

Sensitized Radiolytic Isomerization of Stilbene

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RECENT investigations into energy transfer mechanisms in the radiolysis of solutions in benzene^{1,2} led to diverging opinions regarding the species involved. In view of the good understanding of direct and sensitized reversible photo-isomerization in stilbene,^{3,4} the latter appeared promising in investigating possible energy transfer reactions taking place in radiolysis, in particular in dilute ($<10^{-4}$ molar) organic solutions.

Irradiation of solutions of stilbene in aliphatic hydrocarbons (isohexane, isopentane, methylcyclohexane) was found to result mainly in irreversible decomposition, with only little concurrent isomerization. However, in benzene solutions the isomerization was found to be the predominant reaction.

Solutions of either *cis*- or *trans*-stilbene in benzene, contained in optical quartz cells, were thoroughly evacuated. The cells were sealed off and then exposed to radiation from either a 200 Kv X-ray machine or a cobalt-60 source. The

isomeric composition of the solutions was determined spectrophotometrically in the same cells as a function of irradiation time, as illustrated by the curves in Figure 1. The dose rate was about 3×10^{17} ev/min. ml. *G*-Values for the isomerizations were calculated from the dose rate and the initial slopes of the experimental curves. Some results are summarized in the Table.

As seen in the Table, the presence of oxygen or anthracene sharply reduces the rate of radiolytic isomerization in very dilute solutions, this effect becoming smaller with increasing stilbene concentration. On the other hand naphthalene, phenanthrene, and triphenylene all enhance the isomerization rates in both directions. In their presence a radiation-stationary state is approached in which the ratio *cis/trans* is about 1.6 (*cf.* Figure 1). Biacetyl enhances the *trans* → *cis* conversion more than the reverse reaction, and the stationary state contains about 72 per cent *cis*.

The *G*-values in the presence of the enhancing

¹ R. B. Cundall and P. A. Griffiths, *Discuss. Faraday Soc.*, 1963, **36**, 111; *Trans. Faraday Soc.*, 1965, **61**, 1968.

² J. Nosworthy, *Trans. Faraday Soc.*, 1965, **61**, 1138.

³ G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsel, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, 1964, **86**, 3197.

⁴ S. Malkin and E. Fischer, *J. Phys. Chem.*, 1964, **68**, 1153.

compounds increase with the latter's concentration and approach limiting values which in the case of naphthalene are as given in the Table. They can be reached at concentrations above about 3×10^{-3} molar naphthalene, and are independent of the concentration of stilbene.

these added solutes and "active" benzene. If this product does *not* react with stilbene, the isomerization will be attenuated, while if it reacts with stilbene, the isomerization rate will be either not affected or enhanced, depending on the relative lifetimes of "active" benzene and "active" product.

TABLE

G (isomerization) Values, for solutions of stilbene in benzene, in the absence or presence of sensitizers or inhibitors, irradiated with X-rays

Concentration of stilbene moles/l.	Degassed	Aerated	<i>G</i> (isomerization)		
			10^{-3} molar Anthracene	5×10^{-3} molar Naphthalene	5×10^{-3} molar Biacetyl
<i>cis</i> , 5×10^{-5}	0.037	0.019	0.005	0.27	0.12
<i>cis</i> , 5×10^{-4}	0.12	0.10	—	0.28	—
<i>trans</i> , 5×10^{-5}	0.033	0.005	0.01	0.45	0.36
<i>trans</i> , 5×10^{-4}	0.15	0.14	—	0.44	—

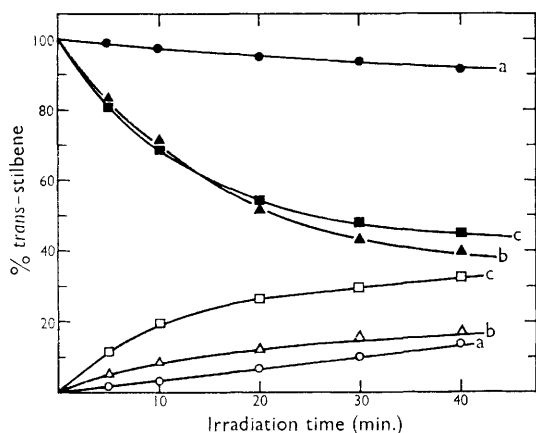


FIGURE 9

Change of isomeric composition with time of irradiation. 5×10^{-5} M-solutions of *cis*- or *trans*-stilbene in benzene. (a) no additives, (b) with 5×10^{-3} M-naphthalene, (c) with 10^{-3} M-biacetyl.

The results can be explained by assuming that absorption of radiation by stilbene leads to the formation of an active species able to react with stilbene to bring about isomerization. Added solutes will compete with stilbene for "active" benzene molecules. The way in which such competition affects the isomerization reaction will depend on the product of the reaction between

The results given above indicate that anthracene and oxygen belong to the former class, while the remaining added compounds belong to the latter. A plausible explanation would be that the "active" benzene is in the triplet state, known to have a very short lifetime^{1,2,5} of 10^{-7} to 10^{-8} sec. Collisions with the added organic solutes result in formation of the respective triplet molecules, having lifetimes⁶ of about 10^{-4} sec. and thus standing a very much higher chance of encountering stilbene molecules during their lifetime. In the case of anthracene, the energy of the triplet state⁷ is too low (42 Kcal./mole) to bring about isomerization in either direction. With naphthalene and the other aromatic hydrocarbons found to enhance the isomerization the triplet levels are high enough^{7,8} (61–67 Kcal./mole) to cause isomerization. Here the net effect of adding these compounds at sufficiently high concentrations, to ensure the efficient scavenging of the triplet benzene molecules, is a conversion of short-lived benzene triplets (at an energy level⁹ of about 85 Kcal./mole) into long-lived triplets. Biacetyl occupies an intermediate position, enhancing the *trans* → *cis* conversion much more than the *cis* → *trans* conversion. This may be explained at least qualitatively by the fact that its triplet (55 Kcal./mole) is above that of *trans*-stilbene (48 Kcal./mole) but somewhat below that of *cis*-stilbene (about 57 Kcal./mole), as shown by Hammond *et al.*³ and by Lippert¹⁰ in connection with the

⁵ V. A. Krongaus, *Doklady Akad. Nauk S.S.S.R.*, 1964, **155**, 658.

⁶ G. Porter and F. Wilkinson, *Proc. Roy. Soc.*, 1961, **A**, **264**, 1.

⁷ G. Porter, *Proc. Chem. Soc.*, 1959, 291.

⁸ W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1964, **86**, 4537.

⁹ D. F. Evans, *J. Chem. Soc.*, 1957, 1351.

¹⁰ E. Lippert, *Z. phys. Chem. (Frankfurt)*, 1964, **42**, 125.

photosensitized isomerization of stilbene. The close similarity between the present results and those obtained in photosensitization studies³ is striking. This holds also for the investigation, by Krongaus,⁵ of photoisomerization of stilbene in benzene solutions irradiated at 245 m μ . Light at this wavelength is absorbed predominantly by the solvent benzene, just as the ionizing radiation in our case. Krongaus explained his results by assuming primary formation of triplet benzene molecules, which then transfer their energy to stilbene molecules.

The *G*-value for the formation of triplet benzene may be estimated if it is assumed that all such triplets will transfer their energy to the stilbene, either directly or through the added solutes, and that the excited stilbene molecules have an equal chance to revert to the ground state of either the *cis*- or the *trans*-molecules. This leads to *G*-values of close to unity, in good accordance with the value of 1.1 estimated by Nosworthy² from the fumarate \rightarrow malate radiolytic transformation in benzene solutions.

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