Short Communication

Quenching of excited singlet states by dibenzoyl peroxide and *tert*-butyl peroxybenzoate

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The fluorescence lifetimes of polycyclic aromatic hydrocarbons, substituted naphthalenes and anthracenes were measured as a function of the concentration of dibenzoyl peroxide and *tert*-butyl peroxybenzoate in benzene and acetonitrile. The quenching rate constant is not dependent on the singlet excitation energy of the sensitizers but depends on the oxidation potential of the excited singlet states of the sensitizers as estimated in terms of the difference between their ground state oxidation potentials and the singlet excitation energies. The results are consistent with a quenching mechanism involving the formation of exciplexes with a charge transfer character.

1. Results and discussion

Recently, increasing attention has been paid to the sensitized photolysis of organic peroxides from the mechanistic viewpoint as well as from the standpoint of the photochemical generation of free radicals [1 - 11]. In both singlet and triplet sensitizations the excitation energies of the sensitizers employed are far less than the energies required to excite the peroxides to their electronically excited states, and the mechanisms proposed so far are exciplex formation in singlet sensitization [2, 3] and excitation transfer to peroxide molecules in a vibrationally hot ground state in singlet [4] and triplet sensitization [5, 6].

Recent reports by Encinas and Lissi [4] and by Engel *et al.* [6] prompted us to report our results on the quenching of the fluorescence lifetimes of 16 polycyclic aromatics by dibenzoyl peroxide (BPO) and *tert*-butyl peroxybenzoate (BPB) newly determined by the single-photon counting technique with deconvolution. On the basis of the quenching of the fluorescence intensity of aromatic hydrocarbons by several peroxides and by comparison of their results with our previous results [2] on

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quenching by BPO, Encinas and Lissi [4] proposed excitation transfer to hot ground state peroxide molecules in singlet sensitization, and Engel *et al.* [6] described the quenching of triplet ketones by peroxides including BPO.

Since we proposed, in a previous report [2], that aromatic hydrocarbons such as chrysene efficiently sensitize the decomposition of BPO through the formation of reactive non-emissive exciplexes on the basis of the efficient quenching of the fluorescence intensity of several hydrocarbons by BPO, we have attempted to obtain more reliable quenching rate constants by measuring the quenching of the fluorescence lifetime, first by using the phase shift technique [12], then by using the single-photon counting technique [13] and finally by treatment of the data with deconvolution for which the results are presented below.

In the present work, the fluorescence lifetimes of several polycyclic aromatic hydrocarbons and of a series of substituted naphthalenes and anthracenes were measured in the presence of various concentrations of BPO and BPB in deaerated benzene and acetonitrile solutions. The quenching rate constants k_q determined from Stern–Volmer plots are summarized in Table 1 together with the singlet excitation energies E_s [14] and the oxidation potentials E_{ox} of the sensitizers measured in acetonitrile with respect to an Ag|AgNO$_3$ (0.1 M) electrode.

Inspection of Table 1 indicates that the quenching rate constants are not correlated with E_s in contrast with the report on the fluorescence quenching by di-*tert*-butyl peroxide, *tert*-butyl hydroperoxide and hydrogen peroxide [4]. The present data can be correlated with the oxidation potentials of the excited singlet states of the sensitizers which are estimated as $E_{ox} - E_s$. It is well known that the rate constant for the quenching of an excited singlet electron donor by an electron acceptor correlates well with the free-energy change ΔG for electron transfer between them, which is expressed as [15, 16]

$$\Delta G = E_{ox} - E_{red} - E_s - \frac{e^2}{\epsilon a}$$

where E_{red} is the reduction potential of the electron acceptor, and the term $e^2/\epsilon a$ denotes the coulombic interaction energy between the radical ions at the encounter distance a in a solvent of dielectric constant ϵ.

A plot of log k_q in acetonitrile against ΔG estimated according to the above equation gives the correlation depicted in Fig. 1, curve a, as is quite often found for a photochemical electron transfer process. Furthermore, for quenching in benzene, a plot of log k_q against ΔG estimated in acetonitrile affords a correlation curve (curve b) similar to that observed in acetonitrile.

These results clearly support the previously proposed mechanism in which the sensitization takes place through the formation of exciplexes. However, as Fig. 1 shows, in the region where log k_q decreases with $|\Delta G|$, log k_q changes much more gradually than predicted by the Rehm–Weller

TABLE 1

Quenching rate constants by dibenzoyl peroxide and tert-butyl peroxybenzoate and structural factors of the sensitizers

| Sensitizer | k_q (×10^9 M^{-1} s^{-1}) | | | | E_{ox}[a] (V) | E_s[b] (kJ mol^{-1}) | ΔG[c,d] (kJ mol^{-1}) | |
| | In benzene | | In acetonitrile | | | | | |
	BPO	BPB	BPO	BPB			BPO	BPB
1 Fluorene	23.8	7.4	30.8	32.5	1.45	398	−149	−37
2 Naphthalene	9.2	2.2	18.6	5.1	1.45	381	−132	−20
3 Phenanthrene	6.3	0.13	8.3	0.13	1.43	343	−97	15
4 Chrysene	6.9	0.14	9.4	0.19	1.29	331	−97	14
5 Pyrene	5.5	0.26	10.5	0.42	1.06	322	−111	1
6 Anthracene	8.0	0.51	8.5	1.6	1.03	314	−105	7
7 9,10-diphenylanthracene	3.0	0.49	7.9	0.42	0.97	293	−91	21
8 1-methoxynaphthalene	17.0	5.7	15.8	10.0	1.02	367	−159	−47
9 2-methoxynaphthalene	9.6	3.7	14.6	6.4	1.09	361	−147	−35
10 1-methylnaphthalene	14.0	3.2	16.7	6.7	1.32	374	−138	−26
11 2-methylnaphthalene	8.9	2.7	14.1	4.8	1.38	372	−130	−18
12 2-chloronaphthalene	6.2	–	16.1	–	1.54	371	−113	–
13 1-cyanonaphthalene	5.0	0.66	8.7	0.47	1.78	367	−86	26
14 2-cyanonaphthalene	3.4	0.14	9.1	0.17	1.73	359	−83	29
15 9-cyanoanthracene	2.9	0.0062	4.8	0.0080	1.16	285	−65	47
16 9,10-dicyanoanthracene	0.12	–	0.78	–	1.60	275	−10	–

[a]The oxidation potential measured with respect to an Ag|AgNO$_3$ (0.1 M) electrode in acetonitrile.
[b]The singlet excitation energy from ref. 14.
[c]ΔG (kJ mol^{-1}) = 96.5($E_{ox} - E_{red}$) − E_s − C, where C is neglected because $C = e^2/\epsilon a \leqslant 5$ kJ mol^{-1} (a = 0.7 nm; ϵ = 37.5 for acetonitrile).
[d]The reduction potentials E_{red} of the peroxides are as follows: −1.13 V for BPO and −2.29 V for BPB measured with respect to an Ag|AgNO$_3$ (0.1 M) electrode in acetonitrile.
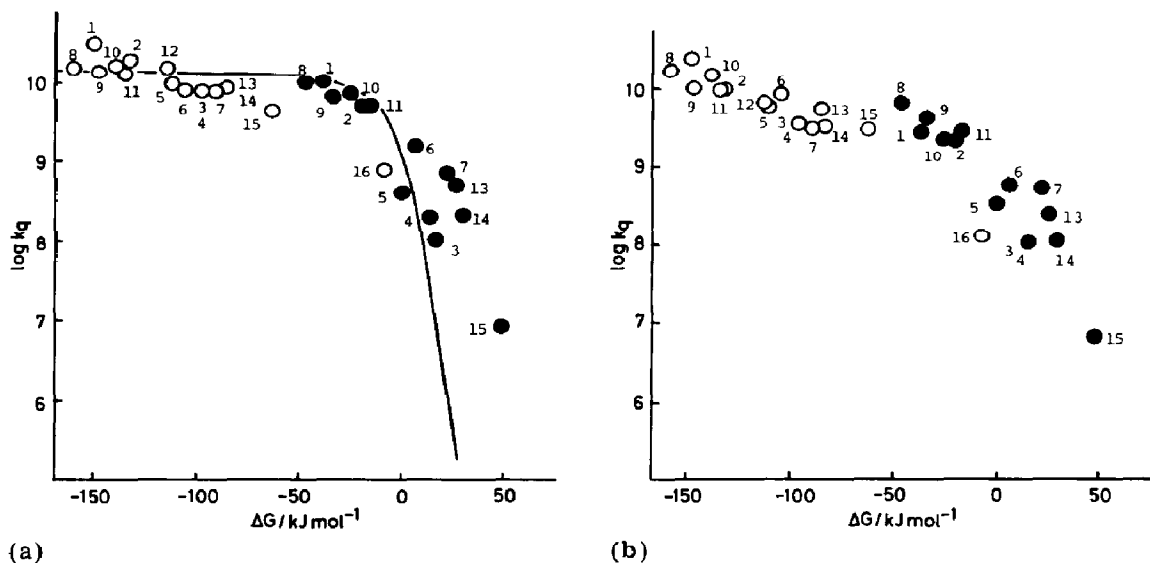
Fig. 1. Quenching rate constants by BPO (○) and BPB (●) as a function of the free-energy change of electron transfer from sensitizer singlets to the peroxides in (a) acetonitrile and (b) benzene (the numerals refer to the sensitizers in Table 1): ———, prediction according to the equation $k_q = 2.0 \times 10^{10}/[1 + 0.25\{\exp(\Delta G^{\ddagger}/RT) + \exp(\Delta G/RT)\}]$, where ΔG and $\Delta G^{\ddagger}$ are the free-energy difference and the free energy of activation between the encounter complex and the ion pair respectively [15, 16].

treatment [15, 16]. This can be taken as indication that the extent of electron transfer is less for quenching by the peroxides than for typical electron transfer [17, 18] and might reflect the fact that the quenching by these peroxides results in their homolytic cleavage but not in overall electron transfer giving ionic products as revealed by the formation of free-radical reaction products including a geminate product, phenyl benzoate from BPO [7, 8], even in acetonitrile. These trends do not seem to be unusual since, for example, the quenching of singlet states (acceptor) by olefins (donor) results in the formation of exciplexes, which may collapse concertedly, but not through zwitterions, to cycloadducts [19]. The different role played by the acyl peroxides (BPO and BPB) as electron acceptors as shown here and by di-tert-butyl peroxide as an energy acceptor as reported by Encinas and Lissi [4] might be attributed to the higher electron acceptor ability of the former as can be estimated by the redox potentials. (The polarographic half-wave potentials of the peroxides were reported as follows [20]: BPO, 0.00 V; BPB, −0.95 V; di-tert-butyl peroxide, less than −2.0 V.)

2. Experimental details

The sensitizers were purified by column chromatography and recrystallization. Their purity was checked by comparing the fluorescence lifetimes with those reported in the literature [14]. BPO was purified by reprecipitation from CH_2Cl_2–CH_3OH. BPB was purified by column

chromatography on Florisil with petroleum ether as eluent and was frozen several times. The solvents, benzene and acetonitrile, were Luminazol from Dojin Chemical Company.

The fluorescence lifetimes of the sensitizers in the presence and absence of a peroxide were measured on a single-photon counting apparatus, an Applied Photophysics SP-3X system, at ambient temperature in benzene and acetonitrile after bubbling with argon for 30 min; the data were deconvoluted with a computer. The redox potentials of the sensitizers and the peroxides were determined by cyclic voltammetry in acetonitrile and were measured with respect to an Ag| AgNO$_3$ (0.1 M) electrode using $(C_2H_5)_4$-NClO$_4$ as a supporting electrolyte.

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