Ionic Intermediates in γ-Irradiated Organic Glasses. Stilbene Anions in 2-Methyltetrahydrofuran

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Studies of ionic intermediates formed by the γ-irradiation of organic glasses at low temperatures have recently been made by several investigators using spectrophotometric and electron spin resonance methods. They have provided significant information about the primary processes in radiation chemistry.

In the present study, the ionic intermediates of *trans*- and *cis*-stilbene produced in 2-methyltetrahydrofuran (MTHF) glasses at 77°K have been investigated by both spectrophotometric and electron spin resonance measurements.

When solutions containing *trans*-stilbene at low concentrations are irradiated with γ-rays, they develop a purplish-brown color, giving the optical absorption spectrum shown in Fig. 1. This spectrum may be attributed to the anion radical of *trans*-stilbene on the basis of the general features of the spectrum and the positions of the absorption maxima ($\lambda_{max}=500$ mμ and 700 mμ), which are essentially the same as those of the chemically-prepared *trans*-stilbene anion radical ($\lambda_{max}=485$ mμ and 694 mμ),[1] where small shifts in wavelength are seen. These band maxima are also in general agreement with those obtained by Dainton and Salmon in γ-irradiated *trans*-stilbene in MTHF at 77°K ($\lambda_{max}=504$ mμ, 561 mμ and 704 mμ),[2] although the 561 mμ band was not clearly observed in the present experiment.

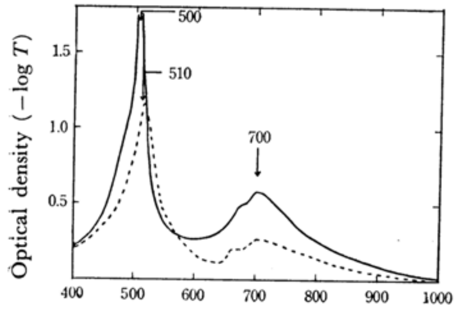

Fig. 1. The absorption spectra of stilbene anion radical in MTHF solution at 77°K.
Conc. of stilbene, 5×10^{-2} mol/*l*
Irradiation dose, 2×10^4 rad
Solid line, *trans*-stlbene; Dotted line, *cis*-stilbene

Under the same experimental conditions, *cis*-stilbene in MTHF gives rise to a reddish-purple color with the absorption spectrum shown in Fig. 1. The spectrum may be attributed to the anion radical of *cis*-stilbene, since the spectrum is somewhat different from that of the anion radical of *trans*-stilbene (see Fig. 1).

In both cases, another conceivable species is the stilbene cation radical, but there is little possibility of this because the contribution of the direct ionization of stilbene to the total ionization is very small at such low solute concentrations, and also because it is unlikely for a positive charge to be trapped in a significant amount by stilbene at low concentrations, since it is known that the positive ion of MTHF does not migrate in the solvent.[3]

The optical density of the 700 mμ band of the *trans*-stilbene anion radical is linear with a dose to about 8×10^4 rad. The optical densities are plotted against the *trans*-stilbene concentrations in Fig. 2. Assuming that the extinction coefficient, ε, of the 700 mμ band is equal to that of the chemically-prepared stilbene anion radical and taking $\varepsilon=7900\ l\ \mathrm{mol}^{-1}\mathrm{cm}^{-1}$,[1] the *G*-values for the formation of the *trans*-stilbene anion radical have been estimated. The highest value thus

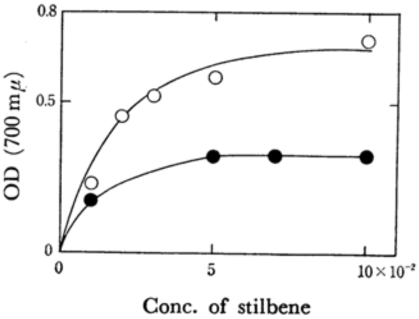

Fig. 2. Optical density (anion) *vs.* concentration of stilbene in MTHF at 77°K.
Irradiation dose, 2×10^4 rad
○, *trans*-stilbene at 700 mμ
●, *cis*-stilbene at 700 mμ

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[1] G. J. Hoijtink and P. H. Meij, *Z. Phys. Chem. N. F.*, **20**, 1 (1959).

[2] F. S. Dainton and G. A. Salmon, *Proc. Roy. Soc.*, **A285**, 319 (1965).

[3] W. H. Hamill, J. P. Guarino, M. R. Ronayne and J. A. Ward, *Discussions Faraday Soc.*, **36**, 169 (1963).

obtained attains 8 at 1×10^{-1} mol/l of *trans*-stilbene in MTHF. This value is unacceptably high as the yield for anion formation, indicating that the extinction coefficient used is probably in error. In order to examine the reliability of our measurements, we have carried out a similar experiment on γ-irradiated MTHF containing biphenyl, since both the extinction coefficient and the *G*-value of the biphenyl anion have been well established.[4] The *G*-value obtained is 2.6 at 6×10^{-2} mol/l of biphenyl; this is in reasonable agreement with that obtained by Hamill *et al.*[4]

The optical density of the 700 mμ band for *cis*-stilbene was also linear with a dose to about 8×10^4 rad. The optical densities are plotted against the *cis*-stilbene concentrations in Fig. 2.

When *cis*-stilbene in MTHF solutions was irradiated at a dose of 10^5 rad at 77°K and then warmed to room temperature, the isomerization of *cis*-stilbene to *trans*-stilbene was not observed. This may indicate that either the isomerization of *cis*-stilbene to *trans*-stilbene does not occur through the anion radical as an intermediate at such a low temperature, or that the charge neutralization of the anion radical of *cis*-stilbene with a positive ion precedes the isomerization.

The γ-irradiation of saturated solutions of *trans*-stilbene in MTHF at 77°K gives rise to the ESR signal shown in Fig. 3. The ESR spectrum is an line with a width between maximum slope of about 12 G; this is in accordance with that of the chemically prepared *trans*-stilbene anion radical in a tetrahydrofuran solution.[5]

Fig. 3. The ESR spectrum of *trans*-stilbene anion radical in MTHF solution at 77°K. irradiation dose, 2×10^5 rad.

The ESR line attributable to the solvent-trapped electron was not observed in a sample containing stilbene at the saturated concentration. This can be interpreted in terms of competitive electron capture by stilbene. These ESR results provide additional evidence for the formation of the stilbene anion radical.

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[4] M. R. Ronayne, J. P. Guarino and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 4230 (1962).

[5] K. Morigaki, K. Kuwata and K. Hirota, This Bulletin, **33**, 958 (1960).