December, 1985] © *1985 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.,* 58, *3641—3642 (1985)* 3641

Laser Photolysis Study on the Duroquinone-photosensitized Isomerization of Stilbenes in Micellar Solution

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(Received April 4, 1985)

Synopsis. Photoinduced electron-transfer reaction between the excited triplet duroquinone and *trans*- and *cis*-stilbenes generates *trans*-stilbene cation radical in SDS micellar solution, suggesting that the *cis-trans* isomerization of stilbene occurs *via* an electron-transfer mechanism.

Recently, an increasing interest has been paid to the photosensitized isomerization of stilbenes in electron-transfer reactions.[1–5] In the present paper, we have studied a photoinduced electron-transfer reaction between duroquinone and stilbenes in sodium dodecyl sulfate (SDS) micellar solution by nanosecond laser flash photolysis. It is shown that the electron-transfer from both *trans*- and *cis*-stilbenes to the excited triplet duroquinone generates only the *trans*-stilbene cation radical in the nanosecond timescale; the *cis-trans* photoisomerization of stilbene mostly occurs *via* an electron-transfer mechanism.

Experimental

Duroquinone (DQ) and *trans*-stilbene (TS) were purified by recrystallization. *cis*-Stilbene (CS) was purified by distillation; its purity was determined to be >95% by gas chromatography. Sodium dodecyl sulfate (for biological use, SDS) was used as supplied. Water was distilled and deionized. The laser flash photolysis measurements were carried out in deaerated solutions at room temperature using a Molectron UV-12 N_2 laser (337 nm) as the exciting light source.[6]

Results and Discussion

Figure 1 shows transient absorption spectra of SDS micellar solutions containing DQ and stilbenes. In the absence of stilbenes, a weak triplet-triplet absorption of DQ appears in the 400—500 nm region.[7,11] In the presence of TS, a new intense band appears at ≈480 nm (the growth and decay rates are 1.1×10^6 and $1.5\times10^4\ s^{-1}$, respectively), which is assigned to the TS cation radical (TS^+).[8] In contrast to this, no appreciable transient absorption due to TS^+ is observed in acetonitrile solution. In the aqueous micellar solution both DQ and TS are mostly solubilized in the micellar phase, since they are almost insoluble in water. This local high concentration of solute molecules in the micellar phase leads to a high efficiency of the electron transfer reaction in the micellar solution. From the plots of the growth rate *versus* the TS concentration shown in Fig. 2A, the apparent bimolecular electron-transfer rate constant was estimated to be $1.6\times10^9\ mol^{-1}\,dm^3\,s^{-1}$ in the present micellar solution. The intercept in the figure deviates slightly from the origin. This is mostly due to the contamination of the T-T absorption intensity of DQ at the lower TS concentrations. Further, the absorption of the duroquinone anion radical ($DQ^{\overline{\cdot}}$), a counter radical, is expected to occur in the 400 nm region.[7] However, it is not observed clearly because of overlap with the absorption bands of the excited triplet duroquinone ($^3DQ^*$) and the TS^+ radical in this wavelength region. The TS^+ radical is mostly formed *via* the photoinduced electron-transfer reaction between $^3DQ^*$ and TS.

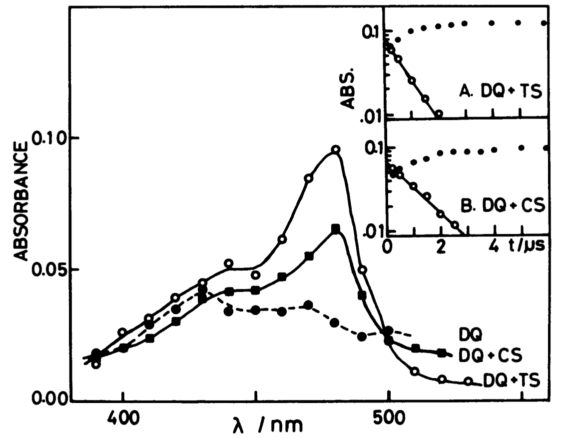

Fig. 1. Transient absorption spectra of 0.4 mol dm^{-3} SDS micellar solutions containing 6×10^{-4} mol dm^{-3} DQ (---●---), DQ and 4×10^{-4} mol dm^{-3} TS (—○—), and DQ and 3×10^{-4} mol dm^{-3} CS (—■—), at 1 μs delay after laser excitation. Inserts show typical time profiles of the absorption intensities at 480 nm for the solutions containing DQ and TS, (A), and DQ and CS, (B).

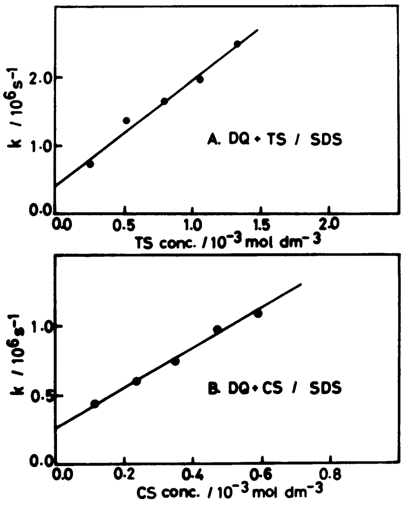

Fig. 2. Concentration dependence of the growth rate, *k*, of the 480 nm band for TS, (A) and CS, (B). The concentrations of SDS and DQ were 0.4 and 5×10^{-3} mol dm^{-3}, respectively.

On the other hand, in a solution containing DQ and

CS, a band appears at ≈480 nm (the growth and decay rates are 0.7×10^6 and $1.5\times10^4\ \mathrm{s}^{-1}$, respectively) as shown in Fig. 1, though the absorption of CS^{+} is reported to appear at 515 nm.[8] Since the band is similar to that of TS^{+} in the figure, it is assigned to the TS^{+} radical. In the photolysis of the micellar solution of DQ and CS, the $CS^{+}\rightarrow TS^{+}$ isomerization occurs rapidly, since no appreciable absorption due to CS^{+} appears in the nanosecond timescale. The apparent bimolecular rate constant for CS was found to be $1.5\times10^9\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$ (see Fig. 2B). This is almost the same as that for TS.

The unusual $CS^{+}\rightarrow TS^{+}$ isomerization has been reported for the photobleaching of CS^{+} in CCl_4 rigid glass at low temperature,[8] for the 9,10-dicyanoanthracene-sensitized oxidation of CS in acetonitrile,[2] and for the electron impact of CS.[9] The present result clearly demonstrates that the TS^{+} radical is also produced by the electron transfer reaction between the excited triplet DQ and CS, whereas generation of TS^{+} *via* a singlet-sensitized reaction is well known.[2]

Furthermore, the formation of CS was detected in a gas chromatograph of the photolysed solution of DQ and TS. The fact suggests that *trans-cis* isomerization of stilbene occurs *via* an electron-transfer mechanism, though triplet sensitized isomerization of stilbene *via* an energy transfer mechanism is well known.[10]

The photoreaction of DQ with TS may be interpreted in the following scheme:[1,3]

$$DQ \xrightarrow{h\nu} {}^1DQ^* \longrightarrow {}^3DQ^* \qquad (1)$$

$${}^3DQ^* + TS \longrightarrow {}^3(DQ^{\cdot-}TS^{\cdot+}) \qquad (2)$$

$${}^3(DQ^{\cdot-}TS^{\cdot+}) \rightleftarrows {}^1(DQ^{\cdot-}TS^{\cdot+}) \qquad (3)$$

$${}^3(DQ^{\cdot-}TS^{\cdot+}) \longrightarrow DQ + {}^3TS^* \qquad (4)$$

$${}^3(DQ^{\cdot-}TS^{\cdot+}) \longrightarrow DQ^{\cdot-} + TS^{\cdot+} \qquad (5)$$

$${}^1(DQ^{\cdot-}TS^{\cdot+}) \longrightarrow DQ + TS \qquad (6)$$

$${}^1(DQ^{\cdot-}TS^{\cdot+}) \longrightarrow DQ^{\cdot-} + TS^{\cdot+} \qquad (7)$$

In the micellar solution of DQ and TS, the electron-transfer between ${}^3DQ^*$ and TS generates a triplet pair of $DQ^{\cdot-}$ and TS^{+}, ${}^3(DQ^{\cdot-}TS^{+})$. Here, we assume the radical ion pair as an intermediate by analogy with the electron-transfer reaction of DQ and diphenylamine in SDS micellar solution.[11] It is expected that there are three processes from the triplet pair; *i.e.*, intersystem crossing to the singlet pair, (3), back electron-transfer to generate the excited triplet TS, (4), and separation into free radicals, (5). *trans-cis* Isomerization may occur *via* the excited triplet TS as suggested by Leshina *et al.*[3]

On the other hand, in the micellar solution of DQ and CS, electron-transfer between ${}^3DQ^*$ and CS generates a triplet pair of $DQ^{\cdot-}$ and CS^{+}, ${}^3(DQ^{\cdot-}CS^{+})$, followed by a rapid isomerization:

$${}^3DQ^* + CS \longrightarrow {}^3(DQ^{\cdot-}CS^{\cdot+}) \longrightarrow {}^3(DQ^{\cdot-}TS^{\cdot+}) \qquad (8)$$

After the generation of ${}^3(DQ^{\cdot-}TS^{+})$, the reaction processes are similar to those mentioned above. Furthermore, since the lifetime of TS^{+} is relatively long (≈65 μs), an apparent *cis-trans* isomerization of TS^{+} may also occur *via* an electron hole transfer from CS to TS^{+} as an inter-micellar process, as proposed for the $[Ru(bpy)_3]^{2+}$ sensitized isomerization of stilbazole in SDS solution,[4] and for the singlet 9,10-dicyanoanthracene-sensitized isomerization of CS in acetonitrile:[5]

$$TS^{\cdot+} + CS \longrightarrow TS + CS^{\cdot+} \qquad (9)$$

Furthermore, the observation of the magnetic field effect (1 T) on the transients was attempted in these micellar solutions. However no detectable effect was observed, suggesting that the triplet-singlet intersystem crossing of the radical ion pair is not the rate-determining step in the reaction. The magnetic field effects on the photosensitized isomerization of stilbene in organic solvents[3] and on the electron-transfer between the excited duroquinone and diphenylamine in SDS solution[11] are reported.

Finally, we believe that the present transient spectroscopic results indicate the importance of $CS^{+}\rightarrow TS^{+}$ isomerization in the triplet sensitized electron-transfer reaction of stilbenes in micellar solution.

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