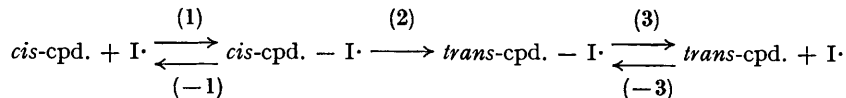


# The Mechanism of the Iodine-catalyzed Thermal Isomerization of Substituted Ethylenes

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FROM previous work on the iodine-catalyzed isomerization of *cis*-cinnamic acid,<sup>1</sup> *cis*-stilbene,<sup>2</sup> and di-iodoethylene<sup>3</sup> it is clear that for all these reactions the following scheme will be valid:



The iodine atoms can be generated either thermally or photochemically.

Noyes, Dickinson, and Schomaker<sup>3</sup> found that in the isomerization of di-iodoethylene the first step is rapidly reversible whereas the second step occurs relatively slowly. Also from kinetic measurements on the isomerization of *cis*-cinnamic esters by Visscher<sup>4</sup> and Kooyman<sup>5</sup> it was concluded that (2) is the rate-determining step.

Until now no evidence has been furnished as to whether a covalently bonded intermediate (*cis*-cpd.-I·) is actually formed during the isomerizations. Therefore we have tried to obtain more information about the nature of the intermediate. For that purpose rates of iodine-catalyzed isomerizations of *cis*-stilbene and four symmetrically *pp'*-substituted *cis*-stilbenes were measured.

Using oxygen-free carbon tetrachloride as solvent the reactions were carried out in ampoules which were sealed under nitrogen and placed in a

thermostat in the dark in order to exclude any photochemical effects.

The reactions were followed spectrophotometrically. As can be seen from the Table rate

constants, calculated from measurements at constant temperature but different iodine concentrations, vary slightly. Similar discrepancies have been reported by other workers and were ascribed to complex formation between iodine molecules and the ethylene compound. Possibly they may also arise from the presence of small amounts of oxygen which has a retarding effect on the reactions. It is clear, however, that electron-donating substituents accelerate the isomerization whereas electron-withdrawing substituents slow it. Activation energies are lowered by all substituents but this decrease is greatest with electron-donating substituents.

It was assumed by Visscher and Kooyman that differences in the rate constants of the isomerization of *cis*-cinnamic esters are due to differences in  $K_1 = k_1/k_{-1}$  rather than to differences in  $k_2$ . Supposing that in our case also substituents influence mainly the equilibrium constant  $K_1$  we

Isomerization rate constants<sup>a</sup> for *p,p'*-di-*X*-*cis*-stilbenes<sup>b</sup>

[I <sub>2</sub> ]	T = 100°			T = 90°			ΔE <sup>c</sup>
	0.02	0.005	0.001	0.02	0.005	0.001	
X + H	2.38	1.99	1.80	0.93	0.82	—	23.3
X = Me	—	3.54	—	1.73	1.58	—	20.5
X = OMe	—	5.57	5.91	—	2.54	2.60	20.5
X = Cl	1.61	1.52	—	0.66	0.62	—	22.7
X = CN	1.29	1.18	—	0.55	—	—	21.7

<sup>a</sup>  $k$  values are derived from  $d[\text{cis-cpd}]/dt = k[\text{cis-cpd}][\text{I}_2]^{1/2}$  and are expressed in  $\text{mole}^{-1/2} \text{l.}^{1/2} \text{h.}^{-1}$ .

<sup>b</sup> Concentration of stilbene in all runs, 0.05 mole/l.

<sup>c</sup> Mean value of the activation energy in kcal./mole, calculated from experiments at the same iodine concentration.

<sup>1</sup> A. Berthoud and Ch. Urech, *J. Chim. phys.*, 1930, **27**, 291; R. G. Dickinson and H. Lotzkar, *J. Amer. Chem. Soc.*, 1937, **59**, 472.

<sup>2</sup> S. Yamashita, *Bull. Chem. Soc. Japan*, 1961, **34**, 487.

<sup>3</sup> R. M. Noyes, R. G. Dickinson, and V. Schomaker, *J. Amer. Chem. Soc.*, 1945, **67**, 1319.

<sup>4</sup> E. A. R. Visscher, Thesis, Leiden, 1963.

<sup>5</sup> E. A. R. Visscher and E. C. Kooyman, *J. Catalysis*, 1963, **2**, 421.

can conclude that in the intermediate (*cis*-cpd.-I) the iodine atom has withdrawn a negative charge from the stilbene molecule. If this inductive effect only was involved a plot of  $\Delta \log k$  against  $\sigma$  should give a linear relationship according to the Hammett equation. It appears, however, that

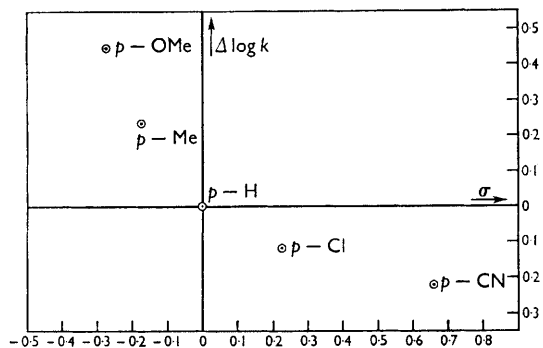


FIGURE 1. Plot of  $\Delta \log k$  against  $\sigma$ , according to Hammett, for iodine-catalyzed isomerizations of *p,p'*-substituted *cis*-stilbenes. Mean  $k$  values of several measurements at different iodine concentrations and at  $100^\circ$  are used (see Table). Values obtained at  $90^\circ$  give a similar curve.

$\Delta \log k$  values of all four substituted stilbenes lie above the appropriate straight line through zero. This increase in rate constant ascribed to an increase in  $K_1$  might be explained by enhanced resonance stabilization in the presence of *para*-substituents if the radical character of the catalytic species has been transferred to the stilbene moiety in the intermediate. Therefore, it is plausible from our results that the iodine atom is actually bound to the stilbene molecule in the intermediate (*cis*-cpd.-I).

In order to eliminate this resonance stabilization and study only the inductive effect the investigation is being continued with *m,m'*-substituted stilbenes.

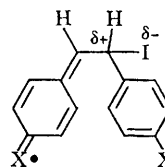


FIGURE 2. Illustration of the resonance stabilization of the radical intermediate *cis*-cpd.-I.

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