Thermal and Photochemical Reactions of the Anion Radical and Dianion of Dibenzothiophen

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The radical anion of dibenzothiophen($DBS^{-\bullet}$) produced by the contact with alkali-metal dissociates thermally at the S–C bond *via* second-order kinetics; the dissociated radical anion accepts an electron from other $DBS^{-\bullet}$ and yields the dianion. Flash photolysis of the dianion in the presence of excess of DBS yields $DBS^{-\bullet}$; one half of $DBS^{-\bullet}$ decays rapidly and the other persists for a long time. The mechanisms of formation and decay are discussed.

It has been reported by Evans *et al.* that the radical anion of dibenzofuran changes into the stable dianion *via* the cleavage of the C–O bond.[1] A similar reaction should occur for the radical anion of dibenzothiophen ($DBS^{-\bullet}$); one of the aims of this study is to compare the rate of cleavage of the C–S bond with that of the C–O bond. In a reaction system where the dianion coexists with the neutral molecule, the concentration of radical anion can be controlled by illumination of the dianion. The mechanisms for the thermal and photochemical processes of the radical anion and dianion of dibenzothiophen are examined.

EXPERIMENTAL

Dibenzothiophen (DBS) was purified by recrystallization. The radical anion of DBS was prepared in highly degassed tetrahydrofuran (THF).[2] The e.s.r. spectra were measured with a Varian E-4 spectrometer and hyperfine splitting constants were estimated by computer simulation. Absorption spectra were measured with a Cary-14 spectrophotometer equipped with a variable-temperature accessory. The flash photolysis apparatus was of standard design; [3,4] the half-duration of the xenon-flash lamp was *ca.* 10 μs and the input energy was *ca.* 100 J.

RESULTS

Thermal Reactions.—Figure 1 shows the absorption spectra of the radical anion of $DBS^{-\bullet}$, K^+ in THF produced by the contact of DBS with potassium metal. $\lambda_{max.}$ 690 nm at room temperature shifted to longer wavelength (705 nm) at −70 °C. $\lambda_{max.}$ at −70 °C is in good agreement with that observed in γ-irradiated MTHF glass.[5] The e.s.r. spectrum was analysed as follows; the hyperfine splitting constants for 1-, 2-, 3-, and 4-H were found to be 4.48, 0.97, 5.08, and 1.45 G, respectively, on the basis of the literature method [6] (the numbering is shown in the Scheme). Since no hyperfine splitting constant attributable to the countercation was observed, the radical anion may be present as part of a solvent-separated ion pair.

The intensity of the blue colour decreased with time after the separation of $DBS^{-\bullet}$ from potassium metal by filtration, and the solution became red; the new absorption band at 515 nm increased (Figure 1). This colour change was accompanied by a decrease in the e.s.r. signal. The rate of decrease in the absorption at 690 nm was found to be second-order (insert of Figure 1); the slope yielded $k_{obs}/\varepsilon_{690\,nm}$ 7.2×10^{-4} cm s^{-1} where k_{obs} and ε refer to the rate constant and molar extinction coefficients of $DBS^{-\bullet}$, respectively. By analogy with the radical anion of dibenzofuran,[1] the decrease of $DBS^{-\bullet}$ may be represented as in the Scheme.

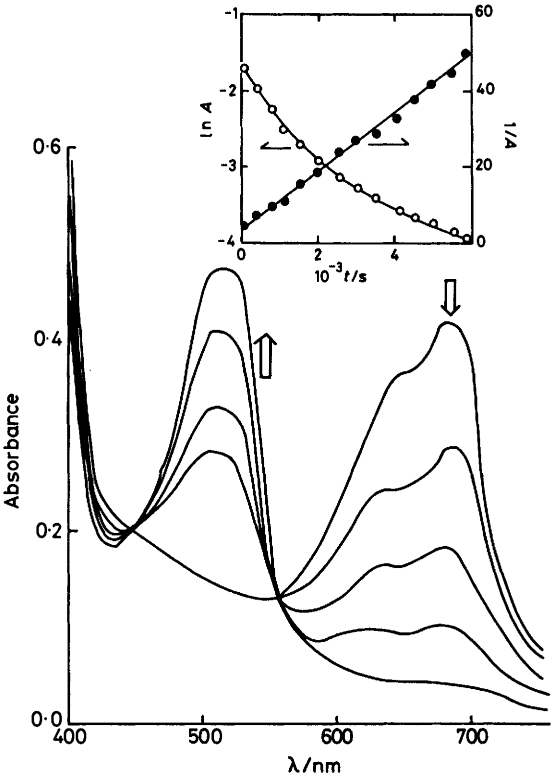


FIGURE 1 Changes of absorption spectra observed at 20 °C (arrows refer to time changes); the anion radical of dibenzothiophen ($\lambda_{max.}$ 690 nm) and the dianion (III) ($\lambda_{max.}$ 515 nm). The initial concentration of the radical anion (I) was 2×10^{-4} mol dm^{-3}; cell length 0.2 cm. Insert: first- and second-order plot of the decrease of the radical anion (I). The perpendicular axis is converted into the absorbance in a 1 cm cell

Assuming a steady-state concentration for (II), equation (1) can be derived. Second-order kinetics [equation (2)] would be anticipated when $k_{-1} \gg k_2[(I)]$; on the other hand, equation (1) obeys first-order kinetics [equation (3)] when $k_{-1} \ll k_2[(I)]$.

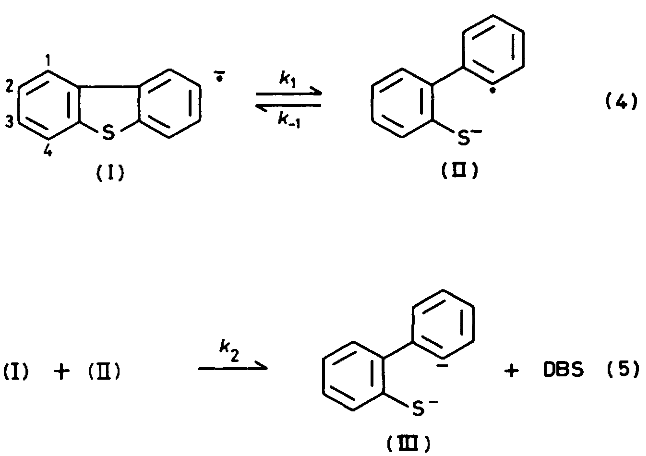
$$-d[(I)]/dt = k_1k_2[(I)]^2/\{k_{-1} + k_2[(I)]\} \qquad (1)$$

$$= (k_1k_2/k_{-1})[(I)]^2 \qquad (2)$$

or

$$= k_1[(I)] \qquad (3)$$

Thus, k_{obs} estimated from the second-order plot can be put equal to k_1k_2/k_{-1}. The k_{obs} value was estimated to be 7.2 $dm^3\ mol^{-1}\ s^{-1}$ from $k_{obs}/\varepsilon_{690\ nm}$ with $\varepsilon_{690\ nm}$ *ca.* $10^4\ dm^3\ mol^{-1}\ cm^{-1}$. The slope of the initial part of the first-order plot yielded an approximate k_1 value, *ca.* $7 \times 10^{-4}\ s^{-1}$. This k_1 value for $DBS^{-\bullet},K^+$ was *ca.* 10 times larger than that for the dibenzofuran radical anion ($6.3 \times 10^{-5}\ s^{-1}$); [1] this may be reasonable since the C–S bond is weaker than the C–O bond.



SCHEME

On the basis of an assumption that electron transfer from an anion radical to a free radical as in reaction (5) is close to the diffusion-controlled limit (*e.g.*, k_2 $10^9\ dm^3\ mol^{-1}\ s^{-1}$), k_{-1} can be calculated to be $10^4\ s^{-1}$. Since [(I)] < *ca.* $10^{-4}\ mol\ dm^{-3}$ under our experimental conditions, the k_{-1} value was always smaller than k_2[(I)]; therefore second-order kinetics were observed. If the concentration of (I) is $>10^{-3}\ mol\ dm^{-3}$, first-order decay kinetics would be anticipated; the first-order kinetics observed for the dibenzofuran radical anion by Evans *et al.* may have resulted from kinetic measurements at high concentration.[1]

With a decrease in temperature, the k_{obs} values decreased; the Arrhenius plot from +20 to −20 °C yielded a straight line (Figure 2), with slope 15 kcal mol^{-1}. Since the k_2 and k_{-1} values correspond to fast reactions, this slope was ascribed to the activation energy of the forward process of reaction (4). This value is *ca.* 5 kcal mol^{-1} smaller than that for the dibenzofuran radical anion (20.2 kcal mol^{-1}); [1] the smaller activation energy of $DBS^{-\bullet}$ may be attributed to the weak bond energy of the C–S bond.

Photochemical Reactions.—Upon illumination with visible light of a solution containing the dianion (III) and DBS resulting from reactions (4) and (5), the radical anion (I) was reformed and the dianion (III) was destroyed. Upon flash photolysis of the dianion (III) in the presence of DBS, transient absorption spectra were observed (Figure 3); in the absorption spectrum immediately after the flash, there was nothing below 640 nm since the large decrease in the absorption of the dianion (III) obscured the initial part of the decay profiles. The decay profile at 690 nm (insert of Figure 3) showed a two-step decay process. The spectrum of the species showing slow decay [Figure 3 (b)] was ascribed to the radical anion (I). The species showing fast decay was also ascribed as the radical anion (I), since the absorption maximum at 690 nm in the spectrum of Figure 3(a) was the same as that of (I). These observations suggest that an electron ejected from the dianion upon photo-illumination was trapped by DBS; reaction (6) then occurred.

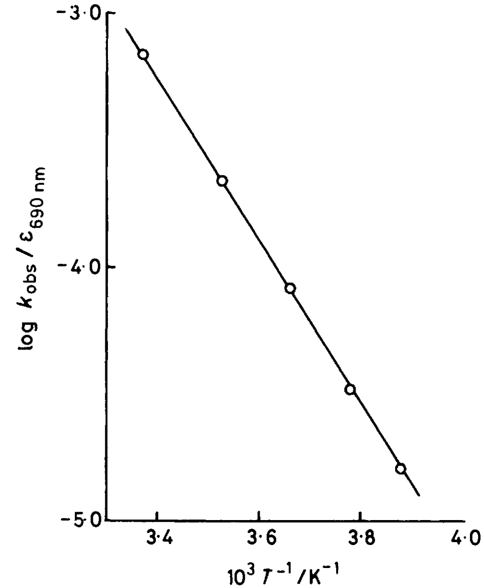


FIGURE 2 Arrhenius plot of log $k_{obs}/\varepsilon_{690\ nm}$; the slope gave 15 kcal mol^{-1}

$$DBS + (III) \underset{k_2}{\overset{h\nu}{\rightleftharpoons}} (I) + (II) \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} 2(I) \tag{6}$$

The fast decay part had second-order kinetics (insert of Figure 3); from the slope ($k/\varepsilon_{690\ nm}$ $1.8 \times 10^5\ cm\ s^{-1}$), k was estimated to be $1.8 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ with $\varepsilon_{690\ nm}$ $10^4\ dm^3\ mol^{-1}\ cm^{-1}$. The value was close to the diffusion-controlled limit. Therefore, the fast decay process for (I) was attributed to reaction (5), since the radical anion (II) may exist

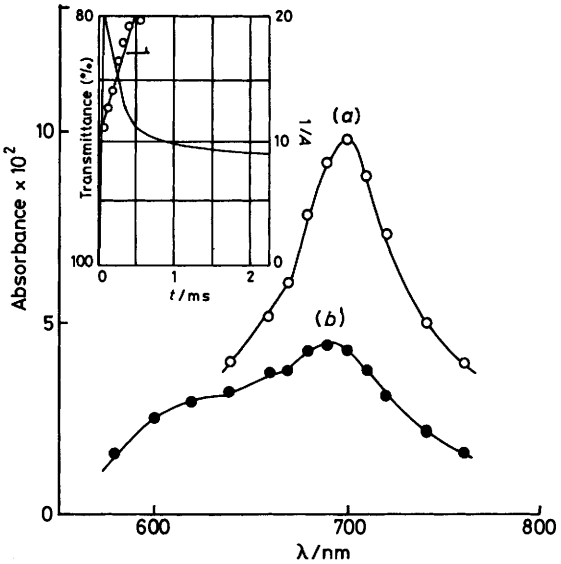


FIGURE 3 Transient absorption spectra observed by flash photolysis ($\lambda_{max.}$ >420 nm) of the dianion (III) ($10^{-4}\ mol\ dm^{-3}$) in the presence of DBS ($10^{-4}\ mol\ dm^{-3}$). (a) Absorbances at 50 μs after flash and (b) absorbances at 1 ms after flash. Insert: the decay profile at 690 nm and the second-order plot of initial part of the reaction

immediately after the flash in larger excess than would be expected from equilibrium (4). The slow decay process was ascribed to the forward process of reaction (4), *viz.* the backward process of reaction (6). The decay rate of the slow process was slightly faster than that observed for the thermal reaction; there may be some reactive species produced by photolysis. These findings suggest that the accumulation of DBS$^{-\bullet}$ was controlled by the illumination of the dianion (III) and DBS.

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