms of the molar fraction, for the formation of a solvated activated complex from the unsolvated activated complex and the polar solvent.

The values of $\alpha_{14}$ for the benzene - nitrobenzene system have been estimated from the equilibrium vapour pressure data to be 0.10.[7] The values for $K$ is so determined that the value calculated for $k$ from Eq. (2) is equal to the experimental results at $x_1 = x_4 = 0.5$.

The value of $K$ for the reaction of piperidine was calculated to be 2.0. This means that, in pure nitrobenzene, the molar ratio of the solvated activated complex and the unsolvated one is 2 : 1.

The solid lines in Fig. 1 are calculated by means of Eqs. (1) and (2). It may be seen that, in the cases of *N*-methylaniline and diphenylamine, the relations between log $k$ and the molar fraction of nitrobenzene are almost linear and agree with the lines calculated by Eq. (1), and that in piperidine the relation agrees well with the upward curved lines calculated by Eq. (2). Therefore, it can be concluded that, in the cases of diphenylamine and *N*-methylaniline, there are no specific interactions between the activated complex and the solvent molecules, whereas in the case of piperidine the activated complex is solvated with the polar nitrobenzene.

The results presented above show that the aromatic amines form a less-ionic intermediate, whereas aliphatic amines form a more-ionic intermediate, in the course of the reaction with benzoyl peroxide; this is in accordance with the previous proposition.[1]

However, even in the case of piperidine the solvent effect is much smaller than in typical ionic reactions, such as the Menschtkin reaction.[7] Kondo and Tokura[9] have also derived a theoretical expression for the activation energies in binary mixed solvents. In the reaction of piperidine with benzoyl peroxide, the solvent effect is too small to make it possible to discuss the changes in the activation energies in relation to the expression. That is, even in the case of highly basic piperidine the ionic character of the activated complex is rather small. Therefore, it is difficult to ascribe the higher reactivity of the aromatic amines only to the formation of the less-ionic activated complex. It is more reasonable to take other factors into consideration.

With regard to this higher reactivity of aromatic amines, another plausible reason is the resonance stabilization of the activated complex. Horner and Steppan[10] have proved that, by the reaction of *N*-ethylaniline with benzoyl peroxide at 20°C, *O*-benzoyl-*N*-ethyl-*N*-phenylhydroxyamine, *N*-benzoyl-*o*-hydroxy-*N*-ethylaniline, and *p*-benzoyloxy ethylaniline are formed; that the latter two products are not formed by the rearrangement of the former, but are formed directly by the reaction with benzoyl peroxide. Further, Denney and Denney[2] have shown that the reaction of diphenylamine with benzoyl peroxide labeled with oxygen-18 in the carbonyl positions forms, as the main product, *N*-(*o*-hydroxyphenyl)-*N*-phenylbenzamide, which contains 55% of oxygen-18 in the carbonyl oxygen and 45% of oxygen-18 in the phenol oxygen, and that, in the case of dibenzylamine, no such equilibration of oxygen-18 occurs. These facts may be evidence of the resonance of the activated complexes from aromatic amines.

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[5] R. G. Pearson, *J. Chem. Phys.*, **20**, 1478 (1952).

[6] Y. Kondo and N. Tokura, This Bulletin, **37**, 1148 (1964).

[7] Y. Kondo and N. Tokura, *ibid.*, **40**, 1433 (1967).

[8] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill, New York (1923); 2nd Ed. (revised by K. S. Pitzer and L. Brewer, 1961), p. 287.

[9] Y. Kondo and N. Tokura, This Bulletin, **40**, 1438 (1967).

[10] L. Horner and H. Steppan, *Ann.*, **606**, 47 (1957).