Triphenylpyrylium Salt as Sensitizer for Electron Transfer Oxygenation not involving Superoxide Anion

Ryoichi Akaba,[a,b]* Shin Aihara,[b] Hirochika Sakuragi,[b] and Katsumi Tokumaru[b]*

[a] *Department of Chemistry, Gunma Technical College, Toriba-machi, Maebashi, Gunma 371, Japan*
[b] *Department of Chemistry, University of Tsukuba, Sakura-mura, Ibaraki 305, Japan*

2,4,6-Triphenylpyrylium tetrafluoroborate sensitized electron transfer oxygenation of adamantylideneadamantane proceeds *via* the reaction of the alkene radical cations with molecular oxygen without participation of superoxide anion.

Considerable effort has recently been focused on electron transfer photo-oxygenation of organic compounds.[1] Our own interest in this field has been centred around possible reactions of alkene radical cations with oxygen.[2] For investigation of these reactions it is desirable to use sensitizers which produce neither singlet oxygen nor superoxide radical anions under the photo-oxygenation conditions.[3] Frequently employed cyanoaromatic sensitizers such as 9,10-dicyanoanthracene (DCA) and 9-cyanoanthracene (CNA) do not meet the requirements.[4] We report here that 2,4,6-triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$) is an appropriate sensitizer for the above purposes.

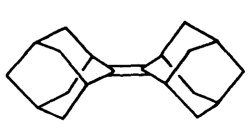
Adamantylideneadamantane (AA) was chosen as a substrate since its radical cation is known to react with oxygen.[5] Results of TPP^+-sensitized oxygenation of AA are summarized in Table 1. Typically, irradiation of a dichloromethane solution (8 ml) of AA (5.0×10^{-2} M) in the presence of $TPP^+BF_4^-$ (2.4×10^{-3} M) with a 650 W halogen–tungsten lamp, through a Pyrex filter with bubbling oxygen, for 10 min, at room temperature, gave exclusively the dioxetane (DO) in 78% yield (based on AA consumed). However, prolonged irradiation (30 min) afforded adamantanone (AN) in 75% yield by decomposition of DO. Addition of 1,4-dimethoxybenzene (0.13 equiv. with respect to AA) quenched the oxygenation appreciably. We propose the mechanism in reactions (1)—(3) for DO formation.†

$$AA + TPP^+ \xrightarrow{h\nu} AA^{+\cdot} + TPP^\cdot \quad (1)$$

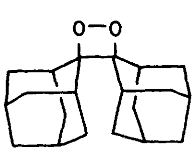
$$AA^{+\cdot} + O_2 \longrightarrow {}^+AA\text{–}O_2^\cdot \quad (2)$$

$${}^+AA\text{–}O_2^\cdot + TPP^\cdot \longrightarrow DO + TPP^+ \quad (3)$$

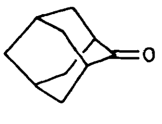
Direct evidence for electron transfer was obtained by means of ns-laser flash photolysis. The laser flash photolysis of $TPP^+BF_4^-$ (1.6×10^{-4} M) with a nitrogen pulsed laser (337 nm) in the presence of AA (6.2×10^{-2} M) in dichloromethane, where 80% of the excited singlet TPP^+ was quenched by AA as determined by quenching of TPP^+ fluorescence by AA, gave a transient absorption (λ_{max} 550 nm). The spectrum was assigned to a pyranyl radical $TPP^\cdot$, the one-electron reduced species of TPP^+, by comparison with the spectrum reported.[6] The formation of $TPP^\cdot$ indicates that electron transfer takes place from AA to the excited singlet TPP^+. From the decay kinetics of the 550 nm band in the absence and presence of oxygen, the rate constant for the process, $TPP^\cdot + O_2$, can be estimated to be less than 10^7 dm^3 mol^{-1} s^{-1}. This is in sharp contrast with the kinetic behaviour of the CNA radical anion in the *trans*-stilbene–CNA system in the presence of oxygen.[7] The present result shows that $TPP^\cdot$ is far less efficient in



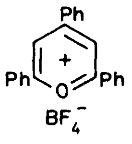
AA



DO



AN



$TPP^+BF_4^-$

---

† TPP^+ decomposes slowly under the experimental conditions. For example, at 54% conversion of AA, 30 times less TPP^+ than AA was consumed. This finding suggests that the following reaction may be involved in the photo-oxygenation, though the quantum yield for DO formation is less than unity: ${}^+AA\text{–}O_2^\cdot + AA \longrightarrow DO + AA^{+\cdot}$.

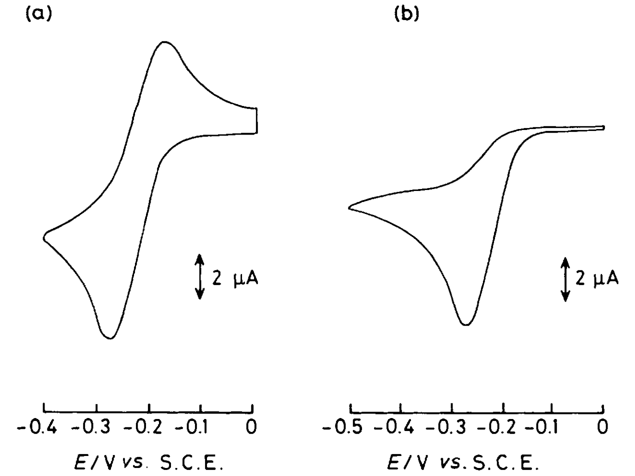


Figure 1. Cyclic voltammograms of $TPP^+BF_4^-$ (1.9×10^{-3} M) in the absence (a) and presence (b) of oxygen in dichloromethane at a 200 mV s^{-1} scan rate with tetrabutylammonium perchlorate (0.1 M) as a supporting electrolyte. (S.C.E. = standard calomel electrode).

Table 1. Product yield on TPP^+-sensitized oxygenation of AA.[a]

Run	Irradiation wavelength/nm	Reaction time/min	% Isolated yield		
			AA	DO	AN
1	>300	10	60	34	Unobs.
2	>300	30	Unobs.	Unobs.	75
3	>300[b]	10	83	7	Unobs.
4	>350[c]	25	52	4	37

[a] Unobs.: product not observed. [b] With 1,4-dimethoxybenzene added. [c] A Toshiba L-39 filter was used.

generating the superoxide radical anion than the CNA radical anion and presumably than the DCA radical anion (*vide infra*).

The reactivity of $TPP^\bullet$ with oxygen was also studied by cyclic voltammetry (CV). Effects of oxygen in TPP^+-sensitized electron transfer reactions have been a matter of controversy.[8,9] Figure 1 shows cyclic voltammograms of $TPP^+BF_4^-$ in dichloromethane in the presence and absence of oxygen. For comparison, those of DCA in acetonitrile were also taken (Figure 2). As shown in Figures 1 and 2, both TPP^+ and DCA exhibited reversible CV curves in the absence of oxygen. In the presence of oxygen, TPP^+ showed typical EC behaviour.[10]‡ In striking contrast, DCA reduction exhibited a catalytic current increase. This huge current increase shows that the DCA radical anion reduces oxygen *via* one-electron transfer to regenerate DCA and to produce the superoxide radical anion. This reaction sequence will continue until all the oxygen molecules near the electrode are converted into the superoxide radical anions. These electrochemical results also support the greater reluctance of $TPP^\bullet$ to undergo electron transfer to oxygen than the DCA radical anion.

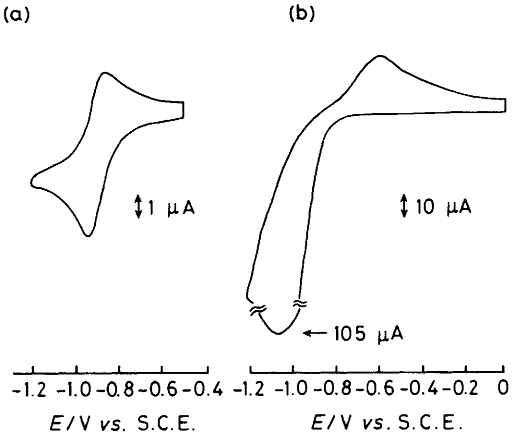


Figure 2. Cyclic voltammograms of DCA (1.5×10^{-3} M) in the absence (a) and presence (b) of oxygen at a 200 mV s^{-1} scan rate with tetrabutylammonium perchlorate (0.1 M) as a supporting electrolyte.

Participation of singlet oxygen in the present oxygenation is ruled out. First, fluorescence from the singlet excited TPP^+ was not quenched significantly by oxygen. Secondly, energetic considerations do not support formation of the triplet TPP^+ (2.3 eV),[11] a potential sensitizer to generate singlet oxygen through back electron transfer in the radical ion pair of $TPP^\bullet$ and $AA^{+\bullet}$ (1.83 eV). Finally, laser flash photolysis of $TPP^+BF_4^-$ (1.6×10^{-4} M) in the presence of low concentrations of AA (0—3.0×10^{-4} M) in dichloromethane under argon gave a transient absorption spectrum assignable to the triplet TPP^+ (λ_{max} *ca.* 850 nm), which was quenched by AA with a rate constant of 1.2×10^{10} dm^3 mol^{-1} s^{-1} and by oxygen saturated in the solvent with $k_q[O_2] = 1.3 \times 10^6$ s^{-1}. Accordingly, under the actual irradiation conditions ([AA] = 5.0×10^{-2} M), the triplet TPP^+, if present at all, is quenched more than 460 times more rapidly by AA than by the dissolved oxygen.

Received, 6th February 1987; Com. 161

References

1 S. L. Mattes and S. Farid, in 'Organic Photochemistry,' vol. 6, ed. A. Padwa, Dekker, New York, 1983, chapter 4, and references therein.
2 R. Akaba, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, 1984, **25**, 665; *Chem. Lett.*, 1984, 1677; M. Tsuchiya, R. Akaba, S. Aihara, H. Sakuragi, and K. Tokumaru, *ibid.*, 1986, 1727.
3 L. Lopez and V. Calo, *J. Chem. Soc., Chem. Commun.*, 1984, 1266.
4 D. C. Dobrowoiski, P. R. Ogilby, and C. S. Foote, *J. Phys. Chem.*, 1983, **87**, 2261; L. E. Marning, C.-I. Gu, and C. S. Foote, *ibid.*, 1983, **87**, 40.
5 S. F. Nelsen and R. Akaba, *J. Am. Chem. Soc.*, 1981, **103**, 2096; E. L. Clennan, W. Simmons, and I. W. Almgren, *ibid.*, 1981, **103**, 2098.
6 F. Pragst, *Electrochim. Acta*, 1976, **21**, 497.
7 L. T. Spada and C. S. Foote, *J. Am. Chem. Soc.*, 1980, **102**, 391.
8 A. Ledwith, in 'Exciplexes,' eds. M. Gordon and W. R. Ware, Academic Press, New York, 1975, p. 220.
9 K. Okada, K. Hisamitsu, and T. Mukai, *Tetrahedron Lett.*, 1981, **22**, 1251; K. Okada, K. Hisamitsu, T. Miyashi, and T. Mukai, *J. Chem. Soc., Chem. Commun.*, 1982, 974.
10 R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.
11 R. Searle, J. L. R. Williams, and D. E. Demeyer, *Chem. Commun.*, 1967, 1165.

---

‡ CV results under oxygen indicate that $TPP^\bullet$ reacts with oxygen on the longer time scale of CV scanning (200 mV s^{-1}) than that of transient spectroscopy (μs) during which the actual photochemical reactions take place.