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Spin Trapping as Applied to Radicals Produced by Chemical Reaction. III.[1) Intermediates of the Reactions of Dibenzoyl Peroxide with Diethylamine and Diphenylamine

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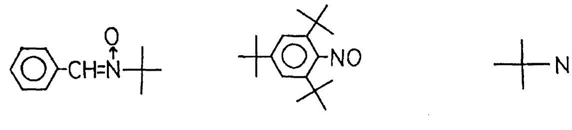
The reactions of dibenzoyl peroxide (BPO) with diethylamine (DEA) and diphenylamine (DPA) have been studied by means of an ESR technique combined with spin-trapping. In the case of the DEA/BPO system, diethylnitroxide was formed, while for the DPA/BPO system diphenylaminyl was detected. Three kinds of traps (*N*-*t*-benzylidene-*t*-butylamine *N*-oxide, 2-methyl-2-nitrosopropane, and 2,4,6-tri-*t*-butylnitrosobenzene) were used. Different kinds of spin-adducts were formed depending on such conditions as the steric circumstances, radical stabilities and solvent effects. The differences in the reaction mechanisms for these systems are discussed.

There has been a vast number of papers concerning the decomposition of diacyl peroxide in the presence of nucleophiles. Especially, the reaction of dibenzoyl peroxide (BPO) with *N*,*N*-dimethylaniline and other nucleophiles[2,3)] has given rise to many arguments concerning the reaction mechanism. Through studies along this line it has been recognized that the reactions of diacyl peroxides with nucleophiles involve ionic as well as radical processes.

Some decades ago, mechanistic studies concerning the decomposition of BPO with iron(II) and amines were carried out in our laboratory.[4,5)] In the latter case, secondary amines (diethylamine (DEA) and diphenylamine (DPA) as well as others) were used. Although we detected ESR signals for the first time, their assignments were unsuccessful at that time. As far as we are aware, mechanistic investigations of the above-mentioned systems seem not to have been done in detail.

The spin-trapping method has been recognized as being a useful tool for detecting and identifying unstable neutral radicals since the late 1960s.[6—9)] Recently, we investigated radicals produced by the photolysis of some 2,2′-azopropanes and radicals formed from the thermal decomposition of di-*t*-butyldiperoxyoxalate in benzene and xylenes.[1)] In these studies, some kinds of traps were used for capturing transient radicals. We found that trapped radical species depend on such conditions as the steric circumstances, stability of the primarily formed radicals and solvents.

We noticed that if we apply the ESR method combined with spin-trapping techniques to the entitled systems, we could obtain additional information concerning the mechanisms so far proposed. The present study started for this reason. We have obtained some new results which should be useful for a better understanding and perspective view of the mechanism. The traps used were as follows (Chart 1):



PBN BNB MNP

Chart 1.

Experimental

Materials. All of the chemicals used were of reagent grade. BPO was purified twice from a chloroform–ethanol mixture. DPA was crystallized from an ethanol solution by adding a small amount of water with stirring. *N*-Phenyl-*N*-(2-hydroxyphenyl)benzamide (PHBA) was prepared according to a method of Denney and Denney;[10)] mp 213—214 °C. DEA, bis(4-methoxyphenyl)amine (MDPA), *m*-chloroperbenzoic acid (CBA), benzene-d_6, and all the traps were used without further purification. Benzene and acetone were dried and purified in the usual manner.

ESR Measurements. A JEOL JES-FE3XG spectrometer equipped with a 100-kHz field modulator and a TE 011 cavity was used for the ESR measurements. About equimolar benzene solutions of BPO and amines (0.02—0.05 $\mathrm{mol\,dm^{-3}}$) were separately charged in an H-shaped Pyrex tube with a side capillary tube for the ESR measurements. When the traps were used, excess amounts (about 3 times of the reagents) were charged in the BPO solution. The tube was connected to a vacuum line and deaerated in the usual manner. Thereafter, the two solutions were mixed and transferred into the capillary. The reaction temperature was kept constant at 25 °C throughout the runs; the signals were recorded on the spectrometer. Spectral simulations were made with an attached computer. The *g*-values were estimated with the aid of a frequency counter and the *g*-value of 2,2-diphenyl-1-picrylhydrazyl.

Results and Discussion

ESR Signals Appearing in the Reaction of BPO with DEA in Benzene in the Absence and Presence of Spin Traps. An ESR signal appeared just after benzene solutions of BPO and DEA were mixed (Fig. 1). This signal was very stable and agreed well with a simulated spectrum with $a_{\mathrm{N}}=1.52$ mT and $a_{\mathrm{H}}=1.02$ mT. Judging from its *g*-value (=2.0059), and referring to the literature,[11,12)] the signal could be assigned to diethyl nitroxide (**1**) unambiguously. The same pattern of the ESR spectrum was observed in a DEA/CBA system in benzene. Incidentally, almost the

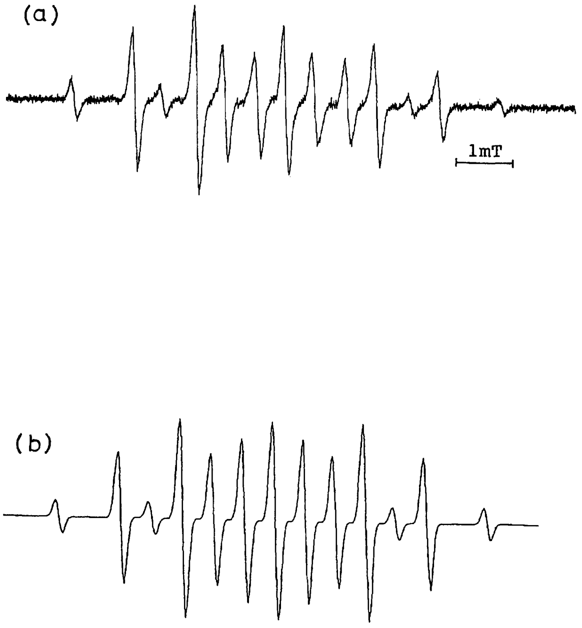


Fig. 1. ESR spectra observed in the reaction of BPO with DEA in benzene at 25 °C (a), and simulated one (b).

same signal pattern was observed for a BPO/dibutylamine system.

When the trap PBN was added, there appeared two kinds of signals besides **1** (Fig. 2a): one was a benzoyloxyl-PBN spin adduct (**2**)[9] with $a_N=1.28$ mT and $a_H=0.14$ mT; the other was a PBN-phenyl spin adduct (**3**) with $a_N=1.44$ mT and $a_H=0.22$ mT.[13] The values of these hyperfine coupling constants (hfcc) are in harmony with the view that the magnitude of the β-H hfcc decreases along with an increase in the bulkiness of the attached groups, and that the magnitude of the nitrogen hfcc decreases with increasing electron-withdrawal of the attached groups.[8,14,15] The simulated spectra obtained with the above-mentioned hfcc's are shown in Fig. 2b. When much more PBN was added, the signal of **3** disappeared, indicating that benzoyloxyl radicals were trapped exclusively before they decomposed into phenyl radicals and CO_2.

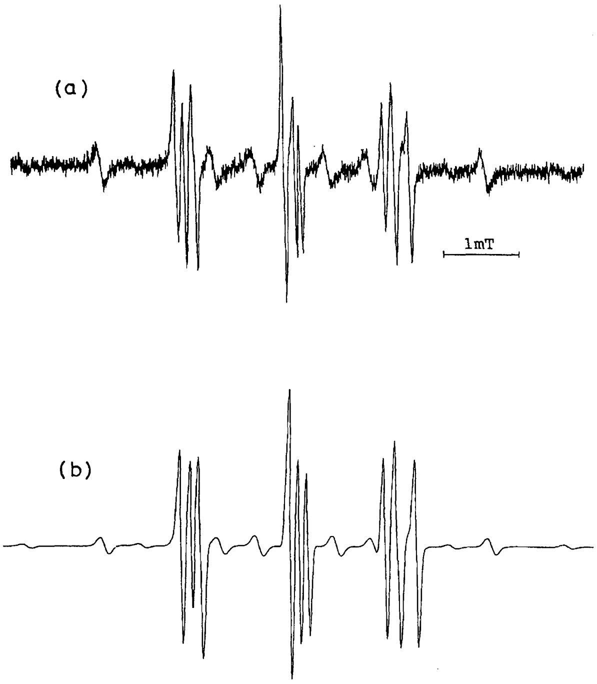


Fig. 2. ESR signals of the DEA/BPO system in the presence of PBN in benzene (a), and simulated one (b).

In the presence of MNP, a triplet appeared besides **1**, as shown in Fig. 3. Perkins et al.[16] reported that only nitroxide which had arisen by scavenging benzoyloxyl radicals from BPO was detected; this is in accordance with our observation. Hence, a radical trapped by MNP must be the benzoyloxyl radical. Contrary to the case of PBN, phenyl radicals were not captured by MNP, suggesting a high reactivity of MNP, on one hand, and the stable nature of benzoyloxyl with respect to decarboxylation on the other hand.

The ESR spectrum of the solution containing BNB is shown in Fig. 4a. The signal comprised two components: one due to diethylnitroxide **1** and the other a phenyl-BNB spin adduct (**5**). The reason why benzoyloxyl radicals were not trapped could be ascribed to a steric hindrance when they approach BNB; this observation is in agreement with that of Terabe and Konaka.[17] With time, the former signal gradually diminished and the intensity of the signal due to the spin adduct (**5**) increased and became well characterized (Fig. 4b). For the sake of convenience, the structures of the identified radicals are shown below (Chart 2).

Reaction Mechanism. The above-mentioned ESR observations afford useful information regarding the formation, reactivity, and the stability of the reaction intermediates and, hence, the reaction mechanism in this system.

Gambarjan[18] reported that BPO reacts with diethylamine to produce benzoic acid (96%) and *O*-benzoyl-*N*,*N*-diethylhydroxylamine (BDHA) (78%), the latter being obtained as a hydrogensulfate. The fact that the

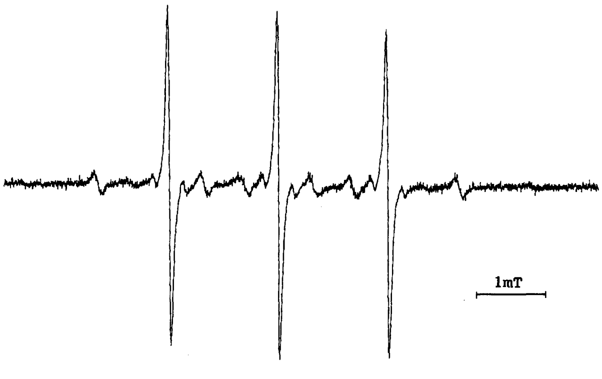


Fig. 3. ESR spectrum of the DEA/BPO system in the presence of MNP in benzene.

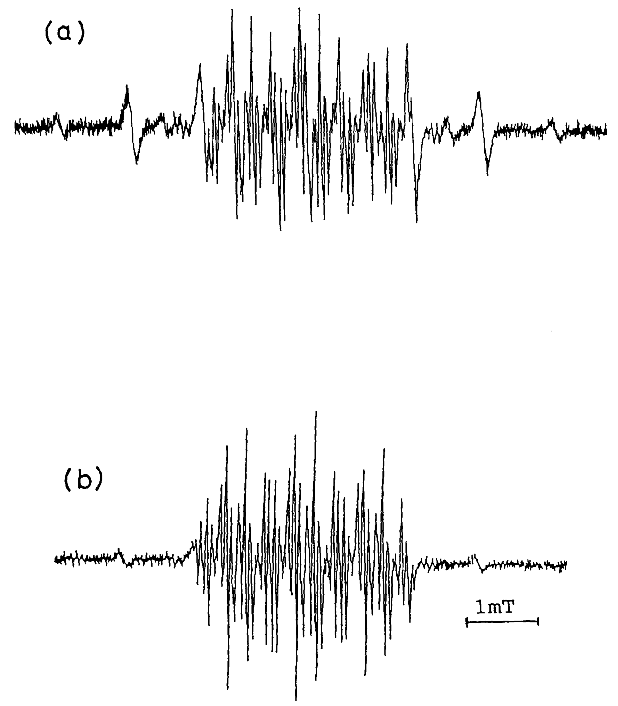


Fig. 4. ESR signals of the DEA/BPO system in the presence of BNB in benzene. Fifty minutes after mixing (a), and four hours after mixing (b).

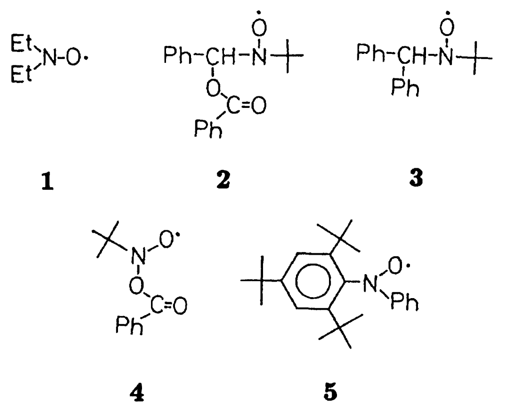


Chart 2.

yield of BDHA is smaller than that of benzoic acid suggests the existence of some side reactions involving radicals. Indeed, Kashino et al.5) found a poorly resolved ESR signal extending over 9 mT in this system. Although they inferred that the radical is of the $-\dot{\mathrm{C}}\mathrm{H}-\mathrm{NH}-\mathrm{R}$ type, the signal must be ascribed to diethylnitroxide. If we take into account the historical background briefly stated at the beginning of the introductory section, the overall reaction scheme in this system could be given below:

Main Reactions:

$$\mathrm{Et_2NH + BPO} \longrightarrow \underset{\mathrm{IP_1}}{[\mathrm{Et_2NH^+OCOPh\ \ PhCOO^-}]}$$

$$\longrightarrow \underset{\mathrm{BDHA}}{\mathrm{Et_2N\text{-}OCOPh}} + \mathrm{PhCOOH}$$

Side Reactions:

$$\mathrm{Et_2NH + BPO} \longrightarrow \underset{\mathrm{IP_2}}{[\mathrm{Et_2NH^{+\bullet}PhCOO^-}]} + \mathrm{PhCOO^\bullet}$$

$$\mathrm{BDHA + PhCOO^\bullet} \longrightarrow \mathrm{Et_2NO^\bullet + PhCO\text{-}O\text{-}COPh}$$

$$\mathrm{2IP_2} \longrightarrow \mathrm{Et_2N\text{-}NEt_2 + 2PhCOOH}$$

$$\mathrm{PhCOO^\bullet} \longrightarrow \mathrm{Ph^\bullet + CO_2}$$

Here, $\mathrm{IP_1}$ and $\mathrm{IP_2}$ denote those ion pairs within solvent cages. In a BPO/*N*,*N*-dimethylaniline system, the formation of a cation radical and $\mathrm{PhCOO^\bullet}$ was proposed by Honer19) as well as Walling and Indictor,20) though the view concerning the formation process is somewhat different. In any case. $\mathrm{Et_2NH^{+\bullet}}$ and $\mathrm{PhCOO^\bullet}$ are formed as indicated above. The formation of benzoic anhydride was evidenced by product analysis. Deaerated benzene solutions of BPO and DEA were mixed at room temperature and allowed to stand for one day. The solution was chromatographed by silica gel, and white crystals were isolated. By comparing its IR spectrum with the authentic one, the formation of benzoic anhydride was confirmed. The observation by Gambarjan that the yield of BDHA is smaller than that of benzoic acid is compatible with the above-mentioned view. It is likely that such species as $\mathrm{PhCOO^\bullet}$ and $\mathrm{Ph^\bullet}$ will abstract β-hydrogens from DEA. However, as far as our ESR study is concerned, no radical other than those stated above was detected. The bimolecular reaction of $\mathrm{IP_2}$ indicated above is likely, but has not yet been affirmed. Induced decompositions of BPO by $\mathrm{PhCOO^\bullet}$ and $\mathrm{Ph^\bullet}$ are a matter of course and are thus omitted from the above scheme.

When a great excess of MNP over the reagents is added, the signal of **1** vanished and only the signal of **4** appeared, suggesting that the radical $\mathrm{PhCOO^\bullet}$ deeply intervened with the formation of **1** (see above scheme).

ESR Signals Appearing in the Reaction of BPO with DPA in the Absence and Presence of Spin Traps. When BPO was mixed with DPA, two kinds of signals appeared (Fig. 5a). The central triplet signal (**6**) with the same intensity (hfcc=0.38 mT) may have arisen from nitrogen-containing radicals, which is considered to be the same as observed by Kashino et al.5) The fine structure extended over 5 mT was found to be due to diphenylaminyl radicals (**7**). Using the reported hfcc values21) for **7** and the value of $a_{\mathrm{N}}=0.38$ mT for **6**, we could reproduce the spectrum (Fig. 5b). The signal of **7** vanished after one hour, while that of **6** was more stable in benzene. Figure 6a shows the ESR signal in acetone just after mixing. With time the intensity of the triplet gradually increased, and bumps of both wings of the triplet gradually appeared at the expense of **7** (Fig. 6b).

When a benzene solution of PHBA was mixed with BPO at an elevated temperature or shaked with $\mathrm{PbO_2}$, a triplet with hfcc=0.38 mT and $g=2.0036$ appeared;

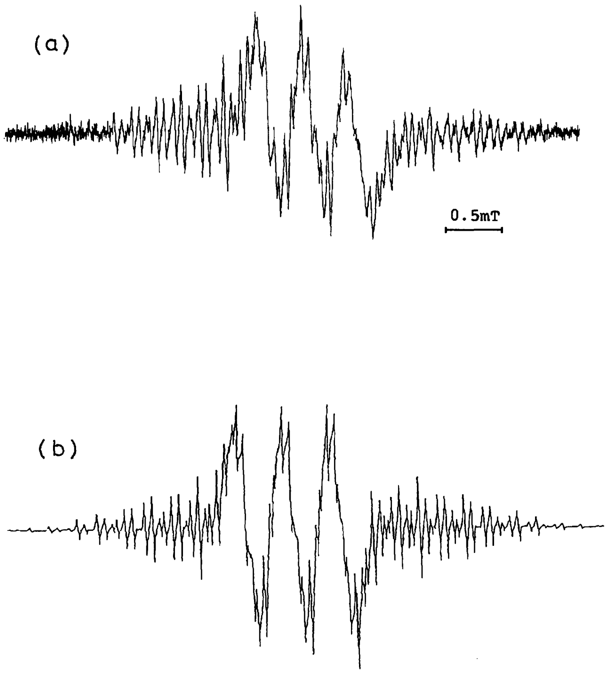


Fig. 5. ESR signals of the DPA/BPO system in benzene. Observed (a), and simulated (b).

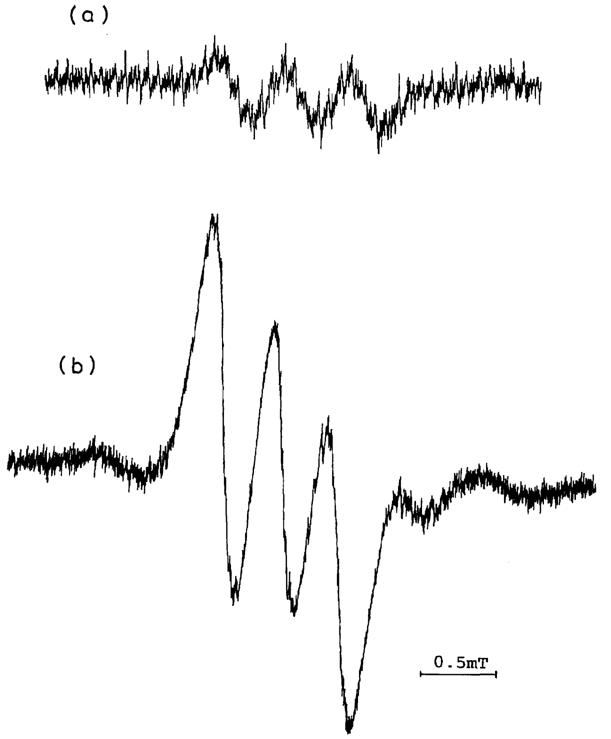


Fig. 6. ESR spectra of the DPA/BPO system in acetone. Three minutes after mixing (a), and three hours after mixing (b).

this agreed with that of **6**. The small a_N-value is characteristic of the phenoxyl radicals having a nitrogen atom in the ortho position,[22] and the g-value is also reasonable for phenoxyls. Therefore, **6** is assignable to the phenoxyl radical from PHBA. However, it is a little bit interesting but hard to explain why the hyperfine structures due to the hydrogens on the phenol-side benzene did not appear.

In order to clarify the above-mentioned solvent effects, MDPA was used in the place of DPA. The observed signal in Fig. 7a could be assigned to the corresponding aminyl (**8**), since the signal agreed well with the simulated one (Fig. 7b) by using the reported hfcc's.[21] No triplet, such as **6**, was observed in this case. Hence, a route to produce the corresponding p,p'-disubstituted PHBA could, if any, be negligible. When the solvent was changed to acetone, a quintet appeared on which the signal of **8** was superimposed (Fig. 7c), and gradually increased. The signal could be ascribed to the cation radical (**9**) of tetrakis(4-methoxyphenyl)hydrazine.[23] The bumps observed in Fig. 6b may, therefore, be due to the corresponding cation radical (Chart 3).

When MNP was added to the BPO/DPA system, only a triplet with $a_N = 1.54$ mT appeared; by inspection, the triplet was assigned to the MNP-benzoyloxyl adduct (**4**), as in the case of the BPO/DEA system. In this sence MNP could be said to be more reactive than PBN, and the benzoyloxyl radicals must have been captured by MNP before they decomposed into phenyl radicals and CO_2. The ESR signal in Fig. 5a drastically changed when BNB was added thereafter. This

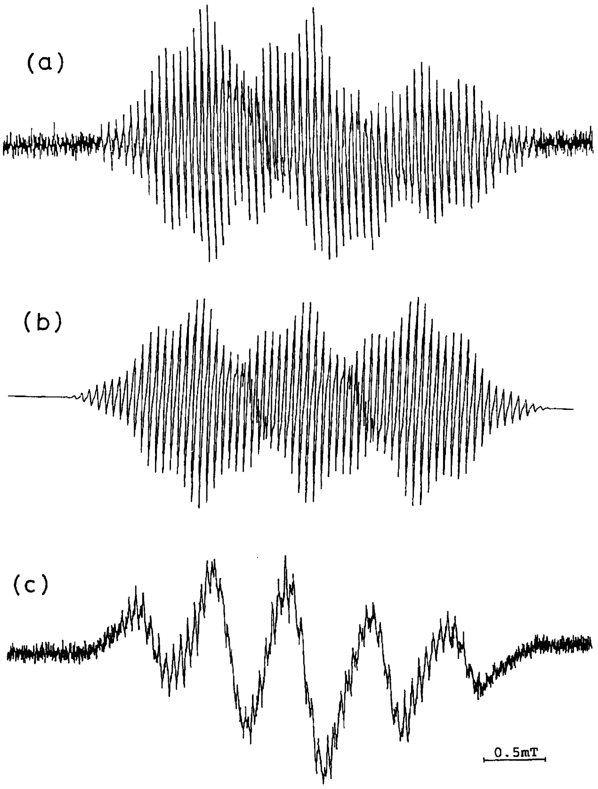
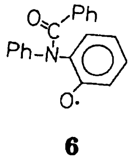


Fig. 7. ESR spectra of the MDPA/BPO system in benzene. Observed (a), simulated (b), and observed ESR signal in acetone (c).



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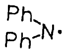

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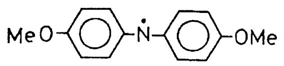

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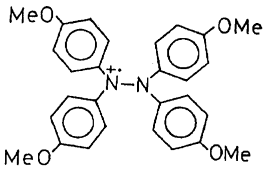

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Chart 3.

is shown in Fig. 8a. It was found by a careful inspection that three kinds of signals are involved. Of these, two are due to **5** and **6**. The same spectra also appeared in benzene-d_6. Hence, the intervention of the solvent can be eliminated. Since the remaining one has a characteristic structure it is very interesting. Each triplet with $a_N=2.65$ mT splits into a doublet due to one proton with $a_H=0.192$ mT, and each doublet further splits to form a fine structure. Judging from its g-value (=2.0055) this signal is considered to be due to a kind of nitroxide radical. It is very interesting to note that the a_N-value is extraordinarily large for usual nitroxide radicals (1.0—1.5 mT). Exceptionally large values of a_N (2.4—2.9 mT) are characteristic of alkoxy-alkylnitroxides.[24] If the steric situation is not taken into account, diphenylaminyl **7** will certainly be trapped by BNB. However, this is impossible due to a very severe steric circumstance. It is therefore likely that the spin adduct has the following structure (Chart 4). In this structure, the steric hindrance at the central nitrogen atom is also severe. It is therefore inferred that as a consequence of nonplanarity at N, the s character of the semioccupied orbital on N is increased, resulting in an extraordinarily large a_N-value.[25] When MDPA was used, such a signal did not appear, which indirectly supports the above view. By a trial-and-error method, we finally succeeded to reproduce the complicated spectra (Fig. 8b). The ESR data obtained in this work are summarized in Table 1.

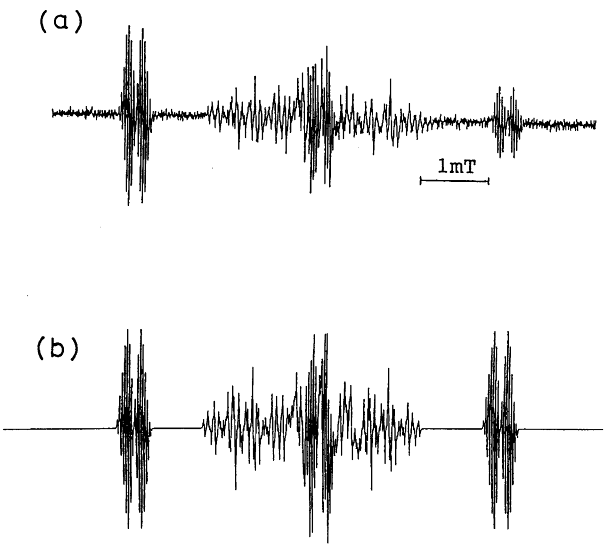

Fig. 8. The change in the ESR signals of Fig. 5a upon addition of BNB. Observed in benzene (a), and simulated (b).

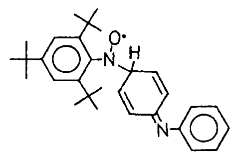

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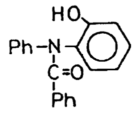
Chart 4.

Reaction Mechanism. On the basis of the information mentioned above, we now discuss the reaction mechanism for the DPA/BPO system. It was assumed[10] that O-benzoyl-N,N-diphenylhydroxylamine (BDA) at first forms by analogy with the case of aliphatic amines. Since the isolation of BDA has not been successful, it is believed to undergo further reactions to finally produce PHBA through the following mechanism.[10]

Main Reactions:

$$\mathrm{DPA+BPO} \longrightarrow [\mathrm{Ph_2NH^+{-}OCOPh\ \ PhCOO^-}]$$
$$\longrightarrow \underset{\mathrm{BDA}}{\mathrm{Ph_2N{-}OCOPh}} + \mathrm{PhCOOH}$$

$$\mathrm{BDA} \longrightarrow [\mathrm{Ph_2N^+\ \ PhCOO^-}] \longrightarrow\!\longrightarrow\!\longrightarrow$$



PHBA

Table 1. ESR Parameters for the Observed Radicals

Radical	a_N/mT	a_H/mT	g-Value
1	1.52	1.02(4H)	2.0059
2	1.28	0.14	2.0062
3	1.44	0.22	2.0061
4	1.54		2.0066
5	0.988	0.286(o-H,2H) 0.092(m-H,2H) 0.261(p-H,1H) 0.063(m-H,2H)	2.0056
6	0.38		2.0036
7	0.880	0.428(p-H,2H) 0.368(o-H,4H) 0.152(m-H,4H)	2.0032
8	0.849	0.347(o-H,4H) 0.118(m-H,4H) 0.059(OMe,6H)	2.0034
9	0.60(2N)		2.0030
10	2.65	0.192(β-H) 0.071(o-H,2H) 0.031(m-H,2H) 0.039(m-H,2H)	2.0055
11	0.966	0.183(o,p-H,6H) 0.079(m-H,4H)	2.0055

Indeed, Gambarjan[26] isolated PHBA in 48% yield.

On the other hand, we observed several radical species, indicating side reactions. As in the case of the DEA/BPO system, the following reaction will take place:

Side Reactions:

$$\mathrm{DPA + BPO \longrightarrow [Ph_2NH^{+\bullet}\ PhCOO^-] + PhCOO^\bullet}$$

$$\mathrm{Ph_2NH + PhCOO^\bullet \longrightarrow Ph_2N^\bullet + PhCOOH}$$

$$\mathrm{Ph_2N^\bullet + [Ph_2N^+\ \ PhCOO^-] \longrightarrow [Ph_2N\text{-}N^{+\bullet}Ph_2\ \ PhCOO^-]}$$

The fate of the ion pair $[\mathrm{Ph_2NH^{+\bullet}\ PhCOO^-}]$ may be similar to that of $[\mathrm{Et_2NH^{+\bullet}\ PhCOO^-}]$. The reaction

$$\mathrm{[Ph_2NH^{+\bullet}\ \ PhCOO^-] \longrightarrow Ph_2N^\bullet + PhCOOH}$$

is likely to occur, since **7** is extraordinarily stable. This process should be independent of the benzoyloxyl radical. As mentioned above, the ESR signal of **7** did not appear in the presence of MNP, suggesting that the benzoyloxyl radical is necessary for the formation of **7**. Therefore, the above reaction could be eliminated. It is reasonable that the benzoyloxyl radical attacks DPA and PHBA and abstracts hydrogen atoms of the $>$NH and –OH groups to form **7** and **6**, respectively. The accumulation of **6** in acetone suggests that the formation of PHBA is via heterolytic processes, as indicated above. The introduction of an electron-donating group, such as –OMe in DPA, would favor heterolytic fission to produce $\mathrm{Ph_2N^+}$, which preferentially reacts with **7** to form the cation radical **9**, rather than a rearrangement reaction leading to **6**.

In order to make situation clearer, CBA was used instead of BPO. In the DEA/BPO system, the formation of **1** was affirmed as expected. In the DPA/CBA system, the ESR signal of **7** did not appear; instead, the signal of diphenylnitroxide (**11**) appeared. Tokumaru and co-workers[27] reported that diphenylamine, when treated with perbenzoic acid, gave diphenylnitroxide. They considered that *N*,*N*-diphenylhydroxylamine is probably an intermediate of the reaction. If this is taken into account, reactions for the DPA/CBA system may proceed as follows:

$$\mathrm{Ph_2NH + \underset{(CBA)}{HOOCOR} \longrightarrow \underset{Ion\ pair}{[Ph_2N^+HOH\ \ RCOO^-]} \longrightarrow Ph_2NOH + RCOOH}$$

$$\mathrm{RCOOOH + PH_2NH \longrightarrow [Ph_2NH^{+\bullet}\ OH^-] + RCOO^\bullet}$$

$$\mathrm{Ph_2NOH + RCOO^\bullet \longrightarrow Ph_2NO^\bullet + RCOOH}$$

Since $\mathrm{Ph_2NOH}$ is stable, it would be attacked by $\mathrm{RCOO^\bullet}$, while in the case of BPO, the unstable product BDA would vanish before being attacked by $\mathrm{PhCOO^\bullet}$ to produce **11**.

Concluding Remarks. We have detected a variety of radicals by means of the ESR method combined with spin trapping. The roles of DEA and DPA for the decomposition of BPO have been clarified. The mechanistic difference between the DEA/BPO and DPA/BPO systems arises for two reasons. One is that the intermediate BDA of the main reaction for the DPA/BPO system is much more unstable than the intermediate BDHA for the DEA/BPO system; the other is that diethylaminyl radicals is very unstable and dimerization occurs before they are caught by the spin traps used.

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