

QUENCHING OF EXCITED SINGLETs BY PEROXIDES AND HYDROPEROXIDES

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Summary

Energy transfer from a variety of aromatic hydrocarbons and ketones to di-*tert*-butyl peroxide, *tert*-butyl hydroperoxide and hydrogen peroxide was examined by following the sensitizer fluorescence yield as a function of the peroxide concentration. For the aromatic hydrocarbons the rate constants range from $1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for benzene to less than $2.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for coronene. The quenching rate constant is almost solvent independent and does not depend appreciably upon the donor properties of substituents but it depends strongly on the sensitizer energy. The results are compatible with a quenching mechanism involving energy transfer to ground state peroxide molecules with an O—O bond length greater than the equilibrium value.

1. Introduction

The photosensitized decomposition of peroxides by excited carbonyls [1] and aromatic hydrocarbons [2 - 7] has been reported in several systems. This type of process has recently received attention because of the role that it could play in the photodegradation of polymers [8]. Despite these investigations the mechanism of the process is still unknown, and exciplex formation [3], charge transfer processes [5 - 7] and the production of vibrationally excited ground state peroxides [8] have all been postulated. Recently, Scaiano and Wubbels [9] carried out an extensive study of the rate of energy transfer from excited carbonyl and aromatic triplets to di-*tert*-butyl peroxide (DTBP) employing a nanosecond laser flash photolysis technique. These workers propose that energy transfer takes place to a repulsive triplet state in a thermally activated ground state peroxide molecule with an oxygen bond length greater than the equilibrium value. Since the excited singlet states of the peroxides are also repulsive [10], a similar mechanism could be operative in the quenching of excited singlet states. In the present work we present data obtained in the deactivation of several excited singlets by DTBP, *tert*-butyl hydroperoxide (TBH) and hydrogen

peroxide (HP). The results obtained are compatible with a mechanism involving transference to vibrationally hot molecules.

2. Experimental details

Fluorescence measurements were carried out in air at room temperature (approximately 20 ± 2 °C) using a 204-S Hitachi-Perkin-Elmer spectrofluorometer. The quenching rate constants were obtained from the slopes of Stern-Volmer plots and published values of the singlet lifetimes [11]. In order to take into account a possible "solvent effect" when substantial amounts of the peroxides were added as quenchers, these measurements were referred to those obtained when similar volumes of water (for HP) or diethyl ether (for DTBP) were added.

All sensitizers employed were of the highest purity commercially available. They were used as purchased or recrystallized and/or sublimed until their absorption and emission spectra matched those reported in the literature.

HP (8.2 M in water, Riedel de Hain) was employed as purchased. DTBP and TBH (Fluka) were used after elution from activated alumina. Merck solvents (Uvasol or fluorescence spectroscopy grade) were employed.

Fluorescence quenching experiments were carried out at the longest possible wavelengths in order to minimize light absorption by the quencher. When this absorption was significant, a double-quenching technique employing carbon tetrachloride and/or oxygen as a second quencher was employed.

The photosensitized decomposition of DTBP was measured in toluene using light of wavelength 366 or 313 nm from a medium pressure mercury lamp. When light of 313 nm was employed the relative concentrations of the naphthalene sensitizer and DTBP were such as to make the light absorption by the peroxide negligible. The *tert*-butanol quantum yield, which under the conditions employed here can be equated to the *tert*-butoxy radical yield, was evaluated employing isocaprophenone [12] ($\phi_{\text{acetophenone}} = 0.24$ at 366 nm) and 2-heptanone [13] ($\phi_{\text{acetone}} = 0.2$ at 313 nm) as actinometers.

3. Results and discussion

3.1. Quenching of aromatic compounds

The results obtained are given in Tables 1 - 5. Table 1 gives the values of the quenching rate constants obtained employing unsubstituted hydrocarbons and carbazole in acetonitrile (DTBP and TBH) and 3:1 acetonitrile: water mixtures (HP). Data previously obtained employing dibenzoyl peroxide (DBP) as a quencher are also included in this table.

TABLE 1
Quenching data for aromatic hydrocarbons

Donor	E_s (kcal mol ⁻¹)	$\lambda_{exc}/\lambda_{emis}$	k_{DTBP}^a ($\times 10^6 M^{-1} s^{-1}$)	k_{TBH}^a ($\times 10^6 M^{-1} s^{-1}$)	k_{HP}^b ($\times 10^6 M^{-1} s^{-1}$)	k_{DBP}^c ($\times 10^9 M^{-1} s^{-1}$)
Perylene	65.8	410/440			2	
Coronene	66.7	380/420	<0.23	<0.06	0.1	
Benzo(<i>ghi</i>)perylene	70.3	380/420	2.1	—	0.6	
Fluoranthene	70.8	370/450	2.5	0.06	0.3	
Dibenz(<i>a,h</i>)anthracene	72.6	360/410	10	<0.3	1.4	
Benz(<i>a</i>)anthracene	74.1	360/410	8	0.2	1.2	
Anthracene	76.3	375/400	12	6.4	14	10
Pyrene	77	360/390	8	0.9	2	6.6
Benz(<i>a</i>)pyrene	78.1	380/430	3.5			
Chrysene	79.2	320/383	15 ^d		5.8	8.8
Phenanthrene	82.9	320/375	10 ^d	6.7 ^d	4.1	
Triphenylene	84.2	350/370	10 ^d		8.2	2.4 ^e
Carbazole	84.8	340/360	130	94	110	
Acenaphthene	88.1	320/340	100	100	125	
Naphthalene	92	315/336	150	95	76	8.4
Fluorene	95	308/320	500	270	570	
Biphenyl	98.7	310/335	450	200	300	
Benzene	110	270/280	1.8 $\times 10^3$		3900	

^a Data obtained in acetonitrile.

^b Data obtained in 3:1 acetonitrile:water mixtures.

^c Data from ref. 3, in benzene.

^d These values have rather large errors (up to a factor of 2.5) owing to the necessity of carrying out a double quenching with very large concentrations of quenchers.

^e Data from ref. 5, in butyl acetate.

TABLE 2
Substituted naphthalenes

<i>Substituent</i>	E_s (kcal mol ⁻¹)	$(k_Q)_{HP}$ ($\times 10^7$ M ⁻¹ s ⁻¹)	$(k_Q)_{DTBP}$ ($\times 10^7$ M ⁻¹ s ⁻¹)	$(k_Q)_{TBH}$ ($\times 10^7$ M ⁻¹ s ⁻¹)
1-CN	88	14	18	5.0
1-CH ₃ O	89	12	17	7.8
1-CH ₃	90	10.5	13	4.7
1-OH	91	20	23	2.8
None	92	8.1	14.5	7.7
2-CH ₃	90	13	15	7.5
2-CH ₃ O	87	6.3	12.5	5.3
2-OH	87	6.7	10	10
2-CN	86	8.0	8	3.8
2-acetate	88	7	12.5	7.0

The data were obtained in acetonitrile solutions.

TABLE 3
Solvent effect in naphthalene quenching

<i>Solvent</i>	k_{DTBP} ($\times 10^7$ M ⁻¹ s ⁻¹)	k_{TBH} ($\times 10^7$ M ⁻¹ s ⁻¹)
Acetonitrile:water (3:1)	15	7.1
Acetonitrile	14	8.3
Ethanol	18	4.8
Benzene	14	—
Cyclohexane	21	—

TABLE 4
Quenching of carbonyl compounds

<i>Compound</i>	k_{HP}^a ($\times 10^7$ M ⁻¹ s ⁻¹)	k_{DTBP}^b ($\times 10^7$ M ⁻¹ s ⁻¹)	k_{TBH}^b ($\times 10^7$ M ⁻¹ s ⁻¹)
2,4-dimethyl-3-pentanone	2.6	11.4	3.4
2,2-dimethyl-3-butanone	7.4	10	3.3
2-adamantanone	6.9	5.4	4.0
1,3-diphenylacetone	15	16	13
Methyl pyruvate	— ^c	0.7	2.4
Biacetyl	— ^c	< 0.05	< 0.02
Benzil	2.3	0.1	0.05
1-phenyl-1,2-propanedione	— ^c	< 0.07	< 0.03
Fluorenone	260	< 0.7	60

^a Acetonitrile:water (3:1) mixture as solvent.

^b Acetonitrile as solvent.

^c Not measurable owing to solvolysis.

TABLE 5
Photofragmentation quantum yields

<i>Sensitizer</i>	<i>DTBP</i> (M)	f_s^a	ϕ_{fragm}
Naphthalene	0.27	0.82	0.6 (0.62) ^b
Benz(a)anthracene	1.63	0.34	0.38
Pyrene	3.26	0.75	0.77
Benzo(ghi)perylene	1.63	0.4	0.28

^aFraction of excited singlets quenched by the peroxide at the concentration employed.

^bThe value in parentheses was given in ref. 9 and ascribed to triplet sensitization.

The data obtained in the present work show noticeable differences from those reported for DBP [3, 5]. The quenching rate constants reported for this peroxide were almost diffusion controlled for all the sensitizers considered. In contrast, the values obtained in the present work are considerably slower and they increase steadily when the sensitizer singlet energy increases. The trend in these results is then similar to that reported by Scaiano and Wubbels [9] for the quenching of excited triplets by DTBP. Furthermore, the data reported in the present work show that the quenching rate constant is almost independent of the solvent (see Table 2), a result similar to that reported for the triplet state quenching [9]. This lack of dependence strongly argues against a dominating mechanism involving a sizable amount of charge transfer, as suggested for quenching by DBP [5]. The results given in Table 3 also provide evidence against a charge transfer mechanism since they show that the substituent characteristics have little effect on the quenching rate. The results shown in Tables 2 and 3 contrast with those obtained employing carbon tetrachloride as the quencher [14]. This compound quenches aromatic hydrocarbons by a charge transfer mechanism, and the rate of naphthalene quenching increases by a factor of 25 when the solvent is changed from cyclohexane to an acetonitrile-water mixture and by a factor of almost 10^2 when the donor is changed from 1-cyanonaphthalene to 1-methoxynaphthalene [14].

Scaiano and Wubbels [9] have proposed a triplet quenching mechanism that involves quenching by peroxide molecules with stretched O—O bonds. Similar "hot band" models for "non-classical" energy transfer have been proposed previously to explain results for alkyl disulphides [15], azides [16] and benzil [17]. In the quenching of triplets by DTBP the "vertical" transference to vibrationally hot molecules would be favoured by the repulsive character of the triplet surfaces. Since the excited singlet surfaces are also repulsive [10], a similar mechanism could be operative in the singlet quenching. The data obtained in the present work employing DTBP as the acceptor are plotted against the singlet donor energy in Fig. 1 which also includes the line that best fits the data of Scaiano and Wubbels [9]. This figure shows that the data obtained in the present work are very similar to

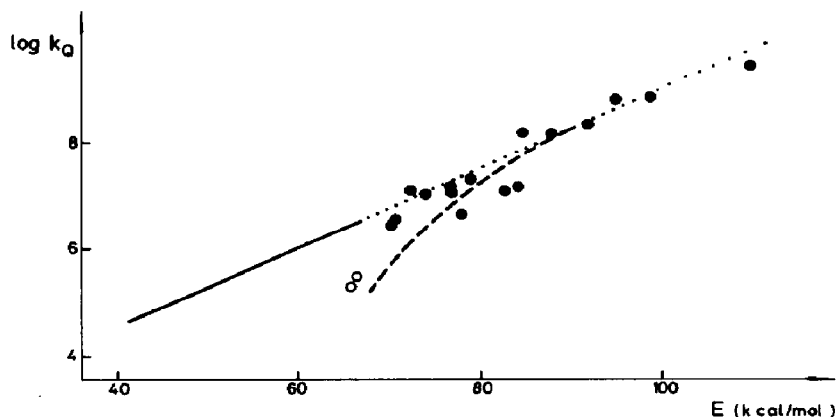


Fig. 1. Dependence of the specific quenching rate constant on the energy of the donor excited state for DTBP at room temperature: ●, present work; ○, estimate of upper limit; —, best fit to the triplet quenching data [9]; — —, values calculated according to eqn. (2).

those expected from an extrapolation of the results of Scaiano and Wubbels [9]. Nevertheless, when both sets of data overlap, the singlet rate constant appears to be slightly slower than that of a triplet of similar energy. This result can easily be explained in terms of the higher energy of the excited energy surfaces of the acceptor for a given configuration [10].

The results of Fig. 1 and Table 1 show that the diffusion-controlled limit is only approached by sensitizers with larger energies. This suggests that the vertical excitation of an unstretched peroxide bond must be larger than $100 \text{ kcal mol}^{-1}$. Semiempirical calculations carried out by Evleth [10] gave an energy of approximately $110 \text{ kcal mol}^{-1}$ for the vertical transition from the equilibrium O—O separation [10].

If the dominant quenching mechanism involves a vibrationally "hot" peroxide molecule, a parallel could be expected between the quenching rate and the absorption coefficient in the peroxide hot bands. In particular, it could be postulated that for a donor of energy E

$$(k_Q)_E \propto \int_0^E \epsilon_E dE \quad (1)$$

where ϵ is the acceptor extinction coefficient. The value of $(k_Q)_E$ relative to that obtained at a reference energy E_{ref} can then be evaluated from

$$(k_Q)_E = (k_Q)_{E_{\text{ref}}} \frac{\int_0^E \epsilon_E dE}{\int_0^{E_{\text{ref}}} \epsilon_E dE} \quad (2)$$

The values of k_Q obtained with a reference energy of 87 kcal mol^{-1} and a $(k_Q)_{87}$ that fits the experimental data are given in Fig. 1. It can be seen that the dependence of k_Q on the donor energy predicted by eqn. (2) approximately agrees with that observed experimentally.

The data obtained employing TBH and HP as acceptors show a similar behaviour to that discussed above for DTBP. Nevertheless, for sensitizers of low energies the values of the quenching rate constants for the hydroperoxides are noticeably smaller than those obtained employing DTBP (see Table 1). This behaviour is contrary to that expected from considerations regarding the steric hindrance of the transference [8, 9]. A possible explanation can be based on the relative relevance of the hot bands. Figure 2 shows the tailing of the absorption spectra of DTBP and HP. This figure shows that at long wavelengths the intensities are larger for the peroxide, indicating that at low energies the excited state is more easily reached in this compound than in HP. This difference could explain the differences observed in the quenching rates.

Comparison of the triplet data obtained by Scaiano and Wubbels [9] and the present results with those reported by Wallace *et al.* [15] for the quenching of aromatic hydrocarbon singlets and aryl ketone triplets by alkyl disulphides shows several noticeable differences: the values of k_Q are larger, the dependence of $\log k_Q$ on the donor energy is higher and the difference between a singlet and a triplet of similar energies is larger for the disulphides than for the peroxides. In terms of the proposed mechanism this implies that the vertical energy is smaller, the S-T separation is larger and the repulsive surfaces are less steep for the disulphides than for the per-

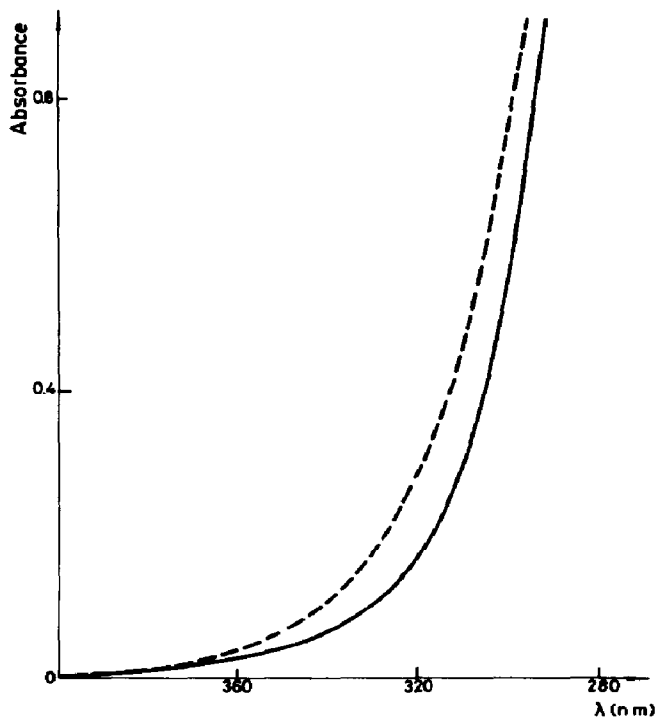


Fig. 2. Absorbance in the long wavelength region: ---, 0.62 M DTBP in acetonitrile; —, 0.62 M HP in acetonitrile.

oxides. The first and the third points are compatible with the relative position of the absorption bands and with the lower energy required to cleave the O—O bond.

3.2. Quenching of carbonyl compounds

Quenching by DTBP has the rates expected if the main reaction path is similar to that discussed for the aromatic hydrocarbons (see Fig. 1). The fact that different types of compounds (aromatic hydrocarbons, carbazole and $n\pi^*$ carbonyl compounds) have rates that depend only on the singlet energy strongly supports the proposed hot band quenching mechanism. Similarly, the values found for the aliphatic ketones and hydroperoxides are also compatible with the proposed mechanism and would suggest that, at least for 2,4-dimethyl-3-pentanone and 2,2-dimethyl-3-butanone, photoreduction is likely to be only a minor process. A similar conclusion has been reached in other systems involving excited carbonyl compounds as donors [1, 8].

Quenching of the singlet state of the styrene-methyl isopropenyl ketone copolymer is faster for TBH than for DTBP, and this result can be explained in terms of the larger steric hindrance of the DTBP process [8]. The results obtained in the present work for the aliphatic ketones indicates that, as in the aromatic compounds, DTBP is a better quencher. The difference between our results and those of Ng and Guillet [8] indicates that, as expected, steric effects are much more important in the system involving macromolecules.

The results obtained employing benzil, methyl pyruvate and fluorenone conform to a different pattern and indicate that hydrogen abstraction from the hydroperoxide could be the main quenching path for these compounds. The different mechanism for benzil and methyl pyruvate can be explained in terms of the tendency of their singlets to photoreduce [18] and the relative weakness of the hydroperoxide O—H bond [19]. Consideration of the results obtained employing fluorenone as the donor must include the possible contribution of a solvent effect to the quenching owing to the sensitivity of its singlet lifetime to solvent changes [20]. Nevertheless, the fact that the quenching rate constants obtained employing hydroperoxides are considerably larger than those of other protic solvents determined under identical conditions (*i.e.* quenching constants of $0.12 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for water and $0.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for isopropanol were obtained) could be attributed to a significant photoreduction contribution to the quenching process.

3.3. Induced photofragmentation yields

The results given in Table 5 indicate that an efficient photocleavage of the O—O peroxide bond takes place in the sensitized singlet process. A similar process takes place in the direct photolysis of DTBP [21] and in the triplet-sensitized process [9]. Furthermore, large values of ϕ_{fragm} have also been reported in the singlet-sensitized decomposition of diacetyl peroxide [7]. The values of ϕ_{fragm} given in Table 5 cannot be employed to obtain a precise value for the fraction of the singlet quenching that leads to O—O

bond rupture in view of the possibility of a triplet-sensitized contribution to this process [9]. Nevertheless, it is interesting to note that the values given for naphthalene and pyrene indicate that a large proportion of the singlet quenching must lead to O—O bond cleavage and that this process is efficient even for sensitizers of relatively low energies.

4. Conclusion

The results obtained in the present work as well as those reported for the triplet quenching [9] can be explained by a mechanism involving quenching by vibrationally hot peroxide molecules. In particular this mechanism is compatible with the absence of a solvent effect on the quenching rate constant, the dependence of the rate constant on the donor energy, the large values of ϕ_{fragm} and the faster rate of quenching by DTBP than by the hydroperoxides.

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