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INTERMEDIACY OF CHARGED SPECIES IN PHOTODECOMPOSITION OF DIAROYL PEROXIDES SENSITIZED WITH AROMATIC HYDROCARBONS IN POLAR SOLVENTS

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Electron transfer upon photosensitization of dibenzoyl and bis(2-thiophenecarbonyl) peroxides with singlet sensitizers in acetonitrile was revealed by trapping of sensitizer (naphthalene) cation radicals with acetic acid and by their direct detection (pyrene cation radicals) by means of laser flash photolysis.

Many photochemical reactions of organic compounds are sensitized by excited singlet states of sensitizers, and the reactions are often proposed to proceed through exciplexes; however, these intermediates are not always detectable by spectroscopy even in non-polar solvents.$^{1)}$ Previously we have shown that aromatic hydrocarbons sensitize decomposition of organic peroxides,$^{2,3)}$ and proposed intermediacy of exciplex intermediates on the basis of fluorescence quenching$^{4)}$ and quantum yield studies.$^{5)}$ We now wish to report that the use of polar solvents revealed electron transfer nature of the exciplex intermediates in the singlet sensitized photolysis of dibenzoyl (BPO) and bis(2-thiophenecarbonyl) peroxide (TPO) by providing characteristic products and spectroscopic evidence for the formation of radical ions.

Naphthalene(0.05 mol/dm^3)-sensitized photolyses of BPO and TPO (0.03 mol/dm^3) were carried out in benzene and acetonitrile in the absence and presence of acetic acid (20 Vol%) under nitrogen atmosphere.$^{6)}$ The products were quantitatively analyzed by GLPC, and are summarized in Tables 1 and 2. The formation of products except for 1-naphthyl acetate is reasonably understood by the usual free radical mechanism as previously postulated,$^{2,3,5,7-9)}$ where phenyl benzoate from BPO is mainly due to geminate recombination of a benzoyloxyl and a phenyl radical arising from successive and/or simultaneous two-bond cleavage of BPO.$^{3)}$ 2-Thiophenecarbonyloxyl radicals from TPO decarboxylate more slowly than benzoyloxyl radicals from BPO.$^{7,8)}$ Therefore, the products arising from thienyl radicals are almost negligible and the reaction mechanism is simpler in the case of TPO, while phenyl radicals from benzoyloxyl radicals react with the solvent and sensitizer to complicate the reaction systems.

It is remarkable that 1-naphthyl acetate was produced, though in a low yield, in the sensitized photolysis of BPO in a mixture of acetonitrile and acetic acid, and also in that of TPO in both of the mixed solvents. Thermolysis of the peroxides in the presence of naphthalene in the mixed solvents did not give the naphthyl acetate. Control experiments irradiating each of naphthalene, 1-naphthyl benzoate, and 1-naphthyl 2-thiophenecarboxylate did not afford 1-naphthyl acetate

Table 1. Product yields in photolysis of BPO in the presence of naphthalene[a)]

Product	Solvent			
	PhH	ACN	PhH-AcOH	ACN-AcOH
PhPh	0.29	0.0	0.31	0.0
$PhCO_2Ph$	0.22	0.05	0.17	0.04
1-PhNp	0.01	0.01	0.03	0.01
$PhCO_2Np$-1	tr	0.04	-	0.02
$PhCO_2Np$-2	tr	tr	-	tr
$MeCO_2Np$-1	0.0	0.0	0.0	0.02
1,1'-NpNp	0.01	0.01	-	0.01
1,2'-NpNp	tr	0.10	-	tr
2,2'-NpNp	0.02	0.0	-	tr

Table 2. Product yields in photolysis of TPO in the presence of naphthalene[a)]

Product	Solvent			
	PhH	ACN	PhH-AcOH	ACN-AcOH
PhPh	0.01	0.0	tr	0.0
2-ThPh	0.01	0.0	0.01	0.0
2-$ThCO_2H$	0.9	1.2	0.9	1.0
2-$ThCO_2Ph$	0.03	0.0	0.01	0.0
2-$ThCO_2Np$-1	0.08	0.11	0.01	0.02
2-$ThCO_2Np$-2	tr	tr	tr	0.0
$MeCO_2Np$-1	0.0	0.0	0.02	0.14
1,1'-NpNp	0.10	0.05	0.09	tr
1,2'-NpNp	0.02	0.03	0.03	tr
2,2'-NpNp	tr	tr	tr	tr

a) Yields based on a mole of BPO or TPO; ACN: acetonitrile; Np: naphthyl; tr: trace (<0.01); -: not determined.

in a mixture of acetonitrile and acetic acid,[6)] confirming that the naphthyl acetate is a primary product in the peroxide photolyses. The formation of naphthyl acetate can be understood in terms of the reaction of naphthalene cation radicals with acetic acid as shown in the following scheme:

$$\begin{array}{rcll} {}^{1}NpH^{*} + RCO_2OCOR & \longrightarrow & {}^{1}(NpH\cdots RCO_2OCOR)^{*} & (1) \\ & \longrightarrow & NpH^{+\cdot} + RCO_2OCOR^{-\cdot} & (2) \\ RCO_2OCOR^{-\cdot} & \longrightarrow & RCO_2\cdot + RCO_2^{-} & (3) \\ NpH^{+\cdot} + AcOH + X^{-\cdot} & \longrightarrow & NpOAc + XH_2 & (4) \end{array}$$

$(X^{-\cdot}$: proton acceptors$)$

The singlet excited naphthalene transfers an electron to a peroxide molecule in the ground state probably through an exciplex intermediate to form a pair of a naphthalene cation radical and a peroxide anion radical.[10,11)] The resulting naphthalene cation radical could be trapped by acetic acid to give 1-naphthyl acetate.[12)]

Fluorescence of aromatic hydrocarbons such as naphthalene and pyrene is efficiently quenched by BPO and t-butyl peroxybenzoate in benzene and acetonitrile; however, the extent of charge transfer in the exciplex intermediates is higher in acetonitrile than in benzene, and some fraction of the exciplexes may undergo electron transfer to give radical ion pairs.[4)] The fact that higher yields of 1-naphthyl acetate were afforded in the polar solvent is consistent with the results of fluorescence quenching.

In the photolysis of TPO 1-naphthyl acetate was formed even in the benzene-acetic acid mixture, and its yield was remarkably higher in the acetonitrile-acetic acid mixture than in the benzene-acetic acid mixture. These indicate that the electron transfer in the exciplex of TPO is more efficient than that of BPO. This finding can be explained by difference in the reduction potentials (E_{red}) of the peroxides;13) E_{red} is -0.95 V for TPO and -1.13 V for BPO as measured in acetonitrile vs. $Ag/AgNO_3$ (0.1 mol/dm^3). As Table 2 indicates, the formation of naphthyl 2-thiophenecarboxylates and binaphthyls is significantly suppressed by the production of 1-naphthyl acetate.

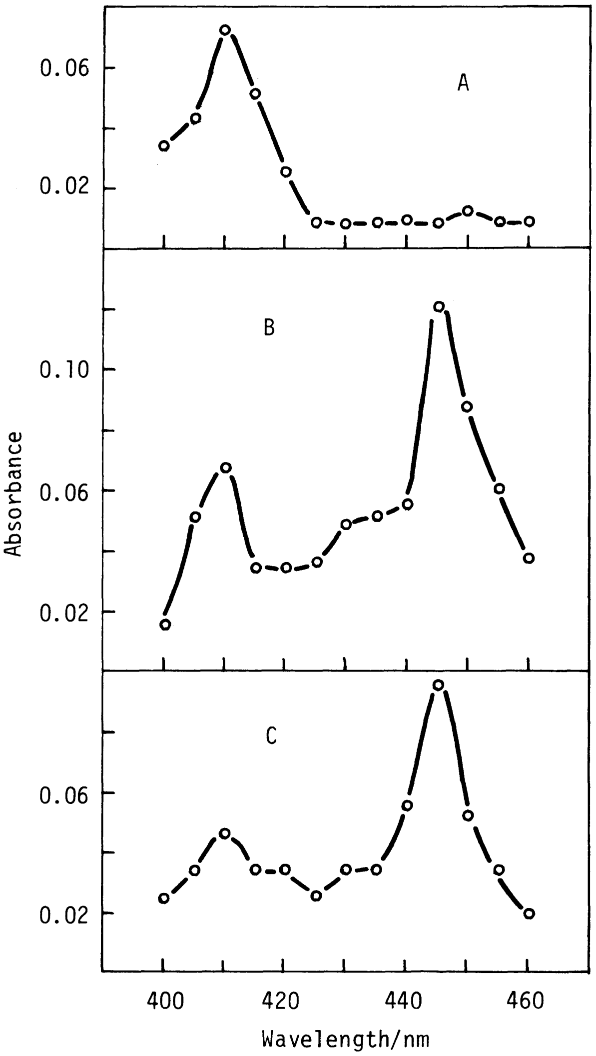

Fig. 1. Transient absorption spectra observed at 4 μs following flash photolysis of pyrene (2.0 x 10^{-5} mol/dm^3) by nitrogen pulsed laser in deaerated acetonitrile in the absence of a quencher (A), in the presence of bis(2-thiophenecarbonyl) peroxide (1.1 x 10^{-3} mol/dm^3) (B), and dibenzoyl peroxide (1.5 x 10^{-3} mol/dm^3) (C).

This fact means that in the absence of acetic acid the ionic intermediates collapse to the starting materials and/or the usual free-radical products.

To get more insight into electron transfer processes in the exciplexes, pyrene-sensitized decomposition of the peroxides was investigated by laser flash photolysis (337.1 nm, 7-ns fwhm, 8 mJ/pulse).14,15) Figure 1 compares transient absorption spectra observed for acetonitrile solution of pyrene (2 x 10^{-5} mol/dm^3) in the absence and presence of BPO (1.5 x 10^{-3} mol/dm^3) and TPO (1.1 x 10^{-3} mol/dm^3) under nitrogen atmosphere.

In the absence of a peroxide the transient absorption spectrum is ascribed to pyrene triplets10,16) (Fig. 1A). In the presence of TPO or BPO the spectrum consists of two components (Figs. 1B and 1C); the shorter wavelength band is due to the pyrene triplets and the longer wavelength band is in good agreement with that of pyrene cation radicals.16) In these cases the pyrene triplets might be formed mainly from the exciplex intermediates17) since the pyrene singlets are efficiently quenched by the peroxides under these conditions.4) Relative intensity of the band due to the pyrene cation radicals was increased with increasing peroxide concentration in the range of (1.5 - 5.0) x 10^{-3} mol/dm^3 for BPO and (0.28 - 2.8) x 10^{-3} mol/dm^3 for TPO. The formation of pyrene cation radicals clearly shows involvement of electron transfer on quenching of pyrene singlets by the peroxides. Flash photolysis of pyrene in benzene in the presence of the peroxides did not afford any absorption bands ascribable to pyrene cation radicals. This is consistent with the results of chemical trapping of naphthalene cation radicals, and the formation of naphthyl acetate from TPO in benzene might be due to interception of the exciplex (contact radical pair) by acetic acid.

It is concluded that the quenching of singlet sensitizers by peroxides such as BPO and TPO is accompanied by electron transfer to give ion radical pairs in polar solvents as revealed by chemical trapping of naphthalene cation radicals and by the transient absorption spectrum of pyrene cation radicals.

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