BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(1), 327—328 (1976)

Absorption Spectrum of the Aggregated Radical Anion of Sulfur Dioxide Produced by γ-Irradiation

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(Received September 18, 1975)

Synopsis. By γ-irradiation of sulfur dioxide in 2-methyltetrahydrofuran at -196 °C, blue glassy solution was obtained, although the monomer radical anion of sulfur dioxide was colorless. The absorption spectrum of the blue species was identical with that of the stable radical anion produced by the amalgam reduction of sulfur dioxide, which was attributed to the dimer or trimer radical anion.

The dimer radical cations formed by the γ-irradiation of aromatic hydrocarbons have been identified by the absorption bands appearing in the longer wavelength region than those of the monomer radical cations.[1] Recently, the dimer radical anions were studied by means of the absorption and ESR spectra.[2] From these studies, it is revealed that if the dimer or trimer radical anion in which an unpaired electron is delocalized was formed, it would be distinguishable from the monomer one by the characteristic absorption band. In this note, we will report that the γ-irradiation of SO_2 gives a colored radical anion at -196 °C, although a monomer one has been known to be colorless.[3]

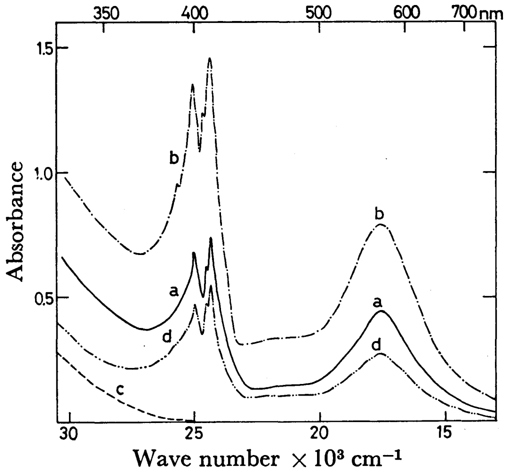

Fig. 1. Absorption spectra of the radical anion formed by γ-irradiation of SO_2 in MTHF at -196 °C (2 mm cell length).
a: $[SO_2]=0.15$ mol/l, b: after thermal annealing of a,
c: $[SO_2]=0.05$ mol/l, d: after thermal annealing of c.

γ-Irradiation of the concentrated SO_2 solution (>0.1 mol/l) in 2-methyltetrahydrofuran (MTHF) at -196 °C gave a blue glassy solution and the absorption bands appeared at 566 nm (band I) and 410 nm (band II) as shown in Fig. 1-a. When the blue glassy solution was warmed slightly, the solution changed to deep blue. By thermal annealing the intensities of the bands I and II, which were observed after recooling to -196 °C, increased with the same proportion without the shift of the positions of the absorption maxima (Fig. 1-b). By the γ-irradiation of the dilute SO_2 solution (<0.05 mol/l), the colorless solution was obtained and only the tail of absorption band appeared at shorter wavelength than 360 nm (Fig. 1-c). By slight melting, this colorless glassy solution turned to a blue solution, whose absorption maxima (Fig. 1-d) were the same as those obtained by the γ-irradiation of the concentrated solution (Fig. 1-a and -b). This suggests that the anionic species, probably monomer radical anion ($SO_2^{\cdot-}$), exists in the γ-irradiated colorless glass and the blue species, probably aggregated radical anion, may be formed by the collision of $SO_2^{\cdot-}$ and SO_2 by thermal annealing. Although the absorption band due to $SO_2^{\cdot-}$ was observed at 360 nm in aqueous solution by means of flash photolysis[3] and pulse radiolysis,[4] any clear peak was not observed at this region in MTHF glass. However, since $SO_2^{\cdot-}$ may interact strongly with H_2O, this difference can be caused by the solvent effect on the electronic transition and the tail of the absorption band shown in Fig. 1-c may be attributed to $SO_2^{\cdot-}$ in MTHF. Since the blue species was also formed by the γ-irradiation of the crystalline SO_2 at -196 °C, the blue species could not attributed to the reaction products formed by MTHF and SO_2. Furthermore, if SO and SO_3 were formed by γ-irradiation at -196 °C, $SO^{\cdot-}$ and $SO_3^{\cdot-}$ and their aggregates with SO_2 such as $SO^{\cdot-}(SO_2)_n$ and $SO_3^{\cdot-}(SO_2)_n$ must be taken into consideration as blue species. However, $SO^{\cdot-}$, $SO_3^{\cdot-}$, and $S_2O_3^{\cdot-}$ were known to be colorless in aqueous solution[3] or in crystalline phase.[5]

The results above indicate the following facts clearly; a) the absorption bands I and II shown in Fig. 1 were attributed to an identical species, since the relative intensities of both bands did not change by the thermal annealing, and b) the blue species increased by thermal annealing was identical with the blue species directly formed by the γ-irradiation of the concentrated solution, since the appreciable shift of the positions of the absorption maxima was not observed by thermal annealing. These results suggest that the blue radical anion can be attributed to the aggregated radical anion of sulfur dioxide, $(SO_2)_n^{\cdot-}$, which may be produced by the following scheme of reactions;

$$n\ SO_2 \rightleftharpoons (SO_2)_n \tag{1}$$

$$\text{MTHF} \xrightarrow{\gamma} \text{MTHF}^+ + e^- \tag{2}$$

$$(SO_2)_n + e^- \longrightarrow (SO_2)_n^{\cdot-} \tag{3}$$

$$SO_2 + e^- \longrightarrow SO_2^{\cdot-} \tag{4}$$

$$SO_2^{\cdot-} + n-1\ SO_2 \longrightarrow (SO_2)_n^{\cdot-} \tag{5}$$

The formation of the blue species by γ-irradiation of the concentrated solution indicates that the self-association of SO_2 occurred in MTHF at -196 °C before irradiation (reactions (1) and (3)),[6] or SO_2 migrated in MTHF glass during γ-irradiation (reaction (5)). Increasing of the blue species by the thermal annealing may suggest that the collision of SO_2 and $SO_2^{\bar{\cdot}}$ (reaction (5)) occurs before $SO_2^{\bar{\cdot}}$ encounters with cationic species in MTHF glass. By the experiments of γ-irradiation, however, any information about a value n in $(SO_2)_n^{\bar{\cdot}}$ could not be obtained.

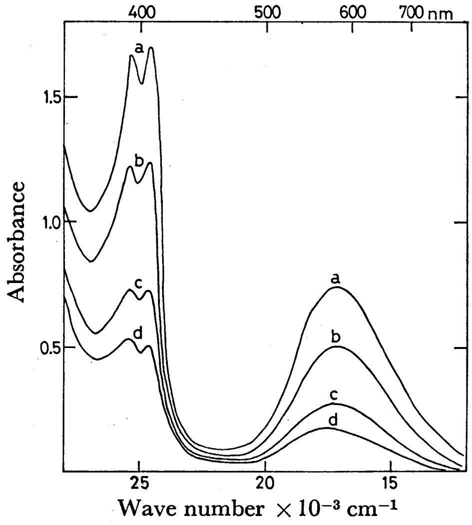

Fig. 2. Absorption spectra of the radical anion formed by sodium amalgam reduction of SO_2 in DMF at various temperatures ($[SO_2]=0.15$ mol/l in 2mm cell). a: 19 °C, b: 0 °C, c: −10 °C, d: −20 °C.

On the other hand, it is reported by Rinker and Lynn that the sodium amalgam reduction of SO_2 gave a stable radical anion having blue color in aprotic solvents.7) The absorption spectrum of the stable species in dimethylformamide (DMF) was shown in Fig. 2. This absorption spectrum was essentially the same as that of the blue species obtained by γ-irradiation of SO_2. There is no doubt about that both blue species are the identical species. For the stable blue species formed by amalgam reduction or by electrolysis, two different structures have been speculated; bonded dimer radical anion ($O_2\bar{S}-\dot{S}O_2 \leftrightarrow O_2\dot{S}-\bar{S}O_2$) by Rinker and Lynn7) and associated trimer ($(SO_2)^{\bar{\cdot}}(SO_2)_2$) by Dinse and Möbius.8)

Before elucidating the structure of the stable blue species, we found that a diamagnetic colorless species coexist with the radical anion in the solution reduced by amalgam. As shown in Fig. 2, with varying temperature the intensities of the two bands at 580 nm (band I) and 400 nm (band II) changed in the same proportion reversibly. Increasing in the intensities of the bands was observed up to 70 °C, and upper limit may exist at higher temperature. With lowering temperature, the intensity of a singlet ESR signal ($g=2.006$) decreased with the same proportion of the intensities of the absorption bands I and II. Thus, it is apparent that the reversible change was caused by the equilibrium between the radical anion and a diamagnetic colorless species, probably a higher aggregate. From this fact it is impossible to elucidate whether the blue species can be attributed to the dimer or trimer radical anion.

It is noteworthy that the absorption spectra of $(SO_2)_n^{\bar{\cdot}}$ resemble that of the disulfone radical anion ($(R-SO_2-SO_2-R)^{\bar{\cdot}}$).9) The dialkyl disulfone radical anion showed the absorption bands at 690 nm and 350 nm, although the dialkyl monosulfone radical anion showed a band at 400 nm. In the disulfone radical anion, the absorption band appearing at 690 nm was assigned to the transition having charge-resonance character, which indicates that an unpaired electron is delocalized between two sulfone moieties. Recently Kerr and Williams studied the radical anion of sulfuryl chloride (SO_2Cl_2) by means of the ESR measurements and proposed that $(SO_2Cl_2)^{\bar{\cdot}}$ can be thought as a resonance hybrid of ($SO_2^{\bar{\cdot}}$, Cl_2) and (SO_2, $Cl_2^{\bar{\cdot}}$) or equivalently, as radical anion complex in which the two molecules share an unpaired electron.10) Supposing that the absorption bands of $(SO_2)_n^{\bar{\cdot}}$ appearing at 560—580 nm were assigned to the transition having charge-resonance character, $(SO_2)_n^{\bar{\cdot}}$ can be thought as that two or three SO_2 molecules share an unpaired electron in the dimer or trimer radical anion.11)

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11) There are some suggestions that the dimer radical anion is more probable than trimer one, although they are not sufficient. One of them is as follows; estimated value $n=2$ in $(SO_2)^{\bar{\cdot}}$ $(SO_2)_n$ by Dinse and Möbius may be slightly larger, since the total intensities of the two ESR signals assigned to the monomer and trimer radical anions decreased with lowering temperature, indicating the formation of the diamagnetic species even by the electrolysis.8)