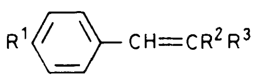
Surface Photochemistry: Photocatalysed Olefin *cis–trans* Equilibrium mediated by CdS

Hussain Al-Ekabi and Paul De Mayo*

Photochemistry Unit, Department of Chemistry, University of Western Ontario, London, Ontario, Canada, N6A 5B7

Six substituted styrenes have been shown to achieve thermodynamic equilibrium *via* a radical-ion mechanism when exposed to the semiconductor CdS excited by light of wavelength shorter than its band gap.

The use of semiconductors for the light-induced generation of fuels is an active area of current research. There has been far less use of semiconductors for other photochemical objectives these consisting, essentially, of oxidative or reductive operations.[1] Amongst the few examples outside these main domains are the CdS powder photocatalysed retrocycloaddition of a homocubane derivative,[2] the dissociation of dianthracene,[3] and the dimerization of phenyl vinyl ether[3] and the gas phase isomerisation of butenes over TiO_2 and ZnO.[4] We now report the photocatalysed thermodynamic equilibration of six substituted styrene derivatives (**1**)—(**6**) mediated by CdS.†



(**1**) R^1 = H, R^2 = H, R^3 = Ph
(**2**) R^1 = H, R^2 = H, R^3 = COMe
(**3**) R^1 = H, R^2 = CN, R^3 = Ph
(**4**) R^1 = OMe, R^2 = H, R^3 = Me
(**5**) R^1 = H, R^2 = H, R^3 = CO_2Me
(**6**) R^1 = H, R^2 = H, R^3 = CN

Irradiation, typically, of 10^{-2} M olefin in methylene dichloride in the presence of CdS (45 mg/5 ml) at $\lambda > 430$ nm (CdS band gap = 2.4 V; *ca.* 520 nm) gave the results indicated in Table 1. The appropriate controls were carried out. The equilibria, approached from both sides lay heavily on the side of the *trans*-isomers. That the equilibrium was thermodynamic was shown by a comparison with iodine photocatalysed[6]

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† The formation of *cis*-stilbene from the TiO_2 mediated oxidation of *trans*-stilbene has been reported:[5] this was probably formed by direct excitation of the *trans*-stilbene under the conditions designated, or photosensitised isomerization by benzaldehyde, a product of the oxidation, or both.

Table 1. Isomeric composition of the thermodynamic *cis–trans* equilibria of (**1**)—(**6**) initiated by CdS or I_2.[a]

Compound	*cis*/% CdS	*cis*/% I_2	*trans*/% CdS	*trans*/% I_2
(**1**)	<1	<1	>99	>99
(**2**)[b]	<1	<1	>99	>99
(**3**)	2	2	98	98
(**4**)	3	3	97	97
(**5**)	<1	<1	>99	>99
(**6**)	25	[37][c]	75	[63][c]

[a] In methylene dichloride: $\lambda > 430$ nm. [b] (**2**) was irradiated at $\lambda > 460$ nm. [c] The thermodynamic equilibrium of (**6**) has been estimated in the gas phase at 352 °C (ref. 13).

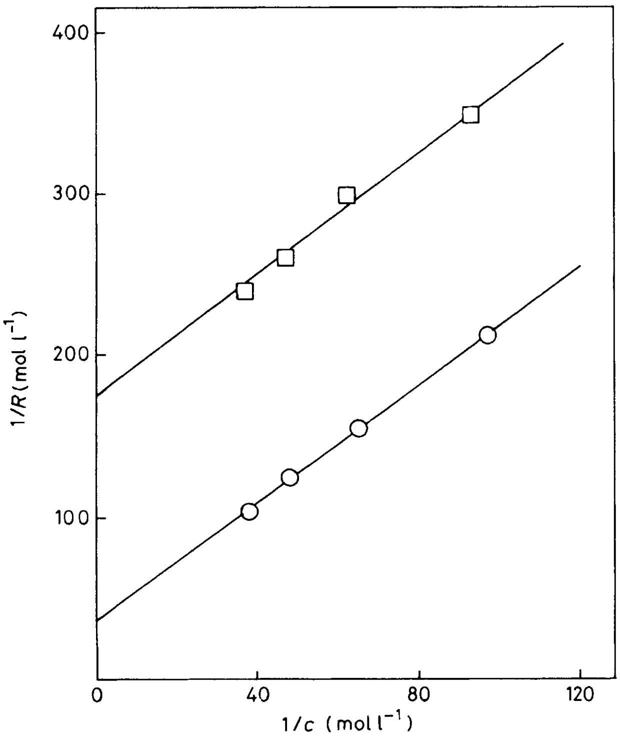

Figure 1. Application of the reciprocal Langmuir–Hinshelwood kinetic treatment ($1/R = 1/k_r + 1/k_rK_1c$) to the isomerizations of (**1**) (○, irradiation periods of 17 min) and (**5**) (□, irradiation periods of 15 min) both with a 1 kW xenon source.

values (Table 1). Only with (**6**) did the iodine technique fail: such failure for some stilbene derivatives has been previously reported.[6]

That the reaction was a surface phenomenon was shown by the fact that, for *cis*-(**1**) and *cis*-(**5**), plots of the reciprocal of the conversion rate (R)‡ against the reciprocal of the olefin concentration (c) were linear with non-zero intercepts, *i.e.*, Langmuir–Hinshelwood kinetics[7] were appropriate (Figure 1).

The most likely mechanism§ for the reaction appeared to be electron-transfer from the olefin to the photogenerated 'hole' on the semiconductor, with the generation of the corresponding radical-cation. One mode of demonstrating the involvement of a radical-cation is the observation of its quenching by an electron donor. The oxidation potential of *cis*-stilbene (**1**) is presumably very close to that of *trans*-stilbene (**1**) ($E^{ox}{}_{\frac{1}{2}} = 1.43$ V *vs.* saturated calomel electrode[8]) and hence its oxidation should be quenched by 1,2,4-trimethoxybenzene ($E^{ox}{}_{\frac{1}{2}} = 1.12$ V[9]). Indeed, in the presence of an equimolar amount of this substance ϕ_0/ϕ (the relative quantum yields of the reaction with and without quencher) was found to be 7.8. As has been pointed out,[10] however, quenching of a surface-induced reaction does not necessarily imply electron transfer: there may simply be competition for the active sites on the semiconductor without any photochemical quenching. To test for this possibility, 1,3,5-trimethoxybenzene ($E^{ox}{}_{\frac{1}{2}} = 1.49$ V[11]), which should be a much poorer electron quencher for stilbene, was used since its adsorption properties should be very similar to that of the 1,2,4-isomer. Indeed, ϕ_0/ϕ was reduced to 1.9, suggesting that both quenching processes may be involved, but that the participation of a radical-cation is certainly implicated.

In other semiconductor-catalysed organic rections[2,3,10] it was found that oxygen accelerates the photocatalytic effect of the semiconductor. In the present study the reverse has been found, the degassed solution of (**1**) reacting 2.9 times faster than the aerated solution. The effect diminishes along the series (**1**)—(**6**). At least two explanations are possible: oxygen may compete with the olefin for active sites; and electron donation to the photoinduced 'hole' by chemisorbed oxygen, a process known to be fast,[12] may compete with radical-ion formation. Degassing may reduce, partially, the surface oxygen concentration.

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‡ The rates, R, were taken, for this purpose, as the conversion per unit time with constant light flux.

§ A 'triplet' mechanism can be excluded since, at the band gap energy (*ca.* 55 kcal/mol) or less, triplet stilbene is known, from energy transfer work, to favour *cis*-stilbene formation. Furthermore, methoxybenzenes have triplet energies too high to permit them to act as quenchers in the manner here reported.