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Electronic Absorption Spectra of the Disulfone Radical Anion. Conjugative Effect of the Sulfone Group

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Synopsis. Disulfone radical anions produced by γ-irradiation show a characteristic absorption band at a longer wavelength region (655—695 nm) than that of the mono-sulfone radical anion (*ca.* 400 nm). The former band is attributed to the charge-resonance originated from the delocalization of an unpaired electron between the linked two sulfone moieties.

The radical anions containing the sulfone group show a pronounced conjugative effect through the sulfone group.[1] The effect was studied by means of the electron spin resonance. We showed that the measurement of the absorption spectrum is useful for elucidating the effect from the absorption band appearing in a longer wavelength region.[2] In this note, we report on our findings that the radical anions of disulfones ($R-SO_2-SO_2-R$) show an absorption band in a longer wavelength region (655—695 nm) than that of the mono-sulfone radical anions such as phenyl methyl sulfone (*ca.* 400 nm). It is expected that the band appearing in a longer wavelength region is related to the effective conjugation of the disulfone moieties.

Experimental

Di-*n*-hexyl disulfone[3] and diaryl disulfones[4] were synthesized by the reported methods. Radical anions containing sulfone moieties were produced by the γ-irradiation (^{60}Co: *ca.* 1 Mrad) of degassed methyltetrahydrofuran (MTHF) glassy solution at 77 K, since the disulfone radical anions formed by the alkali metal reduction were not stable.

Results and Discussion

It is expected that the disulfone radical anion can be produced by γ-irradiation according to the electron (e^-)-capture as follows:

$$\mathrm{MTHF} \overset{\gamma}{\rightsquigarrow} \mathrm{MTHF}^+ + e^- \quad (1)$$

$$e^- + R\text{-}SO_2\text{-}SO_2\text{-}R \longrightarrow (R\text{-}SO_2\text{-}SO_2\text{-}R)^{\bar{\cdot}} \quad (2)$$

A glassy blue solution, obtained by γ-irradiation of diphenyl disulfone, exhibited a strong absorption band at 695 nm and a weak band at 368 nm (Fig. 1a). As a possible species in the blue solution other than the disulfone radical anion, the benzene sulfonyl radical ($Ph-\dot{S}O_2$) might be produced by the direct scission of $-SO_2-SO_2-$ bond or by the dissociative electron attachment process:

$$e^- + R\text{-}SO_2\text{-}SO_2\text{-}R \longrightarrow R\text{-}\dot{S}O_2 + R\text{-}SO_2^- \quad (3)$$

However, the benzene sulfonyl radical, which can be produced by the UV-irradiation of diphenyl disulfone or benzene sulfonyl halides at 77 K, shows an absorption band at 382 nm. Thus, the absorption spectrum of the blue species (Fig. 1a) can be assigned to the diphenyl disulfone radical anion.

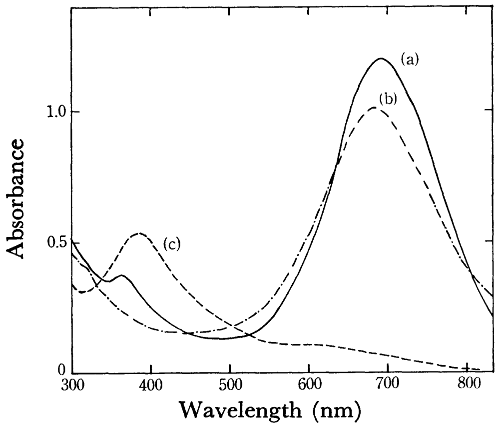


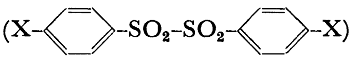
Fig. 1. Absorption spectra of the disulfone radical anions in MTHF at 77 K (5×10^{-3} mol/l in 2 mm cell); (a) diphenyl disulfone, (b) di-*n*-hexyl disulfone, and (c) phenyl methyl sulfone.

The radical anion of di-*n*-hexyl disulfone, an alkyl derivative of disulfone, was also produced by γ-irradiation. It shows a similar spectrum (Fig. 1b) to that of the diphenyl disulfone radical anion. This indicates that the electronic transitions of the disulfone radical anion appearing at *ca.* 690 nm are characteristic of two sulfone moieties and that the π-systems on the phenyl rings do not play an appreciable role in the transition. Moreover, the phenyl methyl sulfone ($Ph-SO_2-CH_3$) radical anion, a mono-sulfone, shows only one absorption band at 398 nm (Fig. 1c). An added electron to this mono-sulfone locates mainly on the sulfone moiety.[2] We see that, in the disulfone radical anion, the absorption band at *ca.* 690 nm results from the linked two sulfone moieties.

It is to be noted that the absorption spectra of the disulfone radical anions resemble those of the [2.2]paracyclophane radical anion (a strong band at 760 nm and a weak band at 360 nm) and biphenyl radical anion (two bands at 625 and 400 nm) as reported by Ishitani and Nagakura.[5] Their theoretical study of the [2,2]-paracyclophane and biphenyl radical anions indicates that the absorption bands appearing in a longer wavelength region than the benzene radical anion are assigned to the charge-resonance band originating from the delocalization of an unpaired electron between two phenyl rings. Thus, in the case of the disulfone radical anion, it can be suggested that the band appearing at *ca.* 690 nm has a charge-resonance character and that an added electron to disulfone is delocalized between the linked two sulfone moieties.

The absorption spectra of the disulfide radical anions were reported by Shida.[6] Since the absorption band of the diphenyl disulfide radical anion appeared in the same region as that of the dialkyl disulfide radical anion (420—435 nm), he indicated that an unpaired electron added to disulfide is localized on the sulfur atoms. Although the diphenyl sulfide radical anion shows an absorption band in the same region as the diphenyl disulfide radical anion, the intensity of the band is reported to be very weak as compared with that of the disulfide.[7] Thus, there is a pronounced difference between the disulfide and disulfone radical anions; in the former the intensity of the band differs from that of mono-sulfide, and in the latter the position of the band differs from that of mono-sulfone. Since it is well established that the σ*-orbital of the disulfide accepts an added electron, the different behavior in the spectra of the disulfone radical anion would be caused by the large π-character of O=S=O bond and/or large d-orbital participation on O=S=O bond.

TABLE 1. ABSORPTION MAXIMA OF THE DIPHENYL DISULFONE



RADICAL ANIONS

X	λ_1 (nm)	λ_2 (nm)
H-	695	368
CH_3-	665	366
CH_3O-	655	360

An abnormal shift by the substituents on the phenyl rings was observed in the absorption band appearing in a longer wavelength region (Table 1). When electron-donating substituents such as CH_3– and CH_3O– are introduced to *para*-positions, the absorption peaks shift towards shorter wavelength. In the case of the *para*-substituted diphenyl disulfide radical anions, however, an opposite tendency was observed by Miyashita, Iino and Matsuda (CH_3O–: 440 nm, CH_3–: 425 nm, and H–: 420 nm).[8] The red shift by the electron-donating substituents observed in the disulfide radical anions agrees with the well-known red shift of the substituted benzene molecules.[9] This is understandable if we assume that the transition energy of the charge-resonance band is approximately proportional to the electron density on each sulfone moiety, which might increase by the electron-donating substituents. Precise molecular orbital calculations might be necessary to elucidate the opposite substituent effect of the disulfone radical anions.

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