Radiation-induced Geometrical Isomerisation of Stilbene in the Gas Phase at 200°

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Summary The addition of 1% SF_6 to *cis*-stilbene has no effect on the initial *G* (*cis–trans*) value for γ-radiolysis in the gas phase.

IN a previous communication[1] from this laboratory, the catalytic effect of SF_6 on the ^{60}Co γ-radiation induced geometrical isomerisation of but-2-ene was described, *G* values (molecules converted/100 ev absorbed) of *ca.* 20,000 being obtained. The investigations are now extended to stilbene vapour at 200°.

The technique used was to irradiate a weighed, de-gassed sample of stilbene sealed in a Pyrex reaction vessel at 200°, the amount of stilbene being sufficiently small for complete vaporisation. *trans*-Stilbene was used as received (Koch-Light Ltd). *cis*-Stilbene was fractionated in a molecular still *in vacuo* at ambient temperature, the middle fraction being used. Analysis by g.l.c. at 200° showed no detectable impurity in the *trans*-stilbene, *cis*-stilbene contained 4·25% *trans*-stilbene and an apparently small quantity of material of lower b.p. A further vacuum-distillation of the *cis*-stilbene over activated 5A molecular sieve had no effect on the results obtained.

Thermal equilibrium in the *cis–trans*-stilbene vapour-phase system over the temperature range 320—341° has been found[2] to lie between 92—94% *trans*-stilbene. On prolonged γ-irradiation at 200° ($1{\cdot}24 \times 10^{21}$ ev g.$^{-1}$) *cis*-stilbene vapour was converted into 96·5% *trans*-stilbene. The thermal contribution alone over the period spent at 200° was calculated to be approximately 3% conversion into *trans*-stilbene. γ-Irradiation of *trans*-stilbene to steady state gave 97·7% *trans*-stilbene. The conversion of *cis*- into *trans*-stilbene was also investigated at short irradiation times where the thermal contribution at 200° is negligible. The results, corrected for the initial presence of 4·25% *trans*-stilbene, are illustrated in the Figure. The addition of 1% SF_6 has no effect on the rate of conversion and an initial $G(cis \rightarrow trans) = 1930$ is obtained from the tangent to the curve at the origin.

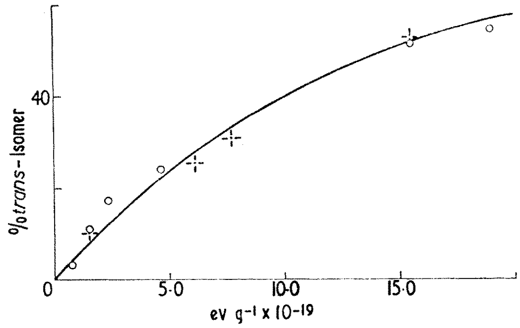

FIGURE. *Radiation-induced* cis–trans-*isomerisation of stilbene; circles*: cis-*stilbene*; *crosses*: cis-*stilbene plus* 1% SF_6.

Studies of the radiolysis of solutions of *cis*-stilbene[3] have shown that for highly purified material in concentrated solution, $G(cis \rightarrow trans) > 200$ indicating a chain reaction for which the following mechanism involving stilbene anions was suggested.[4]

$$e^- + c\text{-stilbene} \longrightarrow t\text{-stilbene}^-$$

$$t\text{-stilbene}^- + c\text{-stilbene} \longrightarrow t\text{-stilbene} + t\text{-stilbene}^-$$

These species have been observed[5] in the pulse radiolysis of stilbene solutions and have been shown to undergo very rapid charge exchange with anthracene, which has a slightly larger electron affinity than stilbene. The addition of CCl_4 which has a much larger electron affinity than stilbene (CCl_4 49,[6] *cis*-stilbene 9·2,[7] *trans*-stilbene 8·7[7] kcal. mole^{-1}), was shown[4] to suppress the rearrangement of *trans*-stilbene thus supporting the suggested electron-capture mechanism.

The present results, showing that the addition of SF_6 (electron affinity[8] SF_6 34 kcal. mole^{-1}) has no effect on *G* init(*cis* → *trans*), can only be correlated with a stilbene anionic chain reaction if the species formed from SF_6 by electron capture can catalyse the isomerisation with the same efficiency as the stilbene anion. Such catalysis would be in agreement with the radiation-induced chain-reaction geometrical isomerisation promoted by SF_6 in but-2-ene.[1] If the chain isomerisation involved stilbene cations, the addition of SF_6 might, by effectively decreasing electron mobility, be expected to increase the lifetime of such cations before neutralisation and hence increase the isomerisation rate. The results do not support this suggestion.

A free-radical chain mechanism may also account for the apparent insensitivity of the system to added SF_6. A mechanism involving the formation of a radical–stilbene complex intermediate has been suggested[5] as complementary to the ionic mechanism in the rearrangement of *cis*-stilbene in concentrated solutions. However, no choice can be made on present evidence.

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