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Reaction Efficiency of Exciplexes in Singlet Sensitized Decomposition of Dibenzoyl Peroxide

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Synopsis. Quantum yields were measured for aromatic hydrocarbon-sensitized decomposition of dibenzoyl peroxide in benzene. For the sensitizers employed, naphthalene, phenanthrene, triphenylene, and chrysene, the ratio of the rate constants for decay and radical formation from intermediate exciplexes was found to be similar (0.2—0.4), indicating that the reactivity of the peroxide moiety in the intermediate is independent of the structural factors of the sensitizers as far as examined.

Exciplexes have been proposed as reactive intermediates in many photochemical reactions though they are not necessarily emissive.[1-3] In some cases the exciplexes may be too reactive to be alive in sufficiently long lifetimes to exhibit emission.[3,4] However, few works have been carried out to actually examine intrinsic reactivity of the exciplexes from the viewpoint of structural factors of sensitizers.[2,5,6]

Previously, singlet excited aromatic hydrocarbons have been revealed to sensitize decomposition of dibenzoyl peroxide (BPO) in solution.[7-9] The reaction was proposed to proceed through short lived reactive exciplexes which either bring about homolytic decomposition of the peroxide moiety into free radicals or deactivate into the original components in the ground state as shown in the following scheme, where Sens and P denote a sensitizer and the peroxide, respectively, and k_q, k_r, and k_d mean the rate constants of the processes concerned.

This paper describes an attempt to determine the relative reactivity of the exciplexes in singlet sensitized decomposition of BPO in relation to structural factors of the hydrocarbon sensitizers.

$$^1\mathrm{Sens}^* + \mathrm{P} \xrightarrow{k_q} {}^1(\mathrm{Sens}\cdot\mathrm{P})^* \quad (1)$$

$$^1(\mathrm{Sens}\cdot\mathrm{P})^* \xrightarrow{k_r} \text{Free radicals} + \mathrm{Sens} \quad (2)$$

$$^1(\mathrm{Sens}\cdot\mathrm{P})^* \xrightarrow{k_d} \mathrm{Sens} + \mathrm{P} \quad (3)$$

Scheme 1.

Results and Discussion

Benzene solutions of a sensitizer (3.0×10^{-3}—$3.0\times10^{-2}\,\mathrm{mol\,dm^{-3}}$) and varying concentrations of BPO (1.2×10^{-3}—$3.1\times10^{-2}\,\mathrm{mol\,dm^{-3}}$) were irradiated under argon atmosphere with 366-nm light (for chrysene as sensitizer) or 313-nm light (for triphenylene, phenanthrene, and naphthalene) isolated from a 400 W high pressure mercury lamp, and the quantum yields for decomposition of BPO were determined at low conversion of BPO (less than 20%) using potassium tris(oxalato)ferrate(III) actinometry.[10]

According to Scheme 1, the quantum yield for disappearance of BPO is expressed by Eq. 4, where τ_S^0 means the lifetime of the singlet excited sensitizer in the absence of the peroxide.

$$\Phi^{-1} = (1 + 1/k_q\tau_S^0[\mathrm{P}])(1 + k_d/k_r) \quad (4)$$

For each sensitizer employed, the reciprocal of the quantum yield is linearly correlated with the reciprocal of the peroxide concentration, and the intercept, $(k_r+k_d)/k_r$, exceeds unity (Fig. 1). This means clearly that the reaction proceeds through formation of some reactive intermediates like exciplexes. The results analyzed according to Eq. 4 are summarized in Table 1.

In Table 1 are also listed the $k_q\tau_S^0$ values determined by fluorescence quenching in benzene using the single photon counting technique,[11] the singlet excitation energies[10] and oxidation potentials[12] of the sensitizers. The $k_q\tau_S^0$ value obtained from the quantum yield measurements for each sensitizer satisfactorily agrees well with that from the fluorescence quenching.

As Table 1 indicates, the observed ratios of the rate constants for decay and radical formation from the exciplexes, k_d/k_r, are not significantly varied (0.21—0.41) among the unsubstituted polycyclic aromatic hydrocarbons employed, naphthalene, phenanthrene, triphenylene, and chrysene. This fact indicates that the reactivity of the peroxide moiety in the intermediate does not depend upon such structural factors of the sensitizers as the singlet excitation energies of the sensitizers, E_S, and the extent of charge transfer from the excited sensitizer to BPO in the exciplex, $E_{ox}-E_S$. This observation might be accounted for by the facts that the low energy (*ca.* 31 kcal mol^{-1}, 1 cal=4.184 J)[13] is required for the cleavage of the peroxide linkage compared to the singlet excitation energies of the sensitizers (Table 1) and that the

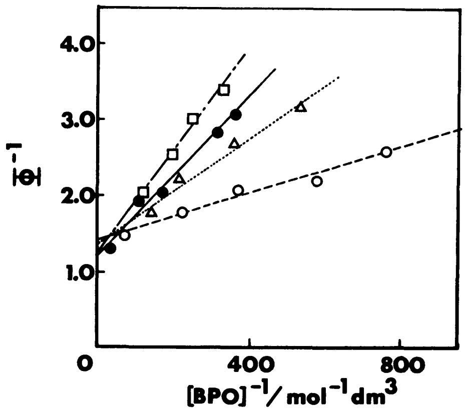

Fig. 1. Stern-Volmer plots of reciprocal quantum yields *vs.* reciprocal concentrations of BPO in aromatic hydrocarbon sensitized decomposition of BPO. Sensitizers: naphthalene (○), triphenylene (□), phenanthrene (△), and chrysene (●).

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TABLE 1. RELATIVE REACTIVITY OF THE EXCIPLEXES IN SINGLET SENSITIZED DECOMPOSITION OF DIBENZOYL PEROXIDE AND STRUCTURAL FACTORS OF THE SENSITIZERS

Sensitizer	k_d/k_r	$k_q\tau_S^0$ a)	$k_q\tau_S^0$ b)	E_S c)		E_{ox} d)	$E_{ox}-E_S$
		$dm^3 mol^{-1}$		kcal mol^{-1}	eV	V	eV
Naphthalene	0.41	930	810	92	3.99	1.87	-2.12
Triphenylene	0.29	200	170	83.4	3.62	1.80	-1.82
Phenanthrene	0.38	400	310	82.8	3.59	1.71	-1.88
Chrysene	0.21	230	240	79.2	3.43	1.56	-1.87

a) From quantum yield measurements. b) From fluorescence quenching.
c) Singlet excitation energy from Ref. 10 d) Oxidation potential *vs.* SCE in CH_3CN with Et_4NClO_4.

overall process of the sensitization gives free radical products arising from benzoyloxyl and phenyl radicals, but not any ionic products at all.[7–9]

Attempts to determine the quantum yields by employing other sensitizers like anthracene, 9,10-diphenylanthracene, pyrene, and perylene were abandoned, since these sensitizers were found to be fairly consumed during the reaction in contrast to the above sensitizers which were recovered more than 80% after the reaction.

Experimental

Materials. Dibenzoyl peroxide was purified by reprecipitation from dichloromethane–methanol. Triphenylene was prepared according to literature.[14] The other aromatic hydrocarbons, naphthalene, phenanthrene, chrysene, anthracene, 9,10-diphenylanthracene, pyrene, and perylene, were commercially available. The aromatic hydrocarbons were purified by column chromatography on silica gel with petroleum ether as eluent and recrystallized from hexane. Benzene (special grade) was distilled before use.

Measurement of Quantum Yields. The quantum yields for disappearance of BPO were determined in benzene under argon atmosphere employing potassium tris(oxalato)ferrate(III) as actinometer. Irradiation was carried out with 366-nm light for chrysene, anthracene, 9,10-diphenylanthracene, pyrene, and perylene and with 313-nm light for naphthalene, phenanthrene, and triphenylene. From a 400 W high pressure mercury lamp 366-nm light was isolated through a Toshiba UV-D36B glass filter and 313-nm light through a Toshiba UV-D33S and a K_2CrO_4/Na_2CO_3 solution filter.[10] The amounts of the remaining BPO were determined by HPLC (column: Zorbax ODS, solvent: $CH_3OH-H_2O=85:15$). Although BPO was decomposed on direct irradiation with 313-nm light, its quantum yield was less than 1% compared with the sensitized decompositions and can be satisfactorily neglected in the present investigation.

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