

Triplet-state Electron-transfer Reactions of Phenylcyclopropane with Quinones

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Photoinduced electron-transfer reactions of phenylcyclopropane **1** with quinones afford cycloadducts **2** and **4** through triplet ion pairs as possible intermediates.

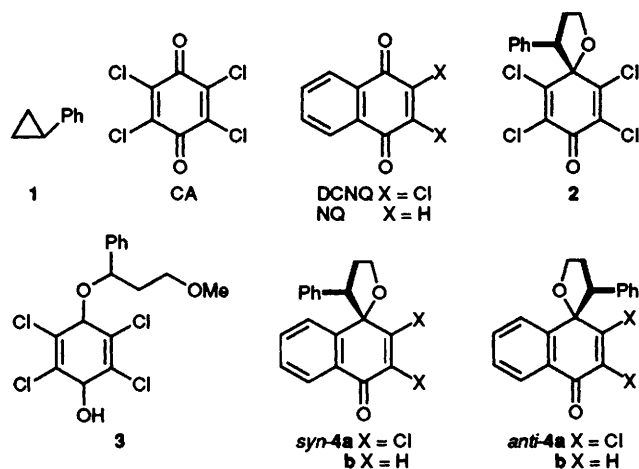
Fluorescence quenching in a polar solvent, acetonitrile, has often been employed to investigate the electron-transfer (ET) photochemistry of arylcyclopropanes.¹ Although singlet ET reactions are sometimes frustrated by fast back ET, nucleophilic cleavage and cycloaddition of arylcyclopropanes can be induced by using singlet acceptors such as cyanoaromatics and phthalimides.

On the other hand, little work has been done on the triplet state ET reactions of arylcyclopropanes. Quinones in the excited triplet state are good acceptors and their utilization for ET induced reactions seems to be more effective and advantageous since back ET deactivation may be minimized by spin inhibition.² We have investigated the triplet state ET reactions of phenylcyclopropane **1** with quinones such as chloranil (CA), 2,3-dichloro-1,4-naphthoquinone (DCNQ), and naphthoquinone (NQ) and found that both solvent polarity and electron-accepting ability of excited quinones are crucial for the formation of cycloadducts **2** and **4**.

Phenylcyclopropane **1** is a good electron donor and the exothermic ET quenching of excited triplet CA (³CA*) is possible. Quenching experiments showed that ³CA* can be efficiently quenched by **1** (k_q 3.9×10^9 dm³ mol⁻¹ s⁻¹) in methylene chloride. When a 10 cm³ solution of **1** and CA (0.10 mmol each) in methylene chloride was irradiated for 30 min, cycloadduct **2** was obtained in 68% isolated yield.† Similar photolysis in benzene also afforded adduct **2** in 64% yield. A preliminary experiment showed that the quantum yield based on the consumption of CA was 0.9 at 366 nm irradiation in methylene chloride. In contrast, only 5% yield of **2** could be obtained in acetonitrile under comparable photolysis conditions despite the fact that both **1** and CA were consumed and that ³CA* was also efficiently quenched by **1** in acetonitrile (k_q 3×10^9 dm³ mol⁻¹ s⁻¹). In the presence of methanol (2.5 mol dm⁻³), however, a novel composite adduct **3** was obtained in 81% yield.†‡

These results indicate that solvent polarity plays a decisive role for the product formation. A simple explanation for these observations is given by invoking triplet ion pairs [**1**^{·+}, CA^{·-}] as intermediates for the formation of **2**. In acetonitrile, ion pairs may be solvated to free ions, so that the formation of **2** becomes disadvantageous.

As shown in Fig. 1(a), we were able to observe transient absorption spectrum due to free ions, CA^{·-} (450 nm) and **1**^{·+} (530 nm) by laser flash photolysis experiments (YAG, 355 nm)



with the **1**-CA system in acetonitrile. The decay monitored at 450 nm (CA^{·-}) followed second-order kinetics with the rate constant of k 6.3×10^9 dm³ mol⁻¹ s⁻¹. The absorption band at 530 nm (**1**^{·+}) was depleted by the addition of 2.5 mol dm⁻³ of methanol. In the absence of methanol **1**^{·+} disappeared faster than CA^{·-} with k 2.4×10^6 s⁻¹, which according to Dinnocenzo *et al.*^{1d} is possibly due to a nucleophilic reaction of **1**^{·+} with the solvent, acetonitrile. These observations are consistent with the result that the low-yield formation of **2** in acetonitrile is replaced by the high-yield formation of **3** on addition of methanol. In methylene chloride much weaker absorptions were observed with the apparent maximum at 448 nm and a tail absorption ranging from 500 to 600 nm. We tentatively assign these absorptions as being due to triplet ion pairs since the decay profile monitored at 448 nm followed principally first-order kinetics with the rate constant of 7.2×10^6 s⁻¹. Moreover, the decay rate became faster (k 1.6×10^7 s⁻¹) with aeration, which is consistent with a triplet multiplicity of the ion pairs. In less polar solvents electron donors such as arenes^{3a-d} and allenes^{3e} are known to form triplet excited complexes with varying degrees of charge transfer.

When we examined the photoreaction of **1** with DCNQ, it was found that cycloadducts *syn*-**4a** and *anti*-**4a** were obtained in acetonitrile in 18 and 17% yield, respectively.† Similar photoreaction in methylene chloride also afforded *syn*- and *anti*-**4a** in 18% yield each. In benzene, however, no formation of the adducts was observed. The ET quenching rates (k_q) decrease from 1×10^9 to 1.2×10^7 to 6.1×10^6 dm³ mol⁻¹ s⁻¹ with decreasing solvent polarity from acetonitrile to methylene chloride to benzene. Similar photoreaction of **1** with NQ in acetonitrile also led to the formation of adducts *syn*- and *anti*-**4b** in 9% yield each.† In methylene chloride, no formation of the adducts was observed.§ The k_q values were 3.1×10^9 and 2.3×10^9 dm³ mol⁻¹ s⁻¹ in acetonitrile and methylene chloride, respectively.

Laser flash photolysis of the **1**-DCNQ system in acetonitrile resulted in transient absorption spectrum with maxima at 402 and 478 nm, and a shoulder around 550 nm [Fig. 1(b)]. The former two maxima are due to anion radical DCNQ^{·-},^{4a} and the latter shoulder can be assigned as being due to **1**^{·+}. The

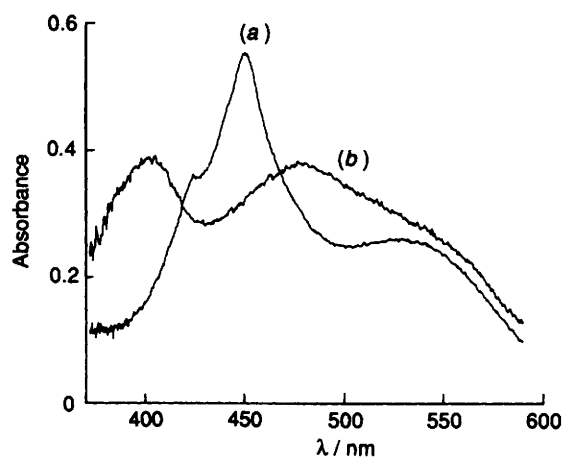


Fig. 1 Transient absorption spectra at 50 ns after the laser flash photolyses of acetonitrile solutions of (a) **1** (5×10^{-2} mol dm⁻³) and CA (4×10^{-3} mol dm⁻³) and (b) **1** (5×10^{-2} mol dm⁻³) and DCNQ (1×10^{-3} mol dm⁻³)

decay profile of $\text{DCNQ}^{\cdot-}$ was biphasic with a fast first-order process followed by a second-order decay. The rate constants for the initial first-order decay and the second-order decay for $\text{DCNQ}^{\cdot-}$ (402 nm) were determined to be $1.8 \times 10^6 \text{ s}^{-1}$ and $9.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. For $1^{\cdot+}$, the decay profile was first order and the rate constant was determined to be $2.6 \times 10^6 \text{ s}^{-1}$.[¶] The fact that the decay of $1^{\cdot+}$ is faster than that of $\text{DCNQ}^{\cdot-}$ may again be due to a nucleophilic reaction of $1^{\cdot+}$ with the solvent, acetonitrile. However, it is noteworthy that the decay of $\text{DCNQ}^{\cdot-}$ contains an initial first order process. This is likely due to decay of ion pairs [$1^{\cdot+}$, $\text{DCNQ}^{\cdot-}$] involving product formation and back ET process.

In addition to solvent polarity, electron-accepting ability of quinones is also an important factor for the adduct formation. There may be a subtle mechanistic difference in the initial ET quenching process depending on the quinones. It is conceivable that the ET quenching of ${}^3\text{CA}^*$ by **1** may occur over longer donor-acceptor distances in acetonitrile to facilitate the production of free ions since the values of free energy change (ΔG) for the ET quenching process is highly exothermic, -42 kJ mol^{-1} .[¶] Under the circumstances the formation of contact ion pairs may be bypassed. On the other hand, DCNQ and NQ are weaker acceptors than CA as indicated by the calculated ΔG values of -29 and -4 kJ mol^{-1} for the ET quenching of ${}^3\text{DCNQ}^*$ and ${}^3\text{NQ}^*$ by **1** in acetonitrile, respectively.[¶] Accordingly, the ET quenching of ${}^3\text{DCNQ}^*$ and ${}^3\text{NQ}^*$ by **1** may proceed with initial formation of ion pairs in a contact form even in acetonitrile.

When both electron-accepting ability of a quinone and the solvent polarity are lower, the initial quenching may proceed with the formation of triplet exciplexes the ionic character of which is not high enough to be classified as ion pairs. As described above, DCNQ failed to give cycloadducts **4a** in benzene while the quenching rate constant is only half of the value in methylene chloride. For NQ , adducts **4b** were formed in acetonitrile but not in methylene chloride despite the fact that the k_q value in methylene chloride is not so small compared with that in acetonitrile.

As has been observed in the photochemistry of quinones with arylalkenes,⁴ degree of charge transfer in an intermediate state is an important factor. In the present cases it is most likely that quinone anion radicals in the photogenerated triplet ion pairs serve as nucleophiles to form cycloadducts **2** and **4**. Not only elongation of the interionic distance but also reduction of the ion pair character would significantly retard the in-cage ionic reaction.

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Footnotes

† Solutions in Pyrex test-tubes were irradiated by using four RUL 3500 lamps. Satisfactory elemental analyses were obtained for all new compounds. They were fully characterized by NMR (${}^1\text{H}$, NOE, ${}^{13}\text{C}$), IR, and MS spectra. Details will be presented in a full paper. **2**, mp 159.0–159.5 °C. **3**, mp 132–133 °C. *syn-4a*, mp 184 °C. *anti-4a*, mp 136 °C. *syn-4b*, mp 131 °C. *anti-4b*, mp 151–152 °C.

‡ The photoreaction of **1** with *N*-methylphthalimides affords cycloadducts and composite adducts analogous to **2** and **4**.^{1c}

§ No reaction was observed in benzene. The lifetime of ${}^3\text{NQ}^*$ in benzene is too short (*ca.* 1 ns or shorter) for preparative photolysis.

¶ The monitoring wavelength was 590 nm, where the absorption due to $\text{DCNQ}^{\cdot-}$ is significantly weak. When monitored at 550 nm, k was $3.0 \times 10^6 \text{ s}^{-1}$.

|| Triplet excited energies of CA , DCNQ and NQ are 205, 242 and 242 kJ mol^{-1} . Reduction potentials of CA , DCNQ and NQ are 0.00, -0.45 and -0.71 V (vs. SCE in MeCN). Oxidation potential of **1** is $+1.81 \text{ V}$ (vs. SCE in MeCN).

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