Photoinduced Electron Transfer Carbon–Carbon Bond Cleavage of Radical Cations of Carbonyl Compounds in Solution. 2,4,6-Triphenylpyrylium Salt-Sensitized Oxygenation of Aralkyl Ketones and Aldehydes

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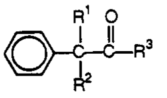
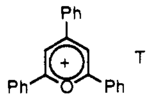
Abstract: Photosensitized electron transfer oxygenation of several aralkyl ketones and aldehydes such as 1,2,2-triphenylethanone and diphenyl- and triphenylethanal has been carried out with 2,4,6-triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$) in dichloromethane. The carbonyl compounds underwent C–C bond cleavage through their cation radicals, generated via electron transfer to the excited singlet state of the pyrylium salt. For example, diphenylethanal afforded benzophenone in 80% yield. Direct evidence for the electron transfer and subsequent formation of a carbocation through C–C bond cleavage was obtained by laser flash photolysis of tetrakis(4-methylphenyl)ethanone in dichloromethane. It is proposed that arylmethyl cations generated by the C–C bond cleavage of the cation radicals undergo electron transfer with pyryl radicals to give arylmethyl radicals, which react with molecular oxygen to afford the final oxygenation products.

Photoinduced electron transfer reactions have gathered growing interest during the last decade.[1] Cation radicals generated by photoinduced electron transfer undergo a diverse set of chemical reactions. Among the competing reaction pathways, C–C bond cleavage is of particular interest since it may provide a unique opportunity to study the chemistry of free radicals and carbocations generated simultaneously.[2] Although extensive studies have been carried out on fragmentation reactions of cation radicals with oxygen functional groups such as ketones and aldehydes in the gas phase,[3] few parallel studies of such cation radicals generated by photoinduced electron transfer in solution have been reported.[4] This may be attributed to the high oxidation potentials of carbonyl compounds and the relatively weak electron-accepting ability of the electron-transfer sensitizers hitherto employed.



	R^1	R^2	R^3
1:	Ph	H	H
2:	Ph	H	Ph
3:	Me	H	Ph
4:	Ph	H	Me
5:	Ph	Ph	Ph
6:	Ph	Ph	H



$TPP^+BF_4^-$

Herein we report our results which demonstrate that carbonyl compounds **1–6** undergo C–C bond cleavage via electron-transfer quenching of the excited states of a 2,4,6-triphenylpyrylium salt, $TPP^+BF_4^-$. Cation radicals formed by the electron transfer undergo bond fission to give arylmethyl cations and benzoyl or formyl radicals, which further react to afford final oxygenation products. The present study represents the first example of photosensitized electron transfer C–C bond cleavage in aralkyl ketones and aldehydes through their cation radicals in solution. Furthermore, we have successfully detected the formation of tris(4-methylphenyl)methyl cation from tetrakis(4-methylphenyl)ethanone cation radical using a laser flash photolysis technique, which is the first direct evidence for the formation of arylmethyl cations through the C–C bond cleavage of a photogenerated cation radical of a carbonyl compound.

Results

Oxygenation Reactions. When a dichloromethane solution (8 mL) of diphenylethanal (**1**) (50 mM) was irradiated for 2 h under oxygen in the presence of $TPP^+BF_4^-$ (5 mM) with a 400-W high-pressure mercury lamp through an appropriate glass filter (>360 nm), benzophenone was obtained in 80% yield based on **1** consumed (92% conversion). Measurements of the absorption spectra of the reaction mixtures before and after irradiation indicated that $TPP^+BF_4^-$ was not consumed appreciably during

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(1) For reviews, see: (a) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 419. (b) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, Chapter 4. (c) Fox, M. A. In *Advances in Photochemistry*; Volman, V. H., Gollnick, K., Eds.; Academic Press: New York, 1986; Vol. 13, p 237. (d) Lewis, F. D. In *Photoinduced Electron Transfer Part C, Photoinduced Electron Transfer Reactions: Organic Substrates*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; p 1.

(2) For recent reports on the C–C bond cleavage of radical cations, see: (a) Okamoto, A.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 2340. (b) Okamoto, A.; Snow, M. S.; Arnold, D. R. *Tetrahedron* **1986**, *42*, 6187. (c) Baciocchi, E.; Bartoli, D.; Rol, C.; Ruzziconi, R.; Sebastiani, G. V. *J. Org. Chem.* **1986**, *51*, 3587. (d) Ci, X.; Lee, L. Y. C.; Whitten, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 2536. (e) Arnold, D. R.; Fahie, B. J.; Lamont, L. J.; Wierzchwski, J.; Young, K. M. *Can. J. Chem.* **1987**, *65*, 2734. (f) Ci, X.; Whitten, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 7215. (g) Maslak, P.; Asel, S. L. *J. Am. Chem. Soc.* **1988**, *110*, 8260. (h) Kellett, M. A.; Whitten, D. G. *J. Am. Chem. Soc.* **1989**, *111*, 2314. (i) Ci, X.; Whitten, D. G. *J. Am. Chem. Soc.* **1989**, *111*, 3459. (j) Sankararaman, S.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1989**, 1800. (k) Maslak, P.; Chapman, W. H., Jr. *J. Chem. Soc., Chem. Commun.* **1989**, 1809. (l) Arnold, D. R.; Lamont, L. J. *Can. J. Chem.* **1989**, *67*, 2119. (m) Sankararaman, S.; Perrier, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 6448. (n) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P.; Mattes, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8973. (o) Dinnocenzo, J. P.; Todd, W. P.; Simpson, T. R.; Gould, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 2462. (p) Popielarz, R.; Arnold, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 3068. (q) Bergmark, W. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1990**, *112*, 4042. (r) Maslak, P.; Narvaez, J. N. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 283. (s) Todd, W. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1991**, *113*, 3601.

(3) For the chemistry of cation radicals of carbonyl compounds in the gas phase, see: (a) Biali, S. E.; Rappoport, Z.; Depke, G.; Eckart, K.; Schwarz, H. *Int. J. Mass. Spectrom. Ion. Processes* **1985**, *63*, 289. (b) Rabin, I.; Biali, S. E.; Rappoport, Z.; Lifshitz, C. *Int. J. Mass. Spectrom. Ion. Processes* **1986**, *70*, 301. (c) Mabud, M. A.; Ast, A.; Verma, S.; Jiang, Y.-X.; Cooks, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 7597 and references cited therein.

(4) For electron-transfer oxidation of ketones by chemical oxidants, see: (a) Stoucy, P.; Ho, T.-L.; Deslongchamps, P. *Can. J. Chem.* **1972**, *50*, 2047. (b) Danieli, B.; Palmisano, G. *Chem. Ind.* **1976**, 565. (c) Okamoto, K.; Takeuchi, K.; Murai, O.; Fujii, Y. *J. Chem. Soc., Perkin Trans. 2* **1979**, 490. (d) Okamato, K.; Takeuchi, K.; Murai, O.; Matsui, S.; Inoue, T.; Kitagawa, T. *Tetrahedron Lett.* **1981**, *22*, 2785. (e) Takeuchi, K.; Murai, O.; Matsui, S.; Inoue, T.; Kitagawa, T.; Okamoto, K. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1301. (f) Kitagawa, T.; Takeuchi, K.; Murai, O.; Matsui, S.; Inoue, T.; Nishimura, M.; Okamoto, K. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1987.

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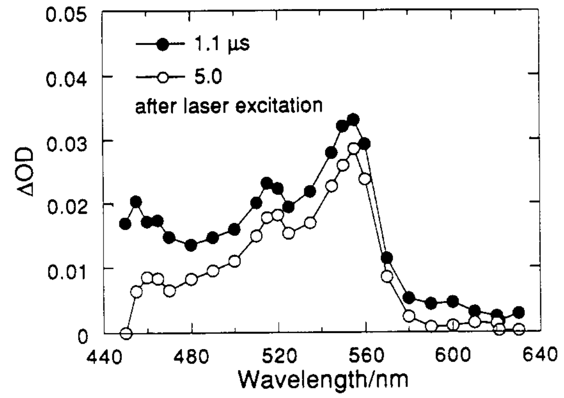

Figure 1. Transient absorption spectra observed on laser pulse excitation of a dichloromethane solution of tetraphenylethanone (**5**) (2.7×10^{-2} M) in the presence of $\mathrm{TPP^+BF_4^-}$ (6.5×10^{-5} M) under argon.

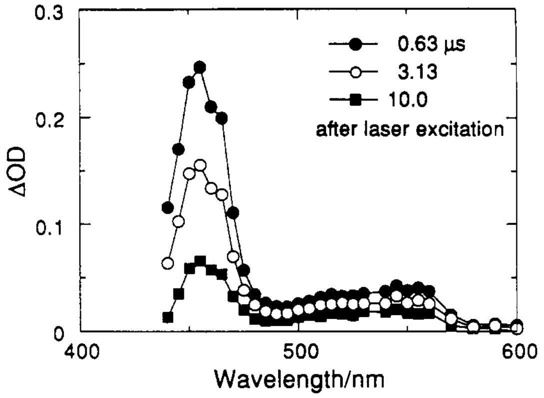

Figure 2. Transient absorption spectra observed on laser pulse excitation of a dichloromethane solution of tetrakis(4-methylphenyl)ethanone (**7**) (2.8×10^{-2} M) in the presence of $\mathrm{TPP^+BF_4^-}$ (6.5×10^{-5} M) under argon.

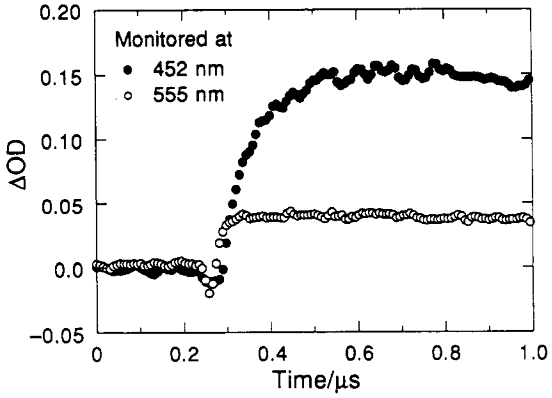

Figure 3. Time profiles of 455- and 550-nm absorption bands monitored in dichloromethane at 452 and 555 nm, respectively.

oxygenation of **1** (ca. 50% conversion). Control experiments established that the sensitizer and irradiation were essential for the oxygenation to occur. 9,10-Dicyanoanthracene ($\sim 10^{-4}$ M), a sensitizer employed frequently for photooxygenation studies,[1a,b] did not induce the reaction of **1** either in CH_2Cl_2 or in CH_3CN. Similar oxygenation was also observed for other aralkyl ketones and aldehydes, **2**–**6**, and the results are summarized in Table I.

To compare the results with those of direct irradiation (>300 nm) in the presence of oxygen, we subjected **1**, **2**, and **5** to direct oxygenation (>300 nm) in CH_2Cl_2. It was found that the oxygenation was fairly slow for **1** (15% conversion for 2 h) and **5** (9% conversion for 3 h) though benzophenone was obtained from both **1** and **5** in very low yields (ca. 5%). However, direct irradiation of **2** in CH_2Cl_2 was relatively efficient, and benzophenone (70% based on **2** consumed) and benzoic acid (50%) were obtained.

The $\mathrm{TPP^+BF_4^-}$-sensitized oxygenation in a more polar solvent, acetonitrile, was also studied for **2**. Thus, irradiation of **2** under similar photooxygenation conditions in CH_3CN gave benzophenone and benzoic acid in 61 and 60% yields, respectively (based on **2** consumed, 97% conversion). It is noted that only a minor amount of benzoyl fluoride (<5%) was formed in CH_3CN. Although the photooxygenation of **2** in CH_3CN proceeded well, as in CH_2Cl_2, no further studies have been done with acetonitrile as a solvent.[5]

Benzoyl fluoride was formed in significant yields when the substrates had a phenyl group attached to the carbonyl group as in **2**, **3**, and **5**. Benzoyl fluoride was identified by comparing the retention times in GLC (two different columns) and by characterization with GC–MS.[6] The effect of the counterion of the sensitizer on the product distribution was also examined using **2** as a substrate, and it was found that the yield of benzoyl fluoride depends significantly on the counterion. When the oxygenation of **2** was sensitized with $\mathrm{TPP^+PF_6^-}$, the yield of benzoic acid increased (59% based on **2** consumed) with a concomitant decrease in the yield of benzoyl fluoride (11%), whereas benzoic acid was obtained in a better yield (66%) when $\mathrm{TPP^+ClO_4^-}$ was employed as sensitizer. Thus, the $\mathrm{TPP^+PF_6^-}$ salt gave a smaller amount of benzoyl fluoride, and in the case of the $\mathrm{TPP^+ClO_4^-}$ salt, where no fluorine source was available, a higher yield of benzoic acid was obtained.

Fluorescence Quenching and Laser Flash Photolysis Studies. In order to get further information on the primary processes of the oxygenation reactions, we have carried out fluorescence quenching experiments. Free energy changes ($\Delta G°$)[7] associated with electron transfer from these substrates to the excited singlet state of $\mathrm{TPP^+BF_4^-}$ have also been estimated. The results are tabulated in Table I. As shown in Table I, the $\Delta G°$ values are negative, and the quenching rate constants, k_q^s, were nearly diffusion-controlled in all the cases studied.

Direct evidence for electron transfer and direction of subsequent bond cleavage of the intermediate cation radicals was obtained by laser flash photolysis (LFP) of tetrakis(4-methylphenyl)ethanone (**7**). Ketone **7** was selected since the absorption bands of arylmethyl cations from **1**–**6**, if generated, would overlap with the ground-state absorption of $\mathrm{TPP^+BF_4^-}$ (λ_{max} 417 nm in CH_2Cl_2) and could not be observed well.[8] Actually, LFP of $\mathrm{TPP^+BF_4^-}$ in the presence of **5** in CH_2Cl_2 produced a transient spectrum due to the pyryl radicals $\mathrm{TPP^•}$ at 550 nm, as previously assigned,[9,10] indicating occurrence of electron transfer from **5** to $^1(\mathrm{TPP^+BF_4^-})^*$; however, no absorption assignable to the triphenylmethyl cation could be detected around 430 nm (Figure 1).[11]

LFP of a dichloromethane solution of $\mathrm{TPP^+BF_4^-}$ (6.5×10^{-5} M) at 408 nm in the presence of **7** (2.8×10^{-2} M) under argon exhibited the transient spectra shown in Figure 2. The intense absorption band at 455 nm can readily be assigned to tris(4-methylphenyl)methyl *cation* ($\mathbf{8}^+$) on the basis of its reported spectrum.[8,12] The 550-nm band is assigned to the pyryl radical. We note that $\mathbf{7}^{•+}$ cleaves preferentially to $\mathbf{8}^+$ and a 4-methylbenzoyl radical,[3c,14] though a cleavage in the opposite direction

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[5] We have found that $\mathrm{TPP^+BF_4^-}$ is not very stable in CH_3CN, especially when it is in the low concentrations (10^{-5} M) which are usually required for laser flash photolysis studies. Detailed solvent effects will be described in a separate paper.

[6] R.A. thanks the late Professor Yoichiro Nagai (Gunma University) for his kindness in making it possible for us to use his instruments (GC–MS).

[7] Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

[8] Olah, G. A.; Pittman, C. U., Jr.; Simmons, M. C. R. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1968; pp 157, 164.

[9] Pragst, F. *Electrochim. Acta* **1976**, *21*, 497.

[10] Akaba, R.; Aihara, S.; Sakuragi, H.; Tokumaru, K. *J. Chem. Soc., Chem. Commun.* **1987**, 1262.

[11] Triarylmethyl radicals usually absorb much shorter wavelength light (<350 nm) in solution.[12,13]

[12] Faria, J. L.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 1277.

[13] McClelland, M. A.; Kanagasabapathy, V. M.; Banait, N. S.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 3966.

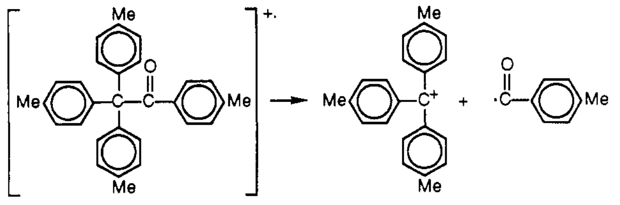
[14] Formation of tris(4-methylphenyl)methyl cation was suggested in the Ce(IV) ion induced oxidation of tetrakis(4-methylphenyl)ethanone in acetic acid. We thank Professor K. Takeuchi, Kyoto University, for drawing our attention to refs 3c–f.

Table I. $TPP^+BF_4^-$-Sensitized Oxygenation of Aralkyl Ketones and Aldehydes[a]

substrate	time/h	conversn/%	products (yield/%)[b]	$E_p^{ox\,c}$/V	$k_q^{s\,d}$/M^{-1} s^{-1}	ΔG°/kcal mol^{-1}
Ph_2CHCHO (**1**)	2	92	Ph_2CO (80)	2.36	4.0×10^9	−1.8
$Ph_2CHCOPh$ (**2**)	3	79	Ph_2CO (66) PhCOF (54) $PhCO_2H$ (22)	2.31	8.7×10^9	−3.0
PhMeCHCOPh (**3**)	3	63	PhCOMe (60) PhCOF (48) $PhCO_2H$ (10)	2.36	2.3×10^9	−1.8
$Ph_2CHCOMe$ (**4**)	3	87	Ph_2CO (64)	2.22	9.3×10^9	−5.1
Ph_3CCOPh (**5**)	2	94	Ph_2CO (72) PhCOF (43) $PhCO_2$ (36) PhOH (38)	2.28	1.4×10^{10}	−3.7
Ph_3CCHO (**6**)	3	94	Ph_2CO (72) PhOH (34)	2.23	1.0×10^{10}	−4.8
$(4\text{-}MeC_6H_4)_3CCOC_6H_4Me\text{-}4$ (**7**)	2	100	$(4\text{-}MeC_6H_4)_2CO$ (71) $4\text{-}MeC_6H_4CO_2H$ (72) $4\text{-}MeC_6H_4OH$ (27) $4\text{-}MeC_6H_4COF$ (24)	1.97	2.0×10^{10}	−10.8

[a] Oxygenation was carried out in dichloromethane at running water temperature under bubbling oxygen. A Toshiba L-39 glass cut filter was used to isolate >360-nm light. Yields of products were determined by GLC. [b] Yields are based on the substrate consumed. [c] Measured in acetonitrile vs SCE. [d] Measured in dichloromethane.

as a minor pathway cannot be ruled out (vide infra). Further support for the direction of the bond cleavage was obtained by comparing the time profiles of the 455- and 550-nm bands (Figure 3). Thus, the time profile of the 455-nm band exhibited growth with first-order kinetics ($\sim 1 \times 10^7$ s^{-1}), while the 550-nm band appeared almost instantaneously after the laser pulse and showed no appreciable decay during the growth of the 455-nm band, indicating that the 455-nm band was formed synchronously with the decomposition of $\mathbf{7}^{\bullet+}$.[15]



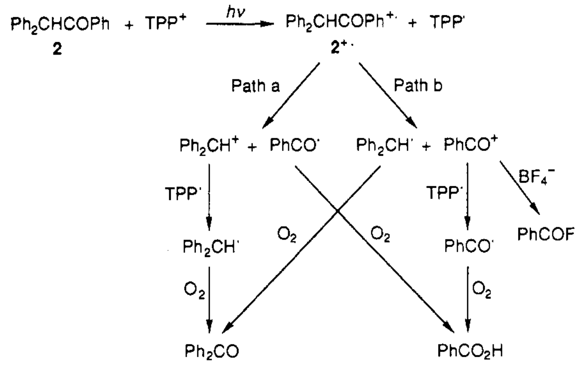
$\mathbf{7}^{+\cdot}$ $\mathbf{8}^+$

To confirm that **7** actually behaves like **1**–**6** under similar oxidative conditions, irradiation of **7** for 2 h in the presence of $TPP^+BF_4^-$ was also performed, and it was found that **7** gave 4,4′-dimethylbenzophenone, 4-methylbenzoic acid, 4-methylphenol, and 4-methylbenzoyl fluoride in 71, 72, 27, and 24% yields, respectively (Table I, 100% conversion).

Discussion

Fluorescence quenching experiments and the negative ΔG° values associated with the electron transfer from the substrates to the excited singlet state of $TPP^+BF_4^-$ [$^1(TPP^+BF_4^-)^*$] suggest the formation of the cation radicals by electron transfer from the carbonyl compounds **1**–**7** to $^1(TPP^+BF_4^-)^*$. Spectroscopic evidence for the electron transfer and direction of subsequent bond cleavage of the intermediate cation radicals was obtained by laser flash photolysis (LFP) of tetrakis(4-methylphenyl)ethanone (**7**). Observation of the absorption spectra assignable to triarylmethyl cations $\mathbf{8}^+$ and the pyryl radicals indicates that the C–C bond cleavage of $\mathbf{7}^{\bullet+}$ also produced 4-methylbenzoyl radicals in addition to $\mathbf{8}^+$. This is the first direct observation of the formation of arylmethyl cations through the bond cleavage of photogenerated cation radicals possessing unsymmetrically substituted C–C σ bonds. Analysis of the buildup curve for the formation of $\mathbf{8}^+$ indicates that the rate constant for the C–C bond cleavage of $\mathbf{7}^{\bullet+}$ is $\sim 1 \times 10^7$ s^{-1}. The observed rate constant is in nearly the same order as reported for the C–Si bond cleavage of (4-methoxybenzyl)trimethylsilyl cation radicals in CH_3CN.[2s] However, it is of interest to point out that, in contrast with our cleavage rate constant on the order of 10^7 s^{-1} in CH_2Cl_2, (4-methoxybenzyl)trimethylsilyl cation radicals were reported to be stable in a laser time (nanosecond) scale even if the cation radicals were generated in CH_2Cl_2 by a cationic salt (*N*-acridinium hexafluorophosphate) sensitized electron-transfer reaction.[2s]

Scheme I



The above results of LFP coupled with those of the oxygenation chemistry indicate that back electron transfer from the pyryl radicals to $\mathbf{8}^+$ must be rapid to afford the tris(4-methylphenyl)methyl radicals which subsequently react with molecular oxygen to give 4,4′-dimethylbenzophenone and 4-methylphenol (vide infra). 4-Methylbenzoic acid could be formed by the reaction of 4-methylbenzoyl radical with molecular oxygen. However, a minor pathway of the bond breaking in $\mathbf{7}^{\bullet+}$ to afford a tris(4-methylphenyl)methyl radical and a 4-methylbenzoyl cation cannot be completely ruled out. This process would explain the formation of 4-methylbenzoyl fluoride (vide infra).

A reasonable overall mechanism for the present oxygenation is outlined in the Scheme I using **2** as a prototype. Thus, electron transfer from **2** to $^1(TPP^+BF_4^-)^*$ generates the cation radical of **2**, $\mathbf{2}^{\bullet+}$, and the pyryl radical, $TPP^\bullet$. The resulting $\mathbf{2}^{\bullet+}$ undergoes C–C bond cleavage to afford a diphenylmethyl cation and a benzoyl radical (path a). Back electron transfer from the pyryl radical to the cation affords a diphenylmethyl radical, which reacts with molecular oxygen to give a diphenylmethylperoxyl radical.[17] The resulting peroxyl radical would finally give benzophenone.

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(15) The absorption band assignable to the cation radical of **8**, $\mathbf{8}^{\bullet+}$, could not be observed. It would be overlapped with the intense absorption band at 455 nm, and also, the molar extinction coefficient might be small since $\mathbf{8}^{\bullet+}$ can be regarded as a derivative of the toluene cation radical.[16]

(16) Hamill, W. H. In *Radical Ions*; Kaiser, E. T., Kevan, L., Eds.; Interscience: New York, 1968; p 399.

(17) The back electron transfer from $TPP^\bullet$ to the diphenylmethyl cation must be diffusion-controlled since the reduction potential of the diphenylmethyl cation (0.35 V/SCE in MeCN)[2p] is much more positive than that of $TPP^+BF_4^-$ (−0.36 V/SCE in MeCN).

Benzoic acid could be formed by the reaction of the benzoyl radicals with molecular oxygen.

An alternative possibility is a bond cleavage in the opposite direction to give a diphenylmethyl radical and a benzoyl cation (path b). The resulting diphenylmethyl radical would then react directly with molecular oxygen to afford a diphenylmethylperoxyl radical. The initially formed benzoyl cation might be reduced by $TPP^{\bullet}$ to afford a benzoyl radical, which finally reacts with molecular oxygen to afford benzoic acid. Therefore, both pathways a and b may well explain the formation of benzophenone and benzoic acid.

The mechanism for the formation of benzoyl fluoride could be very complex.[18] We suggest that path b is mainly operative for the bond cleavage of $\mathbf{2}^{\bullet+}$ in CH_2Cl_2 while $\mathbf{2}^{\bullet+}$ undergoes bond fission through path a in CH_3CN to afford mainly the diphenylmethyl cation and the benzoyl radical. The reaction of benzoyl cation formed in path b with BF_4^- may be an important pathway at the initial stage for benzoyl fluoride formation in CH_2Cl_2.[19]

The following results support the suggested mechanism. Benzoyl fluoride was formed only in a trace amount, if any, in the direct oxygenation of **2** in CH_2Cl_2 in the presence of tetrabutylammonium tetrafluoroborate ($TBBF_4$) as a BF_4^- source. Since the direct irradiation of **2** in CH_2Cl_2 would generate diphenylmethyl radicals and benzoyl radicals via C–C bond homolysis as shown by the formation of benzophenone and benzoic acid, the absence of benzoyl fluoride strongly suggests that the benzoyl radical is not reactive with BF_4^-. The formation of benzoic acid but not benzoyl fluoride in the sensitized oxygenation of **2** in CH_3CN is also consistent with the above mechanism. If the benzoyl radical is a source of benzoyl fluoride, it must also be formed in CH_3CN since the benzoyl radical would certainly be formed in CH_3CN as evidenced by the formation of benzoic acid.[20]

The suggested mechanism is not inconsistent with the observed effects of the counterion on the distribution of benzoyl fluoride and benzoic acid, though the product distribution can also be explained by the reaction of the benzoyl radical with BF_4^- (path a). The higher yield of benzoic acid (>60%) in the $TPP^+ClO_4^-$ salt-sensitized reaction in CH_2Cl_2 could be explained by a rapid one-electron reduction of the benzoyl cation formed by $TPP^{\bullet}$ to afford a benzoyl radical, which would be captured by molecular oxygen, finally giving benzoic acid.

A similar oxygenation mechanism may account for the formation of the oxygenation products of **1**, **3**–**6**, and **7**, though path a, which gives an arylmethyl cation and a formyl, acetyl, or 4-methylbenzoyl radical, is more favored than path b, which gives an arylmethyl radical and a formyl, acetyl, or 4-methylbenzoyl cation, in **1**, **4**, **6**, and **7**. The initial formation of a diphenylmethyl cation and a triphenylmethyl cation in CH_2Cl_2 in the bond cleavage of $\mathbf{1}^{\bullet+}$ and $\mathbf{6}^{\bullet+}$, respectively, may be supported by a comparison of the experimental ionization potentials of the fragment radicals. Thus, the ionization potentials of the triphenylmethyl, diphenylmethyl, and formyl radicals are 7.26,[21] 7.32,[22] and 8.10 eV,[23] respectively, and hence, the bond fission of $\mathbf{1}^{\bullet+}$ or $\mathbf{6}^{\bullet+}$ would favor the formation of the arylmethyl cation and the formyl radical rather than that of the arylmethyl radical and the formyl cation.[24,25] In the cases of **5** and **6**, which contain the triphenylmethyl moiety, the triphenylmethyl radical is formed, and its reaction with molecular oxygen is well-known to give benzophenone and phenol through the reaction of triphenylmethylperoxyl radicals.[29]

Participation of enol forms of **1**–**4** appears unlikely since tetraphenylethanone (**5**) and triphenylethanal (**6**), which have no enolizable hydrogen, gave benzophenone in 67 and 72% yields, respectively, under similar irradiation conditions (Table I). Also, oxygenation of enol forms via dioxetane intermediates should give benzophenone and benzoic acid instead of benzophenone and benzoyl fluoride in the $TPP^+BF_4^-$-sensitized reactions, and therefore, the observed products cannot be explained by such a process.

Conclusion

We have shown that the present $TPP^+BF_4^-$-sensitized reaction of carbonyl compounds may provide a new reaction sequence involving formation of carbocations from the cation radicals of carbonyl compounds, followed by their reduction with $TPP^{\bullet}$ to the respective carbon radicals in solution. It should be emphasized that the present study was first made possible by the strong electron-accepting ability of excited $TPP^+BF_4^-$, which undergoes electron transfer with carbonyl compounds of high oxidation potential in a less polar solvent.

It is also noted that the present photooxygenation reactions involving C–C bond cleavage of cation radicals offer a way of generating and studying the reactivity of the resulting free radicals and carbocations with various substrates. Further studies currently underway in our laboratories, aimed at examining the effects of sensitizers, solvent, additives, counterions, and cation radical structures on the efficiency and direction of C–C bond cleavage,

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(18) We observed that almost all the fluorine atoms in BF_4^- were consumed during the oxygenation of **2**, **3**, and **5**. Therefore, a simple stoichiometric reaction of BF_4^- with benzoyl radicals or benzoyl cations would not explain all the benzoyl fluoride formed. It was also found that in the case of **2**, for example, TPP^+ was mostly decomposed at the end of the reaction, as determined by UV absorption spectra of the reaction mixture.

(19) Another possibility for the formation of benzoyl fluoride in CH_2Cl_2 may be a nucleophilic attack of BF_4^- on $\mathbf{2}^{\bullet+}$ before it undergoes bond fission, as suggested by a reviewer. This is certainly an attractive mechanism which deserves attention. However, at present, the observed results are consistent with the suggested mechanism (path b), and further strong evidence is clearly needed to adopt such a mechanism involving nucleophilic assistance of BF_4^-. Our preliminary laser experiments indicate that the rate constant of the C–C bond cleavage of $\mathbf{7}^{\bullet+}$ generated by $TPP^+ClO_4^-$ was nearly the same as that observed with $TPP^+BF_4^-$, suggesting that nucleophilicity of the counterion of the pyrylium salt seems not to play an important role in the C–C bond cleavage of $\mathbf{7}^{\bullet+}$. Further studies by LFP using some model compounds are in progress on this interesting problem.

(20) The absence of benzoyl fluoride in the $TPP^+BF_4^-$-sensitized oxygenation of **2** in CH_3CN may be accounted for by the higher concentration of oxygen in CH_3CN than in CH_2Cl_2, which would make the rate for benzoic acid formation faster than that for benzoyl fluoride formation. However, this possibility is not likely since addition of $TBBF_4$ (0.05 M) did not help the formation of benzoyl fluoride at all. In striking contrast, addition of $TBBF_4$ increased the yield of benzoyl fluoride significantly in the $TPP^+BF_4^-$-sensitized oxygenation of **2** in CH_2Cl_2. Also, CH_2Cl_2 is less polar than CH_3CN, and hence BF_4^- would be more tightly bound to TPP^+ in CH_2Cl_2 than in CH_3CN. This might cause the faster reaction of benzoyl radical or benzoyl cation with BF_4^- in CH_2Cl_2 than in CH_3CN. Such a proximity effect in the radical ion pairs cannot be ruled out.

(21) Franklin, J. L. In *Carbonium Ions*; Olah, G. A.; Schleyer, P. v. R., Eds.; Wiley: New York, 1968; p 90.

(22) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, Vol. 6, Suppl. 1, 1–188.

(23) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, Vol. 17, Suppl. 1, 64.

(24) In the case of **1**, further evidence for path a was obtained from the consideration of the heats of formation (ΔH_f) of both the fragmentation reactions. Thus, $\Delta H_f(Ph_2CH^{\bullet}) + \Delta H_f(HCO^+)$ and $\Delta H_f(Ph_2CH^+) + \Delta H_f(HCO^{\bullet})$ were estimated to be 245.3 and 227.5 kcal mol^{-1}, respectively, where $\Delta H_f(Ph_2CH^{\bullet})$ = 48 kcal mol^{-1},[23] $\Delta H_f(HCO^{\bullet})$ = 10.7 kcal mol^{-1},[23] $\Delta H_f(HCO^+)$ = 197.3 kcal mol^{-1},[23] and $\Delta H_f(Ph_2CH^+)$ (=216.8 kcal mol^{-1}) was estimated from the sum of $\Delta H_f(Ph_2CH^{\bullet})$ and $I_p(Ph_2CH^{\bullet})$.

(25) Bond dissociation energy in $\mathbf{1}^{\bullet+}$ (BDE) was also estimated to be ≈10 kcal mol^{-1} from the following equation:

$$\mathrm{BDE} = \Delta H_f(Ph_2CHCHO) + I_p(Ph_2CHCHO) - \Delta H_f(Ph_2CH^+) - \Delta H_f(HCO^{\bullet})$$

where $\Delta H_f(Ph_2CHCHO)$ (=9.01 kcal mol^{-1}) was calculated according to Franklin's additivity rule[26] with group equivalent values, and $I_p(Ph_2CHCHO)$ (=9.03 eV) was obtained according to Miller's equation[27] using the oxidation potential of Ph_2CHCHO in acetonitrile. Although the estimation is made for the gas phase, it is reported that bond dissociation energies of cation radicals in the gas phase are often similar to those in solution.[28] R.A. thanks Professor S. Tobita for his helpful discussion on the thermochemistry of decompositions of gaseous ions.

(26) Franklin, J. L.; Dilland, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. In *Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions*; NBS: Washington, DC, 1969.

(27) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916.

(28) Wayner, D. D. M.; Dannenberg, J. J.; Griller, D. *Chem. Phys. Lett.* **1986**, *131*, 189.

(29) (a) Bodner, G. S.; Gladysz, J. A.; Nielsen, M. F.; Parker, V. D. *J. Am. Chem. Soc.* **1987**, *109*, 1757 and references cited therein.

would provide deeper insight into photoinduced cation radical generation and the subsequent bond-cleavage processes.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL 90-FX, a Varian Gemini 200 and/or a Bruker AM-300 NMR spectrometer in $CDCl_3$ and reported in parts per million downfield from TMS. Mass spectra were recorded with a Hitachi M-80A GC–MS system with an ionization voltage of 70 eV. Fluorescence spectra were measured with a Hitachi F-4000 fluorescence spectrophotometer in dichloromethane under argon atmosphere. Oxidation potentials were measured by cyclic voltammetry (CV) in a four-necked CV cell with a platinum disk as a working electrode, a platinum wire as a counter electrode, and a saturated calomel or Ag/AgCl electrode as a reference electrode. A Hokuto HA501 potentiostat/galvanostat, a Hokuto HB104 function generator, and a YEW Model XY recorder were used for the measurements. GLC analyses were carried out with a Shimadzu GC-7A gas chromatograph equipped with a thermal conductivity detector and/or a Shimadzu GC-6AM gas chromatograph equipped with a flame ionization detector. Laser flash photolyses (LFP) were carried out with an excimer laser (Lambda Physik EMG-101, XeCl 308 nm)–pumped dye laser (Lambda Physik FL-3002, DPS Dye, 10 mJ/pulse) at ambient temperature, and the details were described elsewhere.[30]

Materials. 2,4,6-Triphenylpyrylium tetrafluoroborate was commercially available and was recrystallized twice from ethanol before use. The pyrylium perchlorate and hexafluorophosphate were prepared according to the modified procedures of the published methods.[31] Diphenylethanal (**1**), 1,1-diphenyl-2-propanone (**4**), and tetraphenylethanone (**5**) were commercially available. **1** was used as received. **4** and **5** were recrystallized twice from ethanol before use. 1,2,2-Triphenylethanone (**2**),[32] 1,2-diphenyl-1-propanone (**3**),[32] and 1,1,1-triphenylethanal (**6**)[33] were synthesized according to the published procedures, and their IR, ^{1}H NMR, and ^{13}C NMR spectra were consistent with the assigned structures.

Solvents used for the photochemical reactions and cyclic voltammetry were purified as follows. Dichloromethane was washed with sulfuric acid and water, distilled from calcium hydride, and stored over molecular sieves (Wako synthetic zeolite). Acetonitrile was distilled first from phosphorus pentoxide and then from potassium carbonate and stored over the molecular sieves. Dichloromethane for the spectral studies involving LFP was spectral grade Luminasol (Wako) or Uvasol (Merck) and used as received.

Tetrakis(4-methylphenyl)ethanone.[34] 4,4′-Dimethylbenzophenone (14.8 g, 0.07 mol) was dissolved in 1 L of 2-propanol, and a drop of acetic acid was added. The resulting solution was exposed directly to sunlight for 8 days. Evaporation of solvent gave practically pure 1,1,2,2-tetrakis(4-methylphenyl)-1,2-ethanediol (14.8 g, 100%) as a colorless solid. Recrystallization from hexane/dichloromethane gave colorless prisms: mp 179–180 °C (lit.[35] mp 183–184 °C). The ethanediol thus obtained (14.0 g, 0.03 mol) was heated in acetic acid (150 mL) containing iodine (100 mg) for 5 min until all solid materials were dissolved, and the resulting red solution was refluxed for 30 min. The reaction mixture was then poured into water (300 mL). A colorless solid was separated, collected, and recrystallized twice from ethanol to give tetrakis(4-methylphenyl)ethanone as colorless prisms (5.84 g, 44%): mp 140–141 °C (lit.[36] mp 137–138 °C); ^{1}H NMR (90 MHz) δ 2.26 (s, 3 H, CH_3), 2.29 (s, 9 H, CH_3), 6.64–7.20 (m, 14 H, Ar H), 7.44–7.68 (m, 2 H, Ar H); IR (KBr) 3035, 2995, 2879, 1678 (C=O), 1605, 1573, 1504, 1442, 1408, 1221, 1190, 1177, 1120, 1035, 1020, 803, 790, 763, 732 cm^{-1}.

Anal. Calcd for $C_{30}H_{28}O$: C, 89.07; H, 6.98. Found: C, 88.74; H, 6.95.

Photochemical Reactions. Photosensitized electron transfer reactions were carried out in CH_2Cl_2 or CH_3CN solution in a substrate concentration of ca. 5×10^{-2} M and a sensitizer concentration of ca. 5×10^{-3} M unless otherwise indicated. The solution was placed in a ca. 15-mm internal diameter Pyrex tube immersed in a water-cooled bath, and oxygen was bubbled through the solution during the course of the reactions. A Riko 400-W high-pressure mercury lamp was employed as an excitation light source, and a Toshiba L-39 glass cut filter (>360 nm) was used to excite the sensitizers selectively. The oxygenation products were isolated and fully characterized by GC–MS analysis, ^{1}H NMR, and/or ^{13}C NMR spectra, unless otherwise indicated. Yields of the products were determined by GLC with an internal reference, and the sensitivity differences between the products and references (biphenyl or naphthalene) for flame ionization and thermal conductivity detections were corrected. In the case of 4-methylbenzoyl fluoride, the calibration line of benzoyl fluoride was used for the correction.

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Registry No. **1**, 947-91-1; **2**, 1733-63-7; **3**, 2042-85-5; **4**, 781-35-1; **5**, 466-37-5; **6**, 42365-04-8; **7**, 19920-02-6; $TPPBF_4$, 448-61-3; 4,4′-dimethylbenzophenone, 611-97-2; 1,1,2,2-tetrakis(4-methylphenyl)-1,2-ethanediol, 913-86-0.

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(30) Furuuchi, H.; Arai, T.; Sakuragi, H.; Tokumaru, K. *Chem. Phys. Lett.* **1989**, *162*, 211.

(31) Vanallan, J. A.; Reynolds, G. A. *J. Org. Chem.* **1968**, *33*, 1102.

(32) Heine, H.-G.; Hartmann, W.; Kory, D. R.; Magyar, J. G.; Hoyle, C. E.; McVey, J. K.; Lewis, F. D. *J. Org. Chem.* **1974**, *39*, 369.

(33) Cope, A. C.; Trumbull, P. A.; Trumbull, E. R. *J. Am. Chem. Soc.* **1958**, *80*, 2844.

(34) Bachmann, W. E. *Organic Syntheses*; John Wiley & Sons, Inc.: New York, 1943, Collect. Vol. II, pp 71–74.

(35) Gomberg, M.; Bachmann, W. E. *J. Am. Chem. Soc.* **1927**, *49*, 236.

(36) Kitagawa, T.; Takeuchi, K.; Murai, O.; Matsui, S.; Inoue, T.; Nishimura, M.; Okamoto, K. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1987.