Solid–Gas Reactions. Part II.[1] Solid-state *cis–trans* Isomerisation of Alkoxycinnamic Acids in Iodine Vapour

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The *cis–trans* isomerisation of solid *o*-alkoxy-*cis*-cinnamic acids by iodine vapour has been analysed by determination of the rate of the reaction from the change in i.r. transmittance. The isomerisation follows a first-order mechanism. The energy of activation for the isomerisation increases with the density of the solid material. A plot of $\Delta H^‡$ against $\Delta S^‡$ is linear.

A STUDY [1] of the bromination of solid olefins by bromine in the vapour phase has shown that in general addition of bromine proceeds by *trans*-addition to *cis*- and *trans*-substituted ethylenes, and suggested that the abnormal direction of addition to *cis*-substituted styrenes and stilbenes is due to *cis–trans* isomerisation prior to or during addition to *erythro*- or *meso*-dibromides. We now demonstrate such a solid-state *cis–trans* isomerisation by treatment of olefins with iodine vapour. Iodine causes isomerisation (at room temperature) of all those *cis*-ethylenes which give a *meso*- or an *erythro*-adduct with bromine, but fails to do so where bromine is added (at room temperature) in the *trans*-direction (DL or *threo*). In order to clarify the mechanism of *cis–trans* conversion we undertook a more quantitative analysis of the iodine-catalysed reaction of a series of alkoxy-*cis*-cinnamic acids. This particular system, apart from its easy accessibility, is likely to isomerise *via* a common reaction mechanism.

EXPERIMENTAL

The compounds were prepared as described [2,3] and were recrystallised repeatedly. Materials were ground in an agate mortar and sieved to standard mesh size before being introduced into a reaction vessel containing solid iodine; the whole was immersed in a thermostat regulated to ±0·2 °C over the temperature range 20—80 °C. The vessel was rigorously shielded from light. A series of blank experiments confirmed that no thermal isomerisation took place in the absence of iodine over the temperature range employed. Samples of the materials were withdrawn from the reaction chamber, and the percentage of the *cis*- and *trans*-isomers determined by i.r. measurements for potassium bromide pellets (200 mg) with a fixed content of organic material with a Perkin-Elmer 221 spectrophotometer. These analyses were based on the bands characteristic of the *trans*-compound in the region 12—15 μm for the cinnamic acid series, and on calibration curves for each *cis–trans* pair made up in 10% intervals of composition to cover the whole range. The band at 6·05 μm was used as internal standard. Several independent measurements of the same point of the reaction process were carried out in

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[1] Part I, E. Hadjoudis, E. Kariv, and G. M. J. Schmidt, preceding paper.

[2] M. D. Cohen, G. M. J. Schmidt, and F. I. Sonntag, *J. Chem. Soc.*, 1964, 2000.

[3] J. Bregman, K. Osaki, G. M. J. Schmidt, and F. I. Sonntag, *J. Chem. Soc.*, 1964, 2021.

order to check the reproducibility of the i.r. spectra; such measurements demonstrated that the peak height could be determined to better than 1%. The end of the isomerisation was confirmed by i.r. spectrum, m.p., and X-ray powder photographs on a Debye–Scherrer camera of radius 5·7 cm.

RESULTS

Table 1 lists the kinetic data for the *cis*-cinnamic acids. Figure 1 shows a typical plot of the percentage of *trans*-isomer formed from *p*-methoxy-*cis*-cinnamic acid at various temperatures as a function of time; the curves show no evidence of an induction period or of an autocatalytic effect such as might be associated with the formation of a liquid phase due to depression of the m.p. of the reactant by the product. Also, no decomposition occurs since no extraneous absorption bands were observed in any experiment. Figure 2 shows the calibration curve of mixtures of the two isomeric *p*-methoxycinnamic acids.

TABLE 1

First-order rate coefficients for the *cis–trans* isomerisation of cinnamic acids

Substituent	t/°C	10^{-2} k/min^{-1}
o-OMe (1)	50	0·10
	60	0·49
	70	1·80
	80	7·67
o-OMe (2)	50	0·34
	60	0·58
	70	2·55
o-OEt (3)	40	0·38
	50	0·17
	60	0·73
	70	3·20
o-OPr^n (4)	40	0·08
	50	0·41
	60	1·40
	70	4·20
o-OPr^i (5)	20	0·78
	30	2·60
	40	8·60
	50	21·00
p-OMe (6)	20	0·44
	30	1·27
	40	4·30
	50	9·70

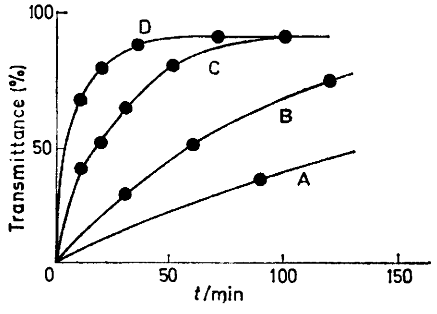

FIGURE 1 The *cis–trans* conversion of *p*-methoxycinnamic acid; A, 20°; B, 30°; C, 40°; and D, 50°

Further analysis of the rate data was attempted. Plots of time against log (% *cis*) follow acceptable straight lines, as shown in Figure 3 for the *p*-methoxy-*cis*-acid from which it proved possible to derive the rate constants listed in Table 1 with an estimated error of 3%. Arrhenius plots based on these values of the rate constants (*e.g.* Figure 4) yield the values of E listed in Table 2 with an uncertainty of 1—2 kcal mol^{-1}. From these values and the rate constants it was possible to derive the entropy [4] $\Delta S^\ddagger$ and the enthalpy of activation $\Delta H^\ddagger$ listed in Table 2 with an

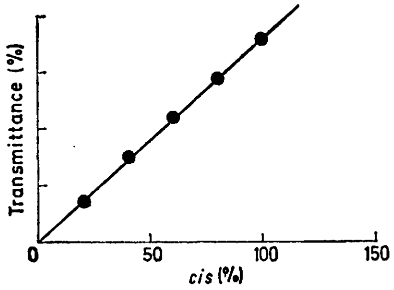

FIGURE 2 Calibration curve of mixtures of the two isomeric methoxycinnamic acid

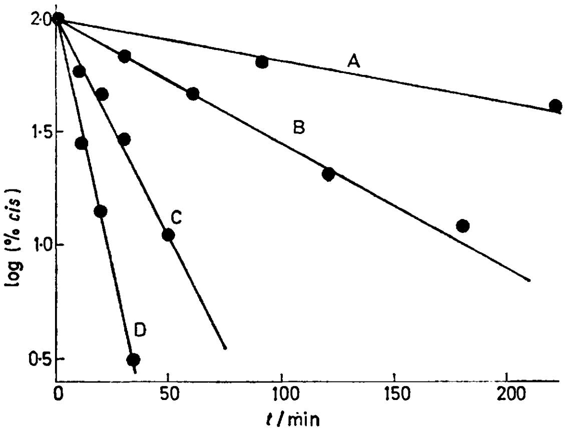

FIGURE 3 First-order kinetic plot of the isomerisation *p*-methoxycinnamic acid; A, 20°; B, 30°; C, 40°; and D, 50°

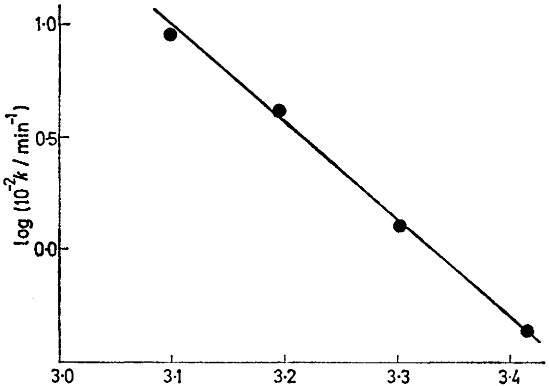

FIGURE 4 Arrhenius plot for *p*-methoxycinnamic acid, E = 20 kcal mol^{-1}

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[4] 'Techniques of Organic Chemistry,' vol. VIII, Part I, ed. A. Weissberger, Interscience, New York, 1961, p. 200.

uncertainty of 0·25—1·25 cal mol^{-1} K^{-1} and 1—2 kcal mol^{-1} respectively.

DISCUSSION

The activation energies refer to a complex sequence of events and a mechanistic interpretation is not possible at this stage. Indeed, the absence of a concentration term involving iodine does not necessarily reflect the role of iodine, which is likely to be ' catalytic ' since no measurable uptake of iodine (<1%) could be recorded during the isomerisation. We therefore interpret our results in the first place in solid-state terms such as crystal density. The chemically related alkoxy-*cis*-cinnamic acids vary in density from 1·15 to 1·43 g cm^{-3} and in crystallographic packing type[2] (see Table 2). The list includes the interesting example of *o*-methoxy-*cis*-cinnamic acid which crystallises in two polymorphic forms of the same packing type but of different densities.

TABLE 2

Structural and activation parameters of *cis*-cinnamic acids

Substituent	M.p. (°C)	Packing type	d/g cm^{-3}	E/ kcal mol^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal mol^{-1} K^{-1}
5-Chloro-2-methoxy	151—152	α	1·43			
(1)	94	α_1	1·27	31·8	31·15	13·61
(2)	89	α_2	1·24	25·5	24·85	−3·42
(3)	101—102	α	1·25	31·3	30·65	13·15
(4)	82—83	β	1·25	25·6	24·95	−2·77
(5)	59—60	β	1·22	20·7	20·05	−10·08
(6)	67—68	α	1·15	20·0	19·35	−15·95

A plot of the Arrhenius energy of activation against density is shown in Figure 5. The energy of activation increases with density until, eventually, isomerisation no longer takes place. A plot of the values of $\Delta H^{\ddagger}$ against those of $\Delta S^{\ddagger}$, gives the linear relation shown in Figure 6. The existence of such a relationship is evidence for a common mechanism for the series of compounds examined.[5] This mechanism should be structure dependent as is shown by the activation energy–density relationship. The effect of density is clearly brought out by the example of *o*-methoxy-*cis*-cinnamic acid: the two crystalline modifications differ markedly in density and possess appreciably different energies of activation. The thermal *cis–trans* isomerisation of *cis*-cinnamic acids in the dissolved phase catalysed by iodine is known; the mechanism of the solid-state reaction presumably follows that suggested for the solution reaction. The energies of activation of isomerisation in solution are in the neighbourhood of the values observed here. However, such correspondence is undoubtedly coincidental; the values determined here may refer to the energy of activation of diffusion of iodine into the lattice, or to the heats of sublimation of these crystals (presumably close to the experimental E values) and hence to the energy required to remove a molecule reactant from its lattice site prior to rearrangement, or, most likely, a combination of all these energy terms.

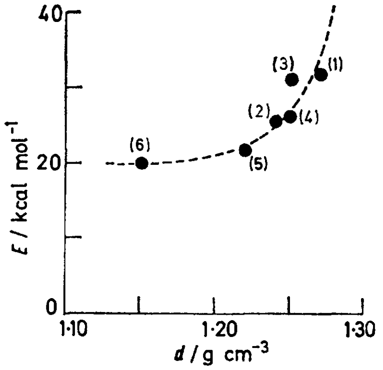

FIGURE 5 The relationship between energies of activation and densities

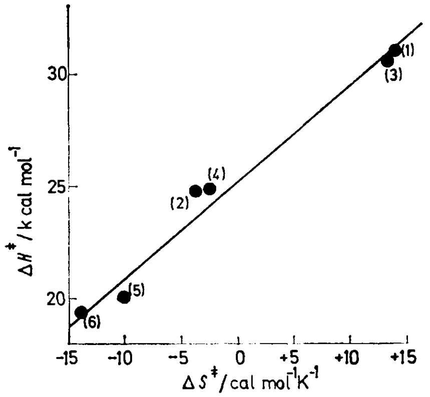

FIGURE 6 The enthalpy–entropy correlation

[1/1929 *Received*, 20*th October*, 1971]

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[5] J. E. Leffler, *J. Org. Chem.*, 1955, **20**, 1202.