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Photoinduced Electron Transfer from Triphenylmethyl Anion or Triphenylsilyl Anion to *p*-Terphenyl

By OSAMU ITO,* TAMOTSU ARUGA AND MINORU MATSUDA

Chemical Research Institute of Non-aqueous Solutions, Tohoku University,
Katahira, Sendai 980, Japan

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The steady illumination of triphenylsilyl anion and *p*-terphenyl (*p*-TP) in tetrahydrofuran yielded the radical anion of *p*-terphenyl (p-TP$^{\cdot -}$), which persisted after cutting off the light. When the triphenylmethyl anion was used, p-TP$^{\cdot -}$ was not observed with the steady illumination; the finding that p-TP$^{\cdot -}$ observed transiently by flash photolysis decayed at a diffusion-controlled rate suggests that the stable triphenylmethyl radical, produced after the donation of an electron to *p*-TP, accepts an electron from p-TP$^{\cdot -}$. On the other hand, since the triphenylsilyl radical is able to produce the disilane whose electron-acceptor ability is less than that of *p*-TP, back electron transfer from p-TP$^{\cdot -}$ to the disilane does not occur and thus p-TP$^{\cdot -}$ persists.

The photoejection process from organic anions and the electron-trapping mechanism of aromatic compounds have been studied extensively in relation to the intermediates of photostimulated $S_{RN}1$ reactions[1-5] and the ion-pair phenomena.[6,7] If back electron transfer occurs after the photoinduced process, then we can control the lifetime of the electron or the radical anions of the aromatic compounds by controlling the illumination. We showed in our previous paper that the radical anions of aromatic compounds were formed efficiently by illumination of the phenylthiolate anion and that the back electron-transfer rates correlate with the reduction potentials of the aromatic compounds.[8] In this paper, we report our findings that the radical anion of *p*-terphenyl (p-TP$^{\cdot -}$) accumulates on steady illumination of the triphenylsilyl anion (Ph_3Si^-), whereas the radical anion is produced only transiently from the triphenylmethyl anion (Ph_3C^-). The cause of these different phenomena is examined.

EXPERIMENTAL

Commercially available triphenylmethyl chloride, triphenylsilyl chloride and *p*-terphenyl (*p*-TP) were purified by recrystallization. Ph_3C^-,Na^+ was produced by contacting Na metal with the chloride in degassed tetrahydrofuran (THF). Ph_3Si,K^+ was produced by contact with Na–K alloy. The light source was a 500 W high-pressure Hg lamp. Absorption spectra of the steady-state solutions were measured by using a Cary 14 spectrophotometer. Absorption spectra of transient species were measured using a flash-photolysis apparatus of standard design;[9] the half duration of the xenon flash lamps was *ca.* 10 μs and the flash energy was *ca.* 100 J. All measurements were made at 23 ± 1 °C.

RESULTS AND DISCUSSION

Ph_3Si^-,K^+ was identified from the absorption band at 360 nm [fig. 1(*a*)].[10] No colour change was observed in the dark by the addition of *p*-TP to Ph_3Si^-,K^+. The solution changed to blue with steady illumination using light of wavelength > 310 nm [fig. 1(*c*) and (*d*)]. The absorption bands at *ca.* 470 and *ca.* 800 nm were attributed

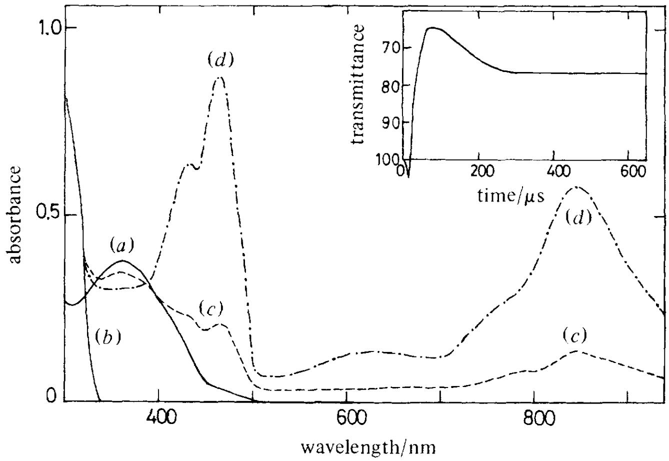

FIG. 1.—Absorption spectra of (*a*) Ph_3Si^-,K^+ (4×10^{-4} mol dm^{-3}) in THF; (*b*) *p*-TP (2.5×10^{-3} mol dm^{-3}); (*c*) steady illumination of the mixed solution of (*a*) and (*b*) with light of wavelength > 310 nm for *ca.* 1 h; (*d*) steady illumination with a 500 W high-pressure Hg lamp with light of wavelength > 310 nm for 15 min. Optical path of the cell is 2 mm. Insert: decay profile at 468 nm observed by flash photolysis of a mixed solution of (*a*) and (*b*) in a 100 mm cylindrical cell.

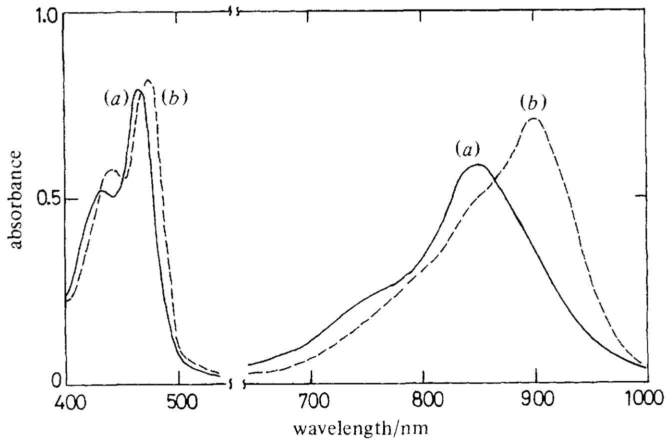

FIG. 2.—Absorption spectra of *p*-$TP^{\cdot -}$($,K^+$); (*a*) at 23 °C and (*b*) at −78 °C in THF. Concentrations of *p*-$TP^{\cdot -}$($,K^+$) is 2.5×10^{-4} mol dm^{-3} in a 2 mm cell.

to the contact ion-pair of *p*-$TP^{\cdot -}$. In fig. 2 the absorption peaks of *p*-$TP^{\cdot -}$ observed at 23 °C were attributed to the contact ion-pair and those at low temperature to solvent separated ion-pair or free ion.[11] The decrease in the absorbance at 360 nm in fig. 1 was ascribed to the consumption of Ph_3Si^-,K^+. After cutting off the light, decay of the absorption bands of *p*-$TP^{\cdot -},K^+$ was not observed within *ca.* 2-3 h.

On flash photolysis of the fresh solution, the decay of the absorption band of *p*-$TP^{\cdot -}$, K^+ was observed initially, as shown in the insert of fig. 1. The absorption showing fast decay was also ascribed to *p*-$TP^{\cdot -},K^+$; the T–T absorption of *p*-TP was not observed under our experimental conditions. The initial concentration of *p*-$TP^{\cdot -},K^+$

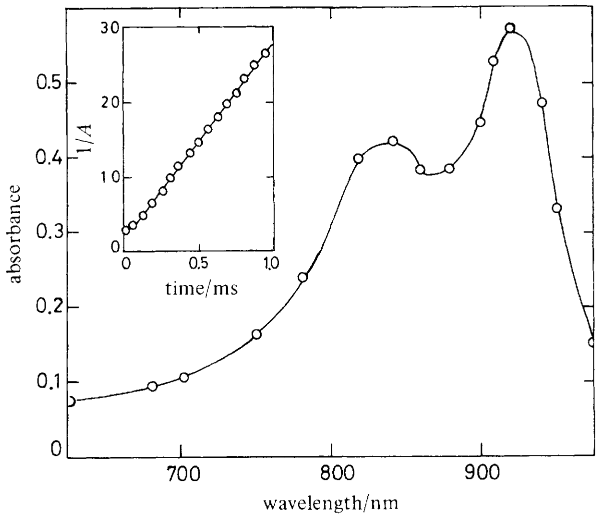

FIG. 3.—Transient absorption spectrum observed by flash photolysis of Ph_3C^-,Na^+ (10^{-4} mol dm^{-3}) in the presence of *p*-TP (5×10^{-4} mol dm^{-3}) in THF; light of wavelength > 310 nm was used. The absorbances 30 μs after flash were depicted. Insert: the second-order plot of the decay curve of *p*-TP$^{\cdot -}$(,Na$^+$) at 845 nm (optical path is 100 mm).

produced by one flash was estimated to be *ca.* 4.3×10^{-7} mol dm^{-3}; *ca.* 40% of *p*-TP$^{\cdot -}$, K$^+$ decayed within 300 μs and the rest persisted for a long time.

With steady illumination of the solution containing Ph_3C^-,Na^+ and *p*-TP, no colour change was observed. Flash photolysis of the solution yielded a transient absorption spectrum as shown in fig. 3. The absorption peak at 830 nm was ascribed to the contact ion-pair (*p*-TP$^{\cdot -}$,Na$^+$) and the absorption peak at 915 nm to the solvent separated ion-pair (*p*-TP$^{\cdot -}$//Na$^+$) or the free ion. Both species co-exist because the concentrations of the ions are low (*ca.* 10^{-7} mol dm^{-3}). Decay of the transient *p*-TP$^{\cdot -}$(,Na$^+$) was very rapid; the second-order plot of the decay curve was linear (insert of fig. 3) and the slope yielded $k/\varepsilon = 2.5 \times 10^5$ cm s^{-1} at 845 nm, where k and ε refer to the rate of constant of the decay process and the molar extinction coefficient of *p*-TP$^{\cdot -}$(,Na$^+$), respectively. The linear second-order plot suggests reaction between *p*-TP$^{\cdot -}$(,Na$^+$) and species of the same concentration as *p*-TP$^{\cdot -}$(,Na$^+$).

For both Ph_3Si^-,K^+ and Ph_3C^-,Na^+, dark electron transfer from these anions to *p*-TP did not occur; this suggests that the reduction potential of *p*-TP (-2.36 V *vs.* SCE)[12] is more negative than that of $Ph_3Si^\cdot$ or $Ph_3C^\cdot$. Photoinduced electron transfer may occur *via* direct photoejection from the anions [mechanism (1)] or *via* electron abstraction from the anions by the excited *p*-TP [mechanism (2)]. Since *p*-TP$^{\cdot -}$ was produced by exciting only the anion (Ph_3M^-), mechanism (1) is more probable than mechanism (2); however, on the flash photolysis of the anions in the absence of *p*-TP, no absorption band for a solvated electron (e^-_{solv}) was observed in the visible region.

$$\left.\begin{aligned} Ph_3M^- &\longrightarrow Ph_3M^\cdot + e^-_{solv} \\ e^-_{solv} + p\text{-TP} &\longrightarrow p\text{-TP}^{\cdot -} \end{aligned}\right\} \quad (1)$$

$$\left.\begin{aligned} p\text{-TP} &\xrightarrow{h\nu} p\text{-TP}^* \\ p\text{-TP}^* + Ph_3M^- &\longrightarrow p\text{-TP}^{\cdot -} + Ph_3M^\cdot . \end{aligned}\right\} \quad (2)$$

The decay process of *p*-TP$^{\cdot -}$ produced transiently by flash photolysis may include back electron transfer from *p*-TP$^{\cdot -}$ to $Ph_3M^{\cdot}$ [reaction (3)],

$$p\text{-TP}^{\cdot -} + Ph_3M^{\cdot} \xrightarrow{k_b} p\text{-TP} + Ph_3M^- \quad (3)$$

since the reaction system of Ph_3C^-, Na^+ and *p*-TP was reproducible by successive flash photolysis. Decay of *p*-TP$^{\cdot -}$ can be expressed by eqn (4)

$$-d[p\text{-TP}^{\cdot -}]/dt = k_b[p\text{-TP}^{\cdot -}][Ph_3M^{\cdot}]. \quad (4)$$

If $Ph_3M^{\cdot}$ is not consumed by other reactions such as recombination to produce $(Ph_3M)_2$, the concentration of $Ph_3M^{\cdot}$ is equal to that of *p*-TP$^{\cdot -}$ at any time; thus eqn (4) can be converted into eqn (5)

$$-d[p\text{-TP}^{\cdot -}]/dt = k_b[p\text{-TP}^{\cdot -}]^2. \quad (5)$$

The k value observed in fig. 3 was ascribed to the rate constant of back electron transfer (k_b) from *p*-TP$^{\cdot -}$(,Na$^+$) to $Ph_3C^{\cdot}$; the value of k_b was estimated to be 5×10^9 mol^{-1} s^{-1} using the value of ε reported in the literature.[11] The value of k_b is close to the diffusion-controlled limit. The decay curve of the initial part of fig. 1 may also be attributed to back electron transfer from *p*-TP$^{\cdot -}$(,K$^+$) to Ph_3Si; although the value of k_b could not be estimated precisely, the rate constant may be similar to the above value.

In the case of the photoreaction system of Ph_3Si^-,K$^+$ and *p*-TP, $Ph_3Si^{\cdot}$ is known to be able to produce the disilane and disiloxane [reactions (6) and (7)][13-15]

$$2Ph_3Si^{\cdot} \xrightarrow{k_r} (Ph_3Si)_2 \quad (6)$$

$$2Ph_3Si^{\cdot} + THF \longrightarrow (Ph_3Si)_2O \textit{ etc.} \quad (7)$$

The recombination rate constant (k_r) close to the diffusion-controlled limit was estimated by analysing the decay curve of the 330 nm absorption band of $Ph_3Si^{\cdot}$ observed by flash photolysis of hexaphenyl disilane at 23 °C; although the ε value was not estimated precisely, the k_r value was calculated to be 3.0×10^9 dm^3 mol^{-1} s^{-1} from $2k_r/\varepsilon = 1.5 \times 10^5$ cm s^{-1} (at 330 nm) using the assumption $\varepsilon = 10^4$ dm^3 mol^{-1} cm^{-1}. The ratio of the disiloxane to disilane was reported to be *ca.* 0.1 from the product analysis.[13-15]

When $(Ph_3Si)_2$ was mixed with *p*-TP$^{\cdot -}$(,K$^+$) produced by contact with K metal, electron transfer from *p*-TP$^{\cdot -}$(,K$^+$) to $(Ph_3Si)_2$ was not observed in the dark. This suggests that the reduction potential of $(Ph_3Si)_2$ is more negative than that of *p*-TP. Our finding that *p*-TP$^{\cdot -}$(,K$^+$) accumulates on steady illumination suggests that $Ph_3Si^{\cdot}$ formed by the donation of an electron is converted into the disilane (or the disiloxane) before the return of the electron from *p*-TP$^{\cdot -}$(,K$^+$).

Electron transfer in the dark was observed by mixing of Ph_3Si^-,K$^+$ with perylene ($E_{1/2} = -1.66$ V), anthracene ($E_{1/2} = -1.94$ V) or pyrene ($E_{1/2} = -2.06$ V);[13] thus aromatic compounds with more negative reduction potentials than that of $Ph_3Si^{\cdot}$ can be used as electron acceptors for the photoinduced electron-transfer system. The *p*-TP$^{\cdot -}$ produced by the photoinduced process from anions such as the phenylthiolate and triphenylstannyl anions decayed at a diffusion-controlled rate; this is due to the fact that the reduction potentials of diphenyl disulphide ($E_{1/2} \approx -1.80$ V)[8] and hexaphenyl distannane ($E_{1/2} = -2.30$ V)[16] are less negative than that of *p*-TP.

In conclusion, we may summarize the conditions necessary for getting a high steady concentration of the radical anions with the photolysis of the anion as follows: (*a*) spontaneous electron transfer from the anion to aromatic compound does not occur in the dark and (*b*) the radical formed from the anion is rapidly converted into a substance having a more negative reduction potential than the aromatic compound.

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