

MECHANISM FOR QUENCHING OF TRIPLET EXCITED SENSITIZERS BY DIAROYL PEROXIDES

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Summary

Rate constants for quenching of triplet excited sensitizers by diaroyle peroxides were determined by monitoring the triplet-triplet absorption of the sensitizers in deaerated carbon tetrachloride at room temperature. The peroxides carrying binuclear aromatic groups such as bis(1-naphthalene-carbonyl) peroxide, bis(2-naphthalenecarbonyl) peroxide and bis(2-phenylbenzoyl) peroxide quench triplet benzophenone with rate constants 10^3 - 10^4 times larger than that of dibenzoyl peroxide (BPO). The rate constants for BPO and its derivatives tend to decrease with decreasing triplet energy of the sensitizer. These results indicate that triplet sensitizers undergo exchange energy transfer to the conjugated electronic systems of the peroxides.

1. Introduction

Organic peroxides are often used as photochemical initiators of free-radical reactions; however, the mechanism for their sensitized dissociation is not yet fully understood. Several investigations aimed at elucidating the mechanism of triplet-sensitized decomposition have already been performed [1 - 4]; the most important part of the task is to gain an understanding of the mechanism through which triplet sensitizers act on peroxides which appear to have higher O-O triplet excitation energies than those of the sensitizers.

In an investigation of the sensitized decomposition of di-*tert*-butyl peroxide Scaiano and Wubbels [3] proposed that, for sensitizers of lower triplet energies than the peroxide excitation energy, energy transfer to a repulsive state of the peroxide occurs from a thermally activated ground state with an O-O bond length greater than the equilibrium value. Engel *et al.* [4] have recently determined the rate constants for the quenching of triplet excited sensitizers by several aliphatic peroxides and for the quench-

ing of triplet 2-acetylnaphthalene by dibenzoyl peroxide, and they explained their results using the same mechanism as that employed by Scaiano and Wubbels [3].

We have also investigated the photolysis of organic peroxides and we now report our results for triplet quenching by dibenzoyl peroxide (BPO), bis(4-chlorobenzoyl) peroxide (ClBPO), bis(4-methylbenzoyl) peroxide (MeBPO), bis(4-methoxybenzoyl) peroxide (MeOBPO), bis(1-naphthalenecarbonyl) peroxide (1-NPO), bis(2-naphthalenecarbonyl) (2-NPO) and bis(2-phenylbenzoyl) peroxide (BpPO). We found that the aromatic groups in the peroxides govern the quenching rate.

2. Results and discussion

The lifetimes of triplet states of the sensitizers 3-methoxyacetophenone (MOA), benzophenone (BP), triphenylene (TR) and 2-acetylnaphthalene (2-AcN) at concentrations in the range $(4 \times 10^{-4}) - (4 \times 10^{-3})$ M were measured by monitoring their triplet-triplet (T-T) absorption on excitation by a nitrogen laser in deaerated carbon tetrachloride in the presence of varying concentrations $((3 \times 10^{-5}) - (3 \times 10^{-2})$ M) of the organic peroxides BPO, ClBPO, MeBPO, MeOBPO, 1-NPO, 2-NPO and BpPO, and the quenching rate constants of the peroxides were determined. Carbon tetrachloride was chosen as an inert solvent to avoid reactions of triplet ketones such as those observed with aromatic solvents [5, 6]. Quantum yields for the BP-sensitized decomposition (0.02 M BP) of BPO and BpPO $((1 - 8) \times 10^{-3})$ M were determined in carbon tetrachloride.

The quenching rate constants k_q of the peroxides are summarized in Tables 1 and 2. Inspection of Table 1 indicates that the peroxides 1-NPO, 2-NPO and BpPO, which carry binuclear aromatic groups, quench triplet BP with rate constants $10^3 - 10^4$ times larger than that of BPO. Biphenyl also

TABLE 1

Rate constants for quenching of benzophenone triplets by diacyl peroxides and reference compounds in carbon tetrachloride at room temperature

Quencher	k_q ($M^{-1} s^{-1}$)
Bis(1-naphthalenecarbonyl) peroxide	6.0×10^9
Bis(2-naphthalenecarbonyl) peroxide	6.9×10^9
Bis(2-phenylbenzoyl) peroxide	6.4×10^8
Dibenzoyl peroxide	3.2×10^5
Dibenzoyl peroxide- d_{10}	5.4×10^5
Di- <i>tert</i> -butyl peroxide	3.8×10^6
Dicumyl peroxide	3.6×10^6
Benzoic anhydride	$(6 - 8) \times 10^4$
Phenyl benzoate	$< 10^4$
Biphenyl	5.2×10^8

TABLE 2

Rate constants k_q ($M^{-1} s^{-1}$) for quenching of triplet states by disubstituted dibenzoyl peroxides

Substituent	E_T^a (kcal mol $^{-1}$)	E_{red}^b (V)	Sensitizer			
			2-AcN (59.3) ^c	TR (66.6)	BP (68.6)	MOA (72.4)
2,2'-(Ph) ₂ -	65.7	-0.56	1.1×10^7	6.6×10^8	6.4×10^8	—
4,4'-(CH ₃ O) ₂ -	80.8	-1.05	2.1×10^6	6.9×10^7	1.4×10^7	2.0×10^8
4,4'-Cl ₂ -	81.7	-0.89	6.3×10^8	4.6×10^8	4.4×10^6	3.9×10^8
4,4'-(CH ₃) ₂ -	82.8	-1.03	9.9×10^5	6.7×10^7	1.9×10^6	9.9×10^7
H-	84.3	-0.96	1.2×10^6	5.6×10^7	3.2×10^5	8.6×10^7

^aTriplet excitation energies of the substituted benzenes corresponding to the aromatic moieties of disubstituted dibenzoyl peroxides.^bReduction potentials with respect to the standard calomel electrode.^cNumerals in parentheses are the triplet excitation energies of the sensitizers in kilocalories per mole [6].

quenches triplet BP with almost the same rate constant as that of BpPO, and naphthalene is known to quench triplet BP with a diffusion-controlled rate constant [7, 8].

Moreover, the rate constant for the quenching of 2-AcN by BpPO is of the order of $10^7 \text{ M}^{-1} \text{ s}^{-1}$ which is an order of magnitude lower than those for TR and BP ($(6 - 7) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). These results suggest that the triplet excitation energy of BpPO is slightly higher than that of 2-AcN and is comparable with or slightly lower than that of biphenyl ($E_T = 66 \text{ kcal mol}^{-1}$ [9]).

It is known that in BpPO the triplet energy transfer takes place to the electronic system conjugated with the biphenyl moiety, and that the resulting triplet peroxide undergoes decomposition efficiently as is shown by a limiting quantum yield as high as 0.62 for BP-sensitized decomposition in carbon tetrachloride [10]. These results for BpPO can be compared with the high quantum yields for photolysis of dibenzoyl peroxides substituted with benzophenone moieties [11] in which the initially excited benzophenone moiety induces the efficient decomposition of the peroxide moiety. Efficient quenching by 1-NPO and 2-NPO must take place in a similar way to that by BpPO.

As indicated in Table 2 the rate constants for quenching by BPO and its derivatives are in the range $(4 \times 10^8) - (3 \times 10^5) \text{ M}^{-1} \text{ s}^{-1}$. The rate constant for quenching of 2-AcN by BPO is almost the same as that reported by Engel *et al.* [4]. For each peroxide the rate constant tends to decrease with decreasing triplet energy of the sensitizer, although BP always gives lower values than TR despite its higher triplet energy[†]. Plots of $\log k_q$ against the triplet energy E_T of the sensitizers are almost linear although there are few data points. The slopes are in the range 0.15 - 0.25 as shown for MeOBPO in Fig. 1 as an example. These values agree with those reported by Engel *et al.* [4] for quenching by several aliphatic peroxides, and are much smaller than the values for typical energy transfer ($1/2.303RT = 0.73$) such as those found for transfer to *trans*-stilbene [13]. The smaller slope implies that the activation energies for the sensitization of the peroxides are lower than usual.

CIBPO exhibits the highest k_q for sensitizers other than BP, whereas for BP MeOBPO shows the highest k_q and BPO shows the lowest k_q for all the sensitizers examined[†]. For each sensitizer a plot of $\log k_q$ against the Hammett σ constants of the substituents of BPO and its derivatives gives a V-shaped relationship with the minimum at BPO as shown in Fig. 2 for 2-AcN.

This behaviour seems to be related to the quenching of the triplet states of BP and its derivatives by substituted benzenes [12]: the plot of $\log k_q$

[†] Among the sensitizers examined, BP seems to behave slightly differently from the others, possibly because of the difference in character of the lowest triplet states: that of BP is (n, π^*) and those of the others are (π, π^*). However, CIBPO is a more efficient quencher of BP than either MeBPO or BPO in contrast with the following sequence of rate constants for the quenching of triplet BP by substituted benzenes (in decreasing order of magnitude): anisole, toluene, benzene, chlorobenzene [12].

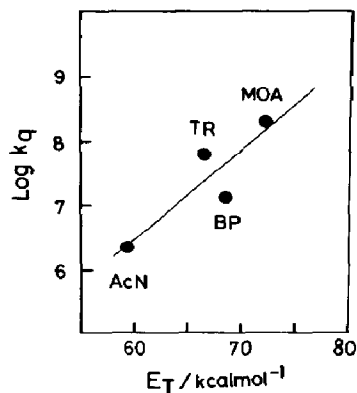


Fig. 1. A plot of $\log k_q$ of bis(4-methoxybenzoyl) peroxide against triplet energies of sensitizers in carbon tetrachloride at room temperature.

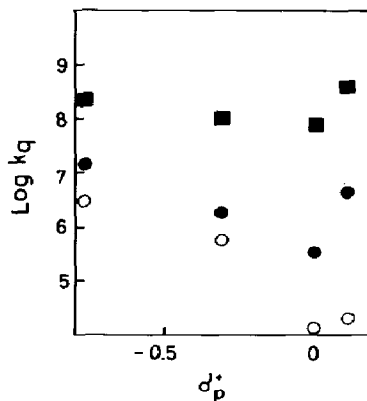


Fig. 2. Plots of $\log k_q$ against the Hammett function σ_p^+ of the substituent of the disubstituted dibenzoyl peroxides in carbon tetrachloride at room temperature: ■, quenching of 3-methoxyacetophenone triplets by diacyl peroxides; ●, quenching of benzophenone triplets by diacyl peroxides; ○, quenching of benzophenone triplets by substituted benzenes [12].

against the Hammett σ constants of the benzene substituents was also V shaped. However, in a series of substituted benzenes, anisole, toluene and chlorobenzene have triplet energies of 80.8 kcal mol⁻¹, 82.8 kcal mol⁻¹ and 81.7 kcal mol⁻¹ respectively, and benzene has the highest energy of 84.3 kcal mol⁻¹. This trend leads to the expectation that k_q for a given triplet sensitizer must be highest for anisole and chlorobenzene and lowest for benzene.

The triplet states of diaryl peroxides can be estimated to lie lower in energy than the corresponding aromatic hydrocarbon moieties since the diaryl peroxides generally exhibit absorption at longer wavelengths than the corresponding aromatic hydrocarbons. Therefore it is reasonable to assume that the triplet energy of a series of substituted dibenzoyl peroxides is highest for unsubstituted BPO and lowest for MeOBPO or ClBPO. It is therefore concluded that in the triplet sensitization of diaryl peroxides triplet excited sensitizers undergo exchange energy transfer to the electronic system conjugated with aryl groups.

It should be noted that the limiting quantum yield for the BP-sensitized decomposition of BPO is 0.21, which is much lower than that of BpPO, *i.e.* 0.62 [10]. This difference seems to indicate that the efficiency of the thermolysis of BpPO is greater than that of BPO [14]. The rate constants for thermolysis in the presence of a radical scavenger at 80 °C were reported as 2.5×10^6 s⁻¹ and 4.2×10^5 s⁻¹ for BpPO and BPO respectively [14].

The above quantum yield of almost 0.2 suggests that the triplet energy transfer induces the decomposition of BPO, but the probability of radiationless deactivation of the excited state of BPO is still almost 80%.

Finally, it should be noted that the present results contribute to an understanding of the mechanism for quenching the triplet excited states by diaryl peroxides which has long been controversial.

3. Experimental details

3.1. Materials

Carbon tetrachloride (Nakarai) was purified in the following manner [15]. The solvent containing benzophenone (about 1 g dm^{-3}) was irradiated using a 400 W high pressure mercury lamp, and was then distilled carefully. This procedure was repeated twice. 1-NPO, 2-NPO and BpPO were prepared from the corresponding acids using *N,N'*-dicyclohexylcarbodiimide and hydrogen peroxide in ether [16]. The other diacyl peroxides were prepared from the corresponding acid chlorides using hydrogen peroxide. The diacyl peroxides were purified by reprecipitation from methanol-dichloromethane.

3.2. Flash photolysis

The triplet lifetimes of sensitizers excited using a nitrogen laser (337.1 nm; full width at half-maximum, 8 ns; 4 mJ pulse^{-1}) were measured by monitoring the T-T absorption at 530 nm for BP, at 430 nm for 2-AcN, at 420 nm for TR and at 370 nm for MOA. The laser excitation was at 90° with respect to the analysing beam from a xenon lamp. The sample was put in a quartz cuvette ($10 \text{ mm} \times 10 \text{ mm}$) and deaerated by bubbling with high purity dried argon. More details of the flash photolysis instrument will be reported elsewhere.

3.3. Quantum yields

The quantum yields for the BP-sensitized photolysis of BpPO and BPO in carbon tetrachloride were obtained by irradiation with 366 nm light which was isolated by passage through a Toshiba UV-D36A glass filter. The disappearance of the peroxide was determined on a JASCO Trirotar high pressure liquid chromatograph with a Zorbax ODS column 15 cm long.

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