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Photoinduced Electron-Transfer Oxygenation of Arylalkanes. Generation and Oxygenation Pathways of Benzylic-Type Free Radicals from the Cation Radical Deprotonation

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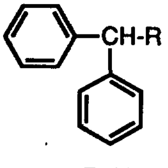
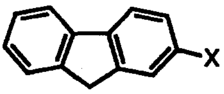
Abstract: *2,4,6-Triphenylpyrylium tetrafluoroborate(TPP$^+$)-sensitized oxygenation has been carried out for several arylalkanes in dichloromethane. Direct evidence for deprotonation of a cation radical was obtained, and interesting structural effects on the deprotonation efficiency was observed.*

Chemistry of cation radicals generated by photoinduced electron transfer (PET) has attracted considerable interest in recent years.[1] Although several groups have reported photoinduced or electrochemically induced deprotonation of cation radicals,[2] there have been few approaches so far to get insight into this important reactions by examining oxygenation of the cation radical-derived free radicals.[2b]

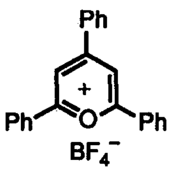
We have recently shown that 2,4,6-triphenylpyrylium tetrafluoroborate (TPP$^+$BF$_4^-$) is a unique sensitizer to generate organic cation radicals in solution.[3] TPP$^+$ has also been found useful to generate the cation radicals of compounds with higher oxidation potentials (>2.0 V/SCE) such as ketones and aldehydes.[4] In a preliminary form, we wish to report here our results on TPP$^+$BF$_4^-$-sensitized electron-transfer oxygenation of several arylalkanes in dichloromethane. The present study is based on a combined approach of product studies in the presence of oxygen and laser flash photolysis (LFP) to elucidate the nature of deprotonation reactions of the arylalkane cation radicals.



1: R=H
2: R=Ph



3: X=H
4: X=Br



TPP$^+$ BF$_4^-$

Typically, irradiation of a dichloromethane solution of diphenylmethane **1** (5×10^{-2} M) in the presence of TPP$^+$ (5×10^{-3} M) by a 400-W high-pressure mercury lamp with a glass cut filter (>360 nm) with bubbling oxygen for 2.5 h gave benzophenone in 94% yield (100% conversion). Photooxygenation of **1** (5×10^{-2} M) in the presence of lower concentration of TPP$^+$ (1×10^{-3} M) under otherwise the same conditions for 1.5 h gave benzo-

Table 1. Results of TPP$^+$-Sensitized Oxygenation of Aralkyl Hydrocarbons **1**–**4** in CH_2Cl_2,[a] Oxidation Potentials in CH_3CN, and Fluorescence Quenching Rate Constants (k_q) in CH_2Cl_2.

Compound	TPP$^+$ /M	Reaction Time/h	Conversion /%	Product Yield/%[b]	Oxidation Potential/V[c]	k_q /M^{-1} s^{-1}	ΔG /kcal mol^{-1}
1	1×10^{-3}	1.5	40	benzophenone 76	2.18	1.5×10^{10}	−6.0
1	5×10^{-3}	2.5	100	benzophenone 94			
2[d]	5×10^{-3}	2.5	95	benzophenone 78	2.33	1.3×10^{10}	−2.5
3	6×10^{-3}	2.5	21	fluorenone not detected	1.79	3.5×10^{10}	−15.0
3[e]	5×10^{-3}	2.5	18	fluorenone not detected			
3[f]	5×10^{-3}	0.8	30	fluorenone not detected			
4	5×10^{-3}	2	95	2-bromofluorenone 65	1.89	3.2×10^{10}	−12.7

a) All reactions were carried out with a 400-W high-pressure mercury lamp with bubbling oxygen at water-running temperature unless otherwise indicated. b) Based on the hydrocarbons consumed. c) V vs. SCE. d) Phenol was also obtained in 48% yield. e) With tetrabutylammonium perchlorate (0.5 M). f) A 2-kW Xe lamp was employed for excitation.

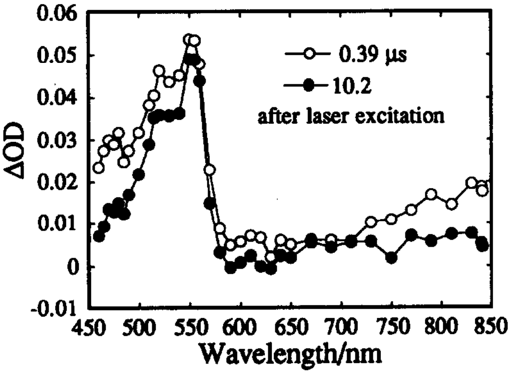


Figure 1. Transient absorption spectra obtained on LFP of TPP$^+$ (6.4×10^{-5} M) in the presence of **2** (2.9×10^{-2} M) in CH_2Cl_2 under argon.

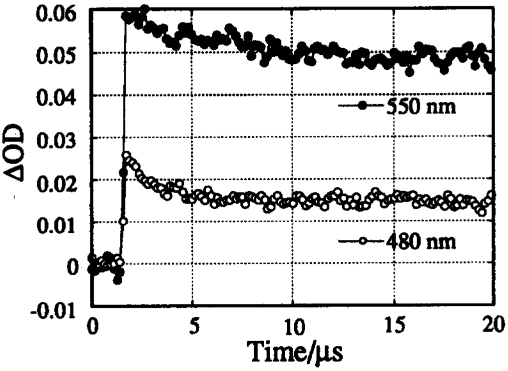


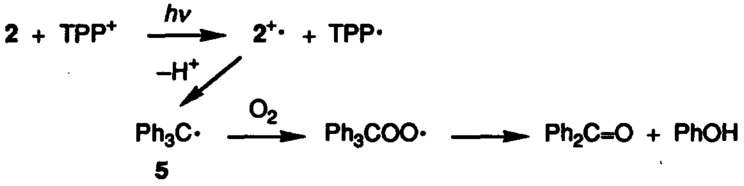
Figure 2. Time profiles at 480 and 550 nm. For conditions, see the caption of Figure 1.

phenone in 76 % yields (based on **1** consumed, 40%) with complete TPP$^+$ bleaching. The results suggest that TPP$^+$ actually acts as a catalyst, and ca. 20 times less TPP$^+$ than **1** was consumed. Similar oxygenation was also carried out for triphenylmethane **2**, fluorene **3**, and 2-bromofluorene **4**, and the results were summarized in Table 1. Oxidation potentials in CH_3CN and fluorescence quenching rate constants (k_q) in CH_2Cl_2 for **1**–**4** are also tabulated in Table 1 together with free energy changes (ΔG) associated with the electron transfer from **1**–**4** to the excited singlet state of TPP, $^1TPP^{+*}$.

Table 1 shows that **1** and **2** are reactive to give benzophenone, while **3**, a planar analogue of **1**, does not give any amount of fluorenone. Neither irradiation of **3** in the presence of tetrabutylammonium perchlorate (0.5 M), which may increase the yield of free radical ions,[5] nor the irradiation with a higher light intensity (2-kW Xe lamp) afforded fluorenone (columns 5 and 6 in Table 1). It is also noted that, while **3** failed to give fluorenone, a 2-bromo group greatly accelerates the oxygenation, as is shown by the formation of 2-bromofluorenone from **4** in a modest yield.

In order to obtain direct evidence for PET and for the subsequent deprotonation of the cation radicals, LFP of **2** and **3** has been carried out in CH_2Cl_2. LFP of TPP$^+$ (6.4×10^{-5} M) in the presence of **2** (2.9×10^{-2} M) with an excimer laser-pumped dye laser (425 nm) under argon, where ca. 50% of $^1TPP^{+*}$ was quenched by 2,[6] exhibited transient absorption spectra shown in Figure 1. The absorption band centered at 550 nm with a shoulder at ca. 515 nm is readily assigned to the absorption of pyryl radicals (TPP·), one-electron reduced species of TPP^+.[7] The relatively small but significant absorption at ca. 480 nm together with a lower-intensity band starting from ca. 700 nm are also safely assigned to $2^{+\cdot}$ on the basis of the reported results.[8] Quite interestingly, the 480-nm band was found to decay much more rapidly than the 550-nm band (TPP·). The time profiles shown in Figure 2 clearly indicate that the 480-nm band decays completely within ca. 4 μs while during that time the 550-nm band decays only 10% to its original intensity. The observed absorption at the flat region of 480 nm is attributed to the absorption of TPP·. These results support that the initial electron transfer takes place from 2 to $^1TPP^{+*}$, generating TPP· and $2^{+\cdot}$, followed by rapid deprotonation of $2^{+\cdot}$ to give triphenylmethyl radical 5 though the ground state absorptions of TPP^+ and 2 hampered its spectral detection.[9] The 480-nm band was found to fit nicely first-order kinetics to give a deprotonation rate constant for $2^{+\cdot}$ in CH_2Cl_2 to be 5×10^5 s^{-1} (τ = 2 μs). In view of the large difference in reactivity between 3 and other hydrocarbons, LFP of 3 was also performed. LFP of TPP^+ (5.8×10^{-5} M) in the presence of 3 (4.6×10^{-2} M) in CH_2Cl_2, where ca. 80% of $^1TPP^{+*}$ was quenched by 3, gave the transient spectra (not shown) which exhibits the absorption bands attributed to TPP· and fluorene cation radicals $3^{+\cdot}$ (640 nm).[10] However, the decays of these two bands are similar to each other, and no evidence was found that indicates deprotonation of $3^{+\cdot}$.

On the basis of the above results, we propose the following mechanism for the product formation with 2 as a prototype as shown in Scheme 1. Thus, irradiation of 2 in the presence of TPP^+ generates $2^{+\cdot}$, which deprotonates to afford 5. The resulting 5 reacts with molecular oxygen to give rise to a triphenylmethylperoxyl radical, which further decomposes to give benzophenone and phenol finally.[11] A similar mechanism may explain the formation of the observed products from 1 and 4.



$$\begin{tikzcd}
2 + TPP^+ \arrow[r, "h\nu"] & 2^{+\cdot} + TPP\cdot \arrow[dl, "-H^+"'] & & \\
\underset{5}{Ph_3C\cdot} \arrow[r, "O_2"] & Ph_3COO\cdot \arrow[r] & Ph_2C{=}O + PhOH &
\end{tikzcd}$$

Scheme 1

The fact that 1, 2, and 4 gave the respective carbonyl compounds while 3 failed to afford fluorenone deserves attention in view of their structures and of the high thermodynamic acidity of $3^{+\cdot}$ ($pK_a = -17$) and $4^{+\cdot}$ (−17).[12] The product and LFP results suggest that $3^{+\cdot}$ formed is not kinetically acidic enough to undergo deprotonation to afford the fluorenyl radical.[13] It is also of interest to note that $4^{+\cdot}$, which was found to be reactive, has the same pK_a as $3^{+\cdot}$. Apparently, the 2-bromo group in the fluorene skeleton increases the kinetic acidity, which eventually results in the deprotonation.

In conclusion, we have shown that TPP^+ is useful to generate the cation radicals of hydrocarbons whose oxidation potentials are relatively high (>2.0 V/SCE) such as 1 and 2, and to follow their subsequent deprotonation. We have also demonstrated that the thermodynamic acidity (pK_a) does not necessarily predict the kinetic acidity of the cation radicals as observed in the present PET-deprotonation-oxygenation sequence in solution. Works are now under way to shed more light onto the cation radical-derived oxygenation reactions.

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6 **2** would not undergo the electron transfer with ^{3}TPP^{+} since ΔG associated with the electron transfer from **2** to ^{3}TPP^{+} is moderately endothermic (+9. 0 kcal mol^{-1}).[3b-d]

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13 Preliminary molecular orbital calculations (PM3-UHF) suggest that the positive charge is developed on the ipso-carbon in $\mathbf{1}^{+\cdot}$, which may enhance the deprotonation while such situation could not be observed in $\mathbf{3}^{+\cdot}$. Details will be reported elsewhere.

14 We thank Mr. M. Ogata (Upjohn Pharmaceuticals, Co. Ltd.), Professor A. Sugawara, and Dr. T. Segawa (Tsuruoka College of Technology) for their measuring NMR spectra. Professor S. Tajima and Mr. K. Ogino kindly performed GC-MS experiments.

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