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Novel Transient Absorption of Irradiated DMSO in Carbon Tetrachloride as Studied by Pulse Radiolysis

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Transient absorption spectra with a maximum at 400 nm have been observed in the pulse radiolysis of dimethyl sulfoxide in carbon tetrachloride solutions. The transients are attributed to the complexes formed in reaction of chlorine atom with dimethyl sulfoxide based on spectral and kinetic studies.

Radiolysis of liquid carbon tetrachloride has provided a wide variety of reactive species such as cations, chlorine atoms and $CCl_3\cdot$ radicals.[1] However,

$$CCl_4 \longrightarrow {}^{\cdot}CCl_4^{+\cdot},\ Cl^-,\ CCl_3^{+\cdot},\ CCl_3\cdot,\ Cl\cdot \text{ etc} \qquad (1)$$

the G-values of these species have been reported as 0.096,[2] 7–8.3 and 7,[3] respectively, the behavior of such reactive species has not been well understood. In this report we describe the formation of a novel transient absorption species of dimethyl sulfoxide(DMSO) irradiated in carbon tetrachloride and its mechanism.

All sample solutions were bubbled with argon and were sealed in a quartz cell. The pulse radiolysis system which utilizes 45-MeV, 10 ns electron pulses as an excitation source was used to detect the optical absorption change.

Figure 1 shows transient absorption spectra obtained in carbon tetrachloride solution containing 8.75×10^{-4} M(mol dm^{-3}) DMSO. After the disappearance of 320 and 500 nm bands[1,4] which originate from the irradiated carbon tetrachloride, the 400 nm band grows in and decays with a half lifetime of several μs. Assignment of this band to anions or cations of DMSO can be excluded since their absorption bands are reported to peak at 350[5] and 600 nm,[6] respectively. The effects of DMSO concentration and the dose rate on the formation kinetics have been examined to understand the reaction mechanism. Figures 2 and 3 show the optical absorption changes observed at 400 nm as a function of time. As shown in Fig. 2, the half lifetime of the grow-in of the 400 nm band decreases with increasing DMSO concentration and the grow-in curves follow a first order law. On the contrary, the dose rate change has no effect on the half lifetime as shown in Fig. 3. These results strongly suggest that only one reactive species which has been produced on irradiation of solvent carbon tetrachloride reacts with DMSO with a rate constant of $(7.0 \pm 0.5) \times 10^9$ M^{-1} s^{-1}. In order to clarify which species reacts with DMSO, irradiation of DMSO in other chlorinated hydrocarbons such as chloroform, dichloromethane and 1,2-dichloroethane has been carried out. The 400 nm band has also been observed in all these solvents after irradiation of DMSO. These facts

evidence that chlorine atoms react with DMSO leading to the formation of the novel 400 nm transient absorption. This assignment can also reasonably explain the effect of alcohols which suppress the formation of the 400 nm band and the transient 430 nm band observed on radiolysis of DMSO in bromotrichloromethane as complexes of DMSO and bromine atom. The complex may be characterized by a sulfur-chlorine bond. In this connection, it is interesting to note that three electron bond radicals, $R_2S\therefore X$ with X = Cl, Br and I were reported to possess an absorption spectrum with a maximum around 400 nm.[7)]

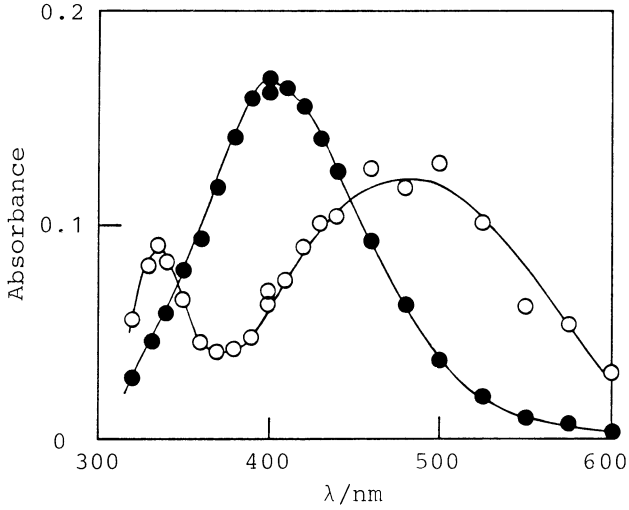

Fig. 1. Optical absorption spectra of 8.75×10^{-4} M DMSO in CCl_4 observed immediately (o) and at 500 ns (●) after a 10 ns electron pulse of 135 Gy.

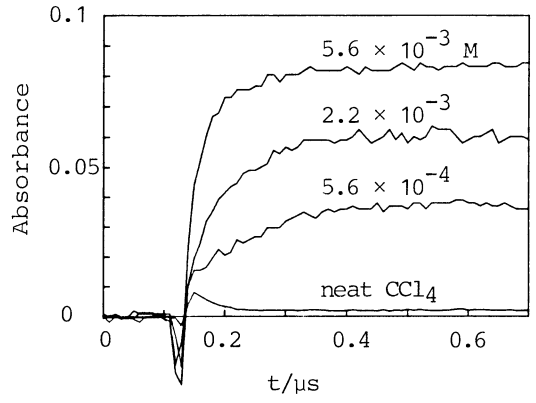

Fig. 2. Absorbance at 400 nm vs. time profiles taken after irradiation of indicated concentration of DMSO at 38 Gy.

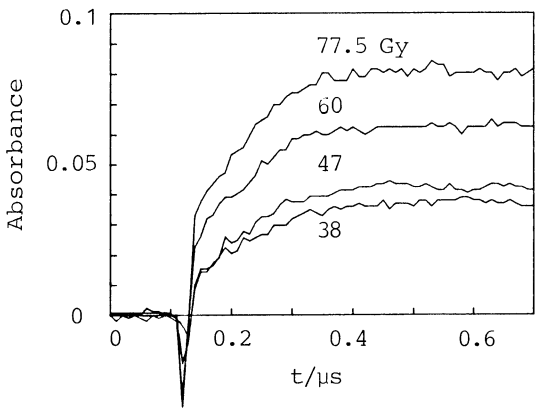

Fig. 3. Absorbance at 400 nm vs. time profiles taken after irradiation of 5.6×10^{-4} M DMSO in CCl_4 at the dose indicated.

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