BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (1), 339—340 (1975)

Extinction Coefficients of Maleate and Fumarate Radical Anions and Relative Yield of *cis-trans* Isomerization in Methanol Glass at 77 K

Ayako TORIKAI, Fumio NAKANO, Kenji FUEKI, and Zen-ichiro KURI
Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464

(Received April 3, 1974)

Synopsis. The photoisomerization of the γ-ray-induced maleate radical anion (DEM$^-$) to the fumarate radical anion (DEF$^-$) has been studied. The molar extinction coefficients of DEM$^-$ and DEF$^-$ have been determined to be $2.4_3\times10^4$ l mol^{-1} cm^{-1} and $3.4_0\times10^4$ l mol^{-1} cm^{-1} respectively. The yield of the isomerization from DEM$^-$ to DEF$^-$ is found to be 0.95.

In a previous paper,[1] we reported the photoisomerization of the maleate radical anion produced in 2-methyltetrahydrofuran (MTHF) glasses by γ-irradiation. The reaction intermediates observed were identified as radical anions. However, some problems remained to be resolved in the previous study. Because of the poor solubility of the *trans* isomer (dimethyl fumarate) to MTHF, for instance, the experiment changing the concentration of the *trans* isomer was not possible, so that the extinction coefficient could not be estimated accurately in that case.

We have now made an attempt to determine the molar extinction coefficients of the radical anions and to estimate the yield of the isomerization in rigid media. We have chosen diethyl maleate or diethyl fumarate-methanol systems in order to have a good solubility of the esters to methanol and for the convenience for optical studies.

Experimental

Spectro-grade methanol containing 5.7 mol% of triply distilled water was used as the solvent. The diethyl maleate (*cis*, DEM) and diethyl fumarate (*trans*, DEF) were purified by passage through an activated aluminum column. The samples were degassed by the freeze-pump-thaw technique. The samples were irradiated with Co-60 γ-rays at 77 K and, in most cases, at a dose rate of 2.0×10^{18} eV/g hr and a dose to 1.0×10^{18} eV/g. The photobleaching of γ-irradiated samples was carried out with visible light from a slide projector. The optical absorption spectra of γ-irradiated samples were measured at 77 K on a Hitachi EPU 2A spectrophotometer.

Results and Discussion

γ-Irradiated pure methanol glass gives an optical spectrum with an absorption maximum at 530 nm; this maximum has been assigned to the trapped electron (e_t) in methanol.[2]

When solutions containing DEM at low concentrations are irradiated, the spectrum shows absorption maxima at 530 and 345 nm (Fig. 1a). Upon an illumination with visible light (λ>490 nm), the 530 nm band diminishes in intensity, while the 345 nm band increases (Fig. 1b). The 345 nm band first shifts to 335 nm upon an illumination with visible light (no filter), while it is bleached by prolonged illumination (Fig. 1c, d). It is obvious from these experimental results that the *cis→trans* isomerization can occur by means of the illumination of visible light at wavelength shorter than 490 nm. The 345 and 335 nm bands are attributable to the DEM and DEF anion radicals respectively, judging from similar results in the previous work.[1] The reaction mechanism is proposed to be:

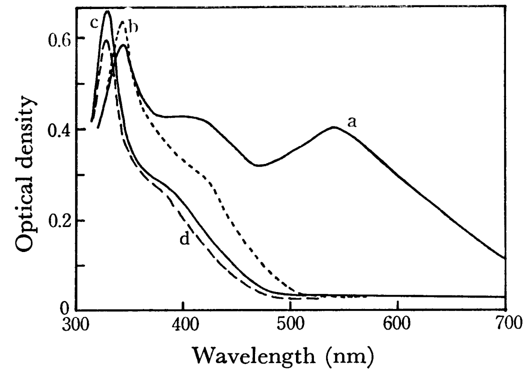

Fig. 1. Absorption spectra of γ-irradiated 0.08 mol% DEM in methanol at 77 K. a: sample γ-irradiated to a dose of 1.0×10^{18} eV/g, b: after 2 min illumination of sample a with visible light (λ—490 nm), c: after 2 min illumination of sample a with a visible light (no filter), d: after 60 min illumination of sample a with visible light.

$$CH_3OH \rightsquigarrow CH_3OH^+ + e_t$$

$$DEM + e \longrightarrow DEM^-$$

$$DEM + e_t \xrightarrow{\lambda>490\,\mathrm{nm}} DEM^-$$

$$DEM^- \xrightarrow{\lambda<490\,\mathrm{nm}} DEF^-$$

$$DEF^- \xrightarrow{h\nu} DEF + e_m$$

The molar extinction coefficients (ε) of the radical anions were determined from the competitive reaction

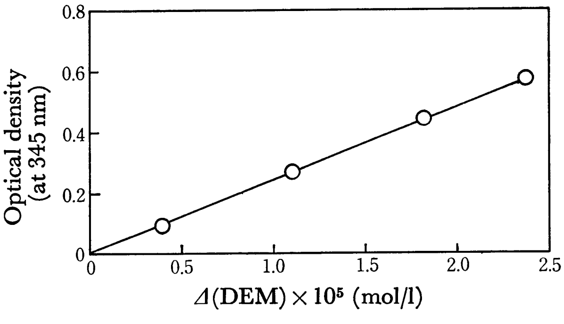

Fig. 2. Plot of optical density at 345 nm *vs.* Δ (DME) for γ-irradiated DEM in methanol at 77 K.

of mobile electrons between the esters and methanol (Fig. 2). Since the extinction coefficient of e_t has been known, the extinction coefficient of DEM$^-$ can be determined by the following method, assuming that the decrease in e_t contributes to the increase in DEM$^-$. In Fig. 2, Δ(DEM) indicates OD—OD$'/\varepsilon(e_t)d$, where OD: optical density at 530 nm in pure methanol glass; OD$'$: optical density at 530 nm in a DEM-methanol glass; $\varepsilon(e_t)$: molar extinction coefficient of e_t at 530 nm, and d: thickness of the cell. The value of $\varepsilon(e_t)$ has been reported to be 1.38×10^4 l mol^{-1} cm^{-1}.[3] The molar extinction coefficient (ε) of the DEM anion radical can be obtained from the slope of the straight line in Fig. 2. The ε of the DEF anion radical can also be obtained by the same method. The molar extinction coefficients of the DEM and DEF radical anions have been estimated to be $2.4_3\times10^4$ l mol^{-1} cm^{-1} at 345 nm and $3.4_0\times10^4$ l mol^{-1} cm^{-1} at 335 nm respectively.

The concentrations of DEM$^-$ and DEF$^-$ can be estimated by using these extinction coefficients. The DEM-methanol solutions were illuminated with visible light ($\lambda>490$ nm) after γ-irradiation at 77 K; the concentrations of DEM$^-$ were estimated at this stage of the experiment. Subsequent illumination of the sample with visible light (2 min) produced DEF$^-$, and the concentrations of DEF$^-$ were estimated. The concentrations of DEM$^-$ and DEF$^-$ obtained in this manner are shown in Fig. 3.

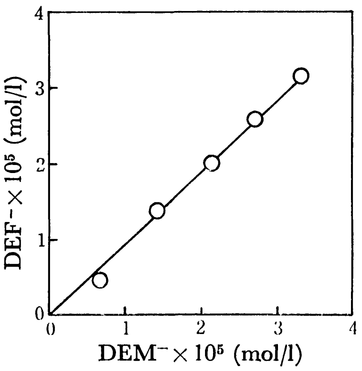

Fig. 3. Plot of the concentration of DEF$^-$ *vs.* the concentration of DEM$^-$ for photoisomerization of γ-irradiated DEM in methanol at 77 K.

The yield of the *cis*→*trans* isomerization is found to be 0.95 from the slope of the straight line in Fig. 3. This means that 95% of the DEM$^-$ produced undergoes the *cis*→*trans* isomerization.

References

1) A. Torikai, T. Suzuki, T. Miyazaki, K. Fueki, and Z. Kuri, *J. Phys. Chem.*, **75**, 482 (1971).

2) F. S. Dainton, G. A. Salmon, and J. Teplý, *Proc. Roy. Soc., Ser. A*, **286**, 27 (1965).

3) A. Habersbergerova, Lj Josimovic, and J. Teplý, *Trans. Faraday Soc.*, **66**, 669 (1970).