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Phenylcyclopropane Cation Radical Revisited: Generation, Direct Observation and Determination of the Rates of Nucleophilic Capture

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Abstract: Phenylcyclopropane cation radical can be generated by photoinduced electron transfer and the rate constants for its nucleophilic capture by methanol and *t*-butanol are determined to be k_{MeOH} 1.1—1.2 × 10^7 and $k_{t\text{-}\mathrm{BuOH}}$ 5.3—5.4 × 10^6 $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, respectively.

The cation radicals of phenylcyclopropanes can be generated by photoinduced electron transfer in solution and they are known to undergo ring opening in the presence of nucleophiles such as methanol.[1—3] The reactions of this type have received considerable attention from synthetic and mechanistic view points and are now recognized as three-electron S_N2 reactions.[2c] On the other hand, only a limited number of investigations[2a,c] have been made as to the direct observation of the cation radical intermediates and measurement of the rates of nucleophilic capture. Herein, we report our experimental results which provide rate constants for nucleophilic capture of phenylcyclopropane cation radical **1**$^{\bullet+}$.

Cation radical **1**$^{\bullet+}$ was generated by pulsed laser flash photolysis (Nd:YAG, 355 nm) of acetonitrile solutions of phenylcyclopropane **1** using either *p*-chloranil (CA) or 9,10-dicyanoanthracene (DCA) as a light-absorbing acceptor. Quenching experiments showed that the triplet excited CA (^{3}CA*) and the singlet excited DCA (^{1}DCA*) were quenched by **1** in acetonitrile with rate constants of 3 × 10^9 and 1.0 × 10^{10} $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, respectively.

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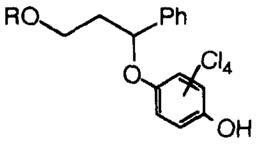
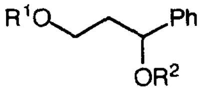


2a: R = Me
2b: R = *t*-Bu

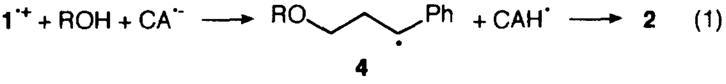


3a: $R^1 = R^2$ = Me, **3b**: $R^1 = R^2$ = *t*-Bu,
3c: R^1 = Me, R^2 = *t*-Bu, **3d**: R^1 = *t*-Bu, R^2 = Me

Fig. 1 shows the transient absorption spectra obtained by laser flash photolysis of an acetonitrile solution of **1** and CA with varying concentration of methanol, 0—2.5 mol $\mathrm{dm^{-3}}$. In the absence of methanol the spectrum consists of two absorption bands (Fig. 1 (*a*)). An absorption at $\lambda_{\max}$ 450 nm with a shoulder at 425 nm is due to anion radical of CA (CA$^{\bullet-}$), which is well known.[4] Another broad absorption with apparent maximum at 530 nm can be assigned as being due to $\mathbf{1}^{\bullet+}$. In support of this assignment is that addition of methanol leads to its depletion as shown in Fig. 1 (*b* – *d*). It is noteworthy that the absorption due to $CA^{\bullet-}$ (450 nm) was also depleted upon addition of methanol and a new absorption appeared at 439 nm (Fig. 1 (*d*)). The newly developed absorption is comparable with the authentic absorption of the semiquinone radical ($CAH^{\bullet}$, λ_{max} 435 nm).[4,5] Similar phenomena were also observed by using *t*-butanol.

We have found that steady-state photolysis of a solution of **1** and CA in acetonitrile containing methanol or *t*-butanol (typically 2.5 mol dm^{-3}) resulted in the formation of composite adducts **2a**[3b] and **2b** in 81 and 54% isolated yields, respectively. The above observations are consistent with the results from the steady-state photoreactions and are in line with the mechanism in eq. (1). The second order rate constant for reaction of $\mathbf{1}^{\bullet+}$ with methanol (k_{MeOH}) was determined to be 1.1×10^7 dm^3 mol^{-1} s^{-1} at 25 °C from the slope of a plot shown in the inset of Fig. 1, where k_{obs} is the decay rate of $\mathbf{1}^{\bullet+}$ monitored at 560 nm.[6] In a similar manner the second order rate constant for reaction with *t*-butanol ($k_{t\text{-}BuOH}$) was obtained to be 5.4×10^6 dm^3 mol^{-1} s^{-1}.

Laser flash photolysis of the **1** – DCA system in acetonitrile also resulted in $\mathbf{1}^{\bullet+}$ (Fig 2, inset). In this case the absorbance due to $\mathbf{1}^{\bullet+}$ (537 nm) was relatively low and overlapping with the absorption due to $DCA^{\bullet-}$ (705, 640 and 500 nm). Oxygen saturation to remove $DCA^{\bullet-}$ is not good enough for kinetic experiments. We



(1)

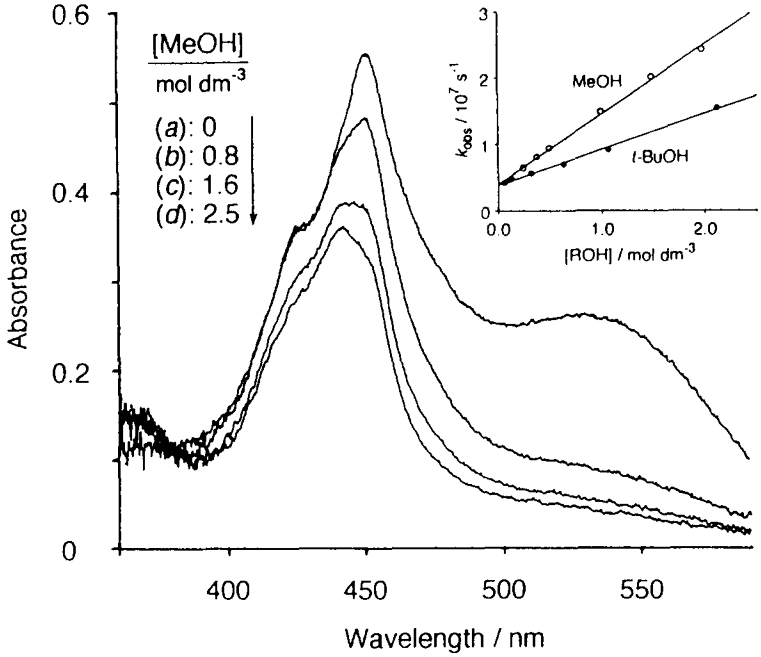
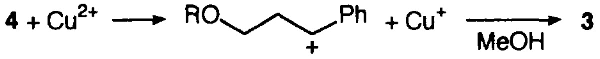


Fig. 1 Transient absorption spectra at 50 ns after the laser flash photolyses of acetonitrile solutions of **1** (1×10^{-2} mol dm^{-3}), CA (4×10^{-3} mol dm^{-3}) and methanol. The inset shows plots of the decay rate monitored at 560 nm *vs.* concentration of added methanol or *t*-butanol.

found that addition of $Cu(BF_4)_2$ resulted in complete depletion of $DCA^{\bullet -}$. Thus the spectrum of $1^{\bullet +}$ became ideal for kinetic experiments (Fig. 2). The rate constants, k_{MeOH} and $k_{t\text{-}BuOH}$, were obtained in a similar manner as described above: $k_{MeOH} = 1.2 \times 10^7$ and $k_{t\text{-}BuOH} = 5.3 \times 10^6$ dm^3 mol^{-1} s^{-1}. These values are in excellent agreement with those obtained by using CA. Steady-state photolysis of a solution of **1**, DCA and $Cu(BF_4)_2$ in acetonitrile containing methanol[7] or *t*-butanol resulted in the formation of **3a** or **3b** in 93 or 86% yield. Apparently Cu^{2+} oxidizes not only $DCA^{\bullet -}$ but also intermediate radical **4**.



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(2)

Finally, competition experiments were carried out in order to confirm the identity of the actual intermediate in pulsed laser photolysis and steady-state photolysis experiments. If the rate constants determined above are correct, competitive photoreactions by using solutions containing an equimolar mixture of methanol and *t*-butanol should give a mixture of **2a** and **2b** in a ratio of $k_{MeOH}/k_{t\text{-}BuOH}$, which is calculated to be 2.0. Indeed, photolysis of the **1**—CA system ($\lambda > 305$ nm) with the alcohols afforded a mixture of **2a** and **2b** in 63 and 27% yield, respectively.[8] The **2a**/**2b** ratio of 2.3 is in good agreement with the prediction from the rate constants. Similar competitive photoreaction of **1** with DCA and $Cu(BF_4)_2$ ($\lambda > 360$ nm) afforded a mixture of **3a—d**,[9]

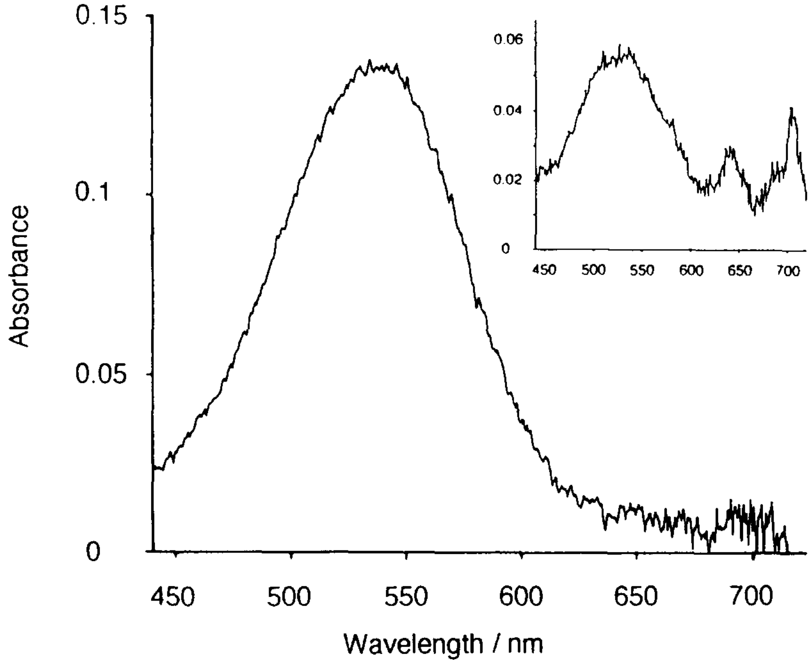

Fig. 2 Transient absorption spectrum at 100 ns after the laser flash photolysis of a solution of **1** (3×10^{-2} mol dm^{-3}), DCA (1×10^{-4} mol dm^{-3}) and $Cu(BF_4)_2$ (1.5×10^{-2} mol dm^{-3}) in acetonitrile. The inset is a spectrum observed upon similar flash photolysis of the **1**—DCA system without $Cu(BF_4)_2$.

whose yields were 30, 4, 5 and 12%, respectively. Again the (**3a** + **3c**)/(**3b** + **3d**) ratio of 2.2 is in good agreement with the prediction from the $k_{MeOH}/k_{t\text{-}BuOH}$ ratio of 2.3 obtained by laser flash photolysis experiments using the **1**—DCA—$Cu(BF_4)_2$ system.

In this study the same reaction systems were utilized in the flash photolyses as well as the steady-state photolysis experiments. As described above, the results from both sets of experiments are in accord with each other. Thus we believe that the present study provides correct values of rate constants for nucleophilic cleavage of $\mathbf{1}^{\bullet+}$ with methanol and *t*-butanol.[10]

Further studies are in progress on the photoinduced electron-transfer reactions of **1** and its derivatives with other nucleophiles. We thank the Ministry of Education, Science, and Culture (Grant No. 06453032 and 07640701) for financial support.

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5 Consistent with the mechanism in eq. (1), the decay monitored at 439 nm followed second-order kinetics with the rate constant of 2.5×10^9 dm^3 mol^{-1} s^{-1} at 25 °C.

6 In order to avoid the tail absorption due to $CA^{\bullet-}$, 560 nm was used as a monitoring wavelength instead of the apparent maxima, 530 nm.

7 Photoinduced nucleophilic cleavage of **1** by using DCA and $Cu(BF_4)_2$ was first reported by Mizuno *et al.*[1c]

8 Typically, a 10 ml acetonitrile solution containing **1** (0.10 mmol), alcohols (2.0 mol dm^{-3} each), and an acceptor (0.10 mmol of CA, or 0.007 mmol of DCA with 0.20 mmol of $Cu(BF_4)_2$) was irradiated by using a 2 kW xenon lamp at 25 °C.

9 Conversion was *ca.* 60%. Formation of **3c** and **3d** is due to the reaction of intermediate **5** with methanol and *t*-butanol, respectively.

10 Recently, Dinnocenzo *et al.*[2a] reported the k_{MeOH} and $k_{t\text{-}BuOH}$ values to be 9.5×10^7 and 1.8×10^7 dm^3 mol^{-1} s^{-1}, which were significantly higher than our values. Apparently there has been a discrepancy to be resolved. Quite recently, however, we have been informed by Prof. Dinnocenzo that they have remeasured the rates and obtained values more or less close to ours.

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