

Preliminary note

Alkyl hydroperoxides as electron donors in photochemical reactions

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Abstract

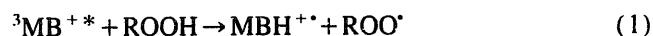
Alkyl hydroperoxides, which are formed as major reaction products during illumination of dyes in the presence of oxygen and an organic substrate, are shown to quench the excited triplet state of the dye by way of an electron-transfer mechanism, leading to the intermediary formation of reactive free radicals. © 1997 Elsevier Science S.A.

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Interaction between triplet excited states of dyes and organic peroxides or hydroperoxides, formed during illumination in the presence of molecular oxygen, is a subject of considerable concern and current importance. These reactions, which may result in formation of reactive free radicals, have many important chemical and biological implications. They are ubiquitous to all photochemical reactions carried out in the presence of oxygen and an organic substrate and play significant roles in the photodegradation of natural and artificial polymers [1], the rancidity of vegetable and mineral oils [2], and photodynamic action [3,4]. Despite the general awareness of the importance of such reactions there are relatively few scientific publications relating to this subject [5] and the current opinion appears to be that hydroperoxides can, depending on the electronic nature of the excited chromophore, have either the O–O or the O–H bond broken, resulting in generation of the corresponding radical pair [6–10]. Most studies have utilized aromatic and/or ketonic sensitizers having high triplet energies, thereby allowing the possibility of both H-atom abstraction and O–O bond fission. H-atom abstraction from alkyl residues on the peroxide and/or from the terminal OOH group is a strong possibility with suitable $n-\pi^*$ excited states. Decomposition of the peroxy bond is reported to arise via a triplet energy transfer from sensitizer to a repulsive triplet state localized on the peroxy bond [9,10], although the latter state has not been identified spectroscopically. Other studies have concluded that O–O bond fission might arise from an electron transfer mechanism [10]. The absence of direct experimental support for electron

transfer, however, compelled these authors to consider a variety of alternative mechanisms to account for dissociation of the peroxide. Indeed we are unaware of any direct observation of electron transfer products arising for photosensitized dissociation of a peroxide.

This communication considers the interaction of the triplet excited state of methylene blue (MB^+) with alkyl hydroperoxides. This dye has been widely used as a photosensitizer for photooxygenation reactions [11,12] and in photobiology [13]. It was selected for the present work because of (i) its low triplet level (1.44 eV) [14] which curtails its ability to abstract a hydrogen atom directly from the hydroperoxide (dissociation energy of O–H bond in hydroperoxides is ca. 3.9 eV) [15], (ii) its inability to transfer excitation energy to the hydroperoxide (triplet energy ca. 2.8–3.0 eV) [16] by an electron-exchange mechanism, and (iii) its high electron affinity and ready participation in light-induced electron-transfer processes [13,17,18]. We now show that electron transfer occurs from *t*-butyl hydroperoxide ($ROOH$)¹ to the triplet state of methylene blue², resulting in quantitative formation of the respective radicals, and that the overall quenching process may be represented by a hydrogen atom-transfer process.



Laser flash photolysis techniques ($\lambda = 532$ nm, pulse duration 10 ns, maximum pulse energy 10 mJ) were used to pro-

¹ Aldrich Cat. No. 18,471-3, ca. 70% Rest Wasser; peroxide concentration as measured by iodometric titration [19] gives a value of 67%.

² Methylene blue chloride, Fluka puriss, was assayed by absorption spectroscopy [20].

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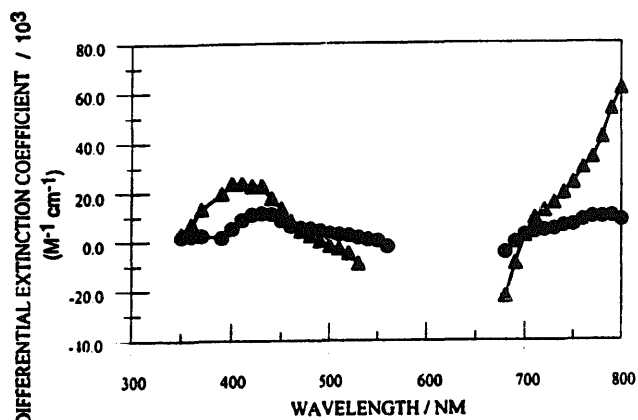


Fig. 1. The differential absorption spectra recorded in deoxygenated chloroform solution of methylene blue following excitation at 532 nm with a 10 ns laser pulse. Spectra refer to: (●) the triplet excited state recorded in the absence of quencher and (▲) the protonated radical cation recorded after the decay of the triplet and in the presence of 0.2M *t*-butyl hydroperoxide. Extinction coefficients have been taken from Ref. [18].

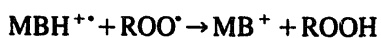
duce the triplet excited state of methylene blue in chloroform solution (Fig. 1). In the absence of molecular oxygen, the triplet state survives for many tens of microseconds; its actual lifetime being set by triplet–triplet annihilation and interaction with the ground state of the dye. In the presence of sufficient quencher, decay of the triplet state occurs via first-order kinetics and the derived rate constant was found to increase linearly with increasing concentration of hydroperoxide. From the gradient of linear plots of the triplet decay rate constant vs. concentration of added hydroperoxide the bimolecular rate constant for triplet quenching (k_Q) was derived to be $(1.1 \pm 0.4) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This rate constant is very much smaller than the diffusion controlled rate limit in chloroform at room temperature ($k_{\text{diff}} = 1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) [21]. In the presence of hydroperoxide, the flash photolysis records show the presence of long-lived intermediate after decay of the excited triplet state. The concentration of this intermediate increases with increasing concentration of hydroperoxide. On long time scales, this long-lived transient species, which exhibits pronounced absorption at 800 nm, decays by way of second-order kinetics. The half-life is on the order of a few milliseconds and decay restores the pre-pulse baseline. Repeated laser photolysis of the same solution, however, showed that the dye was bleached in low quantum yield. From transient absorption spectra recorded after decay of the triplet (Fig. 1) it is clear that the long-lived transient species is the protonated semi-reduced form of the dye as becomes clear by comparison with spectra reported in the literature [22,23].

The laser flash photolysis studies are entirely consistent with electron transfer from the hydroperoxide to the triplet state of the dye and, in order to assess the thermodynamic favourability for this process, cyclic voltammetry studies were made with the reagents in deoxygenated chloroform solution. Upon reductive scans, methylene blue showed a quasi-reversible peak corresponding to a reduction potential of -0.06 V vs. NHE. This derived value is consistent with

literature data collected in other solvents. Oxidative scans made with solutions of the hydroperoxide showed an irreversible peak centred at ca. $+1.29 \text{ V}$ vs. NHE suggesting a rapid chemical transformation of the oxidized form of the substrate. On the basis of these studies it was not possible to determine an accurate value for the oxidation potential of the hydroperoxide but it is apparent that, at least in electrochemical terms, oxidation occurs only at relatively high applied potentials. However, the oxidation potential for the hydroperoxide couple has been estimated by Koppenol at ca. 1 V vs. NHE on the basis of thermochemical calculations [24]. Therefore, the thermodynamic driving force for net electron transfer from hydroperoxide to triplet state dye can be approximated as $\Delta G^\circ \approx -20 \text{ kJ mol}^{-1}$. Thus, the electron-transfer reaction is weakly exergonic and, presumably, the slow rate of reaction reflects this situation.

From the computed initial optical densities of triplet state and semi-reduced form of methylene blue (as extrapolated by curve fitting routines to the centre of the excitation pulse), and using the absorption coefficients given by Kayser and Young [18], the efficiency for formation of the semi-reduced form of the dye can be estimated. Increasing the concentration of *t*-butyl hydroperoxide resulted in a concomitant increase in the yield of radical cation. For example, at $[\text{ROOH}] = 0.2 \text{ M}$, which quenches 69% of triplet MB^+ , the obtained quantum yield of MBH^+ was 0.46 ± 0.05 . Extrapolation to complete triplet quenching gave unitary quantum yield of semi-reduced MB^+ formation. This finding is consistent with the initially formed, caged radical pair undergoing very efficient separation into radicals.

The second-order decay of semi-reduced methylene blue led essentially to regeneration of the ground-state forms of the dye and hydroperoxide.



This bimolecular process restores ground-state MB^+ and is attributed to reverse electron transfer between the primary radicals. Because this process is so fast very few of the initially formed ROO^\cdot radicals escape recombination. Therefore, secondary processes, such as dimerization of ROO^\cdot or dismutation of $\text{MBH}^{+\cdot}$, are minimized. The bimolecular rate constant for this process was found to be $k_2 = (2.7 \pm 0.6) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This rate constant is almost one order of magnitude below the diffusion-controlled limit and may be indicative of slow electron transfer within the geminate cage. This situation, in turn, would support the idea of quantitative dissociation of the caged radicals, as implied above. For chloroform solutions saturated by 1/99 and 5/95 O_2/N_2 mixtures the value of k_2 remains identical to that observed for argon saturated solvent within experimental uncertainties. Furthermore electrochemical studies indicate that the reduced form of MB^+ ($E^\circ = -0.06 \text{ V}$ vs. NHE) is unlikely to be oxidized by molecular O_2 ($E^\circ < -0.2 \text{ V}$ vs. NHE [25]) and is stable against dismutation ($\Delta G^\circ \approx 60 \text{ kJ mol}^{-1}$). It is apparent from these studies that dismutation [18,23] of semi-reduced MB^+ is not

competitive with reverse electron transfer ($\Delta G^\circ \approx -120 \text{ kJ mol}^{-1}$). These overall results are consistent with steady-state irradiations in which it was shown that there is little permanent bleaching of the dye in this system [26].

We have shown that, subject to thermodynamic constraints, hydroperoxides can function as effective triplet state quenchers and that the resulting reaction can involve net electron transfer. Oxidation of the hydroperoxide may be accompanied by loss of the terminal proton, giving rise to an alkyl peroxy radical. Such radicals lack the requisite energy to abstract a hydrogen atom from most organic substrates but they are powerful oxidants. The oxidation potentials of these alkyl hydroperoxides are sufficiently low for the compounds to act as electron donors for many photosensitizers and, in fact, it is likely that electron transfer is a relatively common feature of many such photoprocesses.

It should be noted that continuous exposure of a dye to light in the presence of an organic substrate and molecular oxygen will inevitably result in the formation of hydroperoxides. This is especially significant for the photodegradation of paints, plastics, fabrics, paper, cellulose, dyes, beer, and foodstuffs and for the newly emerging field of photodynamic therapy. These hydroperoxides can initiate light-induced electron-transfer reactions with appropriate dyes that produce more-reactive free radicals, such as alkoxy radicals, and start a chain reaction that will quickly become uncontrollable.

Acknowledgements

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References

- [1] B. Ranby, J.F. Rabek, Photodegradation, Photooxydation and Photostabilization of Polymers, Wiley, New York, 1975, and references cited therein.
- [2] E.N. Frankel, Prog. Lip. Res. 23 (1985) 197.
- [3] J.D. Spikes, in: K.C. Smith (Ed.), The Science of Photobiology, Plenum, New York, 1989.
- [4] C.S. Foote, Future Direction and Applications in Photodynamic Therapy, SPIE Institute Series, vol. IS6, SPIE Optical Engineering Press, Bellingham, WA, 1990, p. 115.
- [5] E.A. Lissi, M.V. Encinas, in: J.C. Scaiano (Ed.), Handbook of Organic Photochemistry, vol. 2, CRC Press, Boca Raton, FL, 1989, p. 111.
- [6] C. Walling, M. Gibian, J. Am. Chem. Soc. 87 (1965) 3413.
- [7] G. Moger, J. Paal-Lucas, D. Gal, Ber. Bunsenges. Phys. Chem. 91 (1987) 794.
- [8] L.C. Stewart, D.J. Carlsson, D.M. Wiles, J.C. Scaiano, J. Am. Chem. Soc. 105 (1983) 3605.
- [9] J.C. Scaiano, G.G. Wubbels, J. Am. Chem. Soc. 103 (1981) 640.
- [10] P.S. Engel, T.L. Woods, M.A. Page, J. Phys. Chem. 87 (1983) 10.
- [11] C. Tanielian, C. Wolff, J. Phys. Chem. 99 (1995) 9831.
- [12] C. Tanielian, R. Mechin, J. Photochem. Photobiol. A 48 (1989) 43.
- [13] S.J. Atherton, A. Harriman, J. Am. Chem. Soc. 115 (1993) 1816.
- [14] K. Gollnick, Ann. N.Y. Acad. Sci. 171 (1970) 89.
- [15] S.W. Benson, R. Shaw, in: D. Swern (Ed.), Organic Peroxides, vol. 1, Interscience, New York, 1971, pp. 129.
- [16] M.G. Kuzmin, L.N. Guseva, Khim. Vys. Energ. 4 (1970) 24.
- [17] T. Ohno, N. Lichtin, J. Phys. Chem. 86 (1982) 354.
- [18] R.H. Kayser, R.H. Young, Photochem. Photobiol., 24 (1976) 395; 24 (1976) 403.
- [19] R.D. Mair, A.J. Graupner, Anal. Chem. 36 (1964) 194.
- [20] K. Bergmann, C.T. O'Konsky, J. Phys. Chem. 36 (1963) 194.
- [21] S.L. Murov, I. Carmichael, G.L. Hug (Eds.), Handbook of Photochemistry, Dekker, New York, 1993.
- [22] K. Kikuchi, S.I. Tamura, C. Iwanaga, H. Kokubun, Y. Usui, J. Phys. Chem. 106 (1977) 17.
- [23] P.U. Kamat, N.N. Lichtin, Photochem. Photobiol. 33 (1981) 109.
- [24] W.H. Koppenol FEBS Lett. 264 (1990) 165.
- [25] D.T. Sawyer, J.S. Valentine, Acc. Chem. Res., 14 (1981) 393.
- [26] (a) C. Tanielian, R. Mechin, M. Shakirullah, J. Photochem. Photobiol. A, 64 (1992) 191; (b) M. Shakirullah, Thèse de Doctorat de l'Université Louis Pasteur de Strasbourg, France, 1987; (c) R. Mechin, Thèse de Doctorat d'Etat, Université Louis Pasteur de Strasbourg, France, 1995.