Surface Photochemistry: Exergonic and Endergonic Photocatalysed Reaction in the CdS-mediated *cis–trans*-Isomerization of *cis*-4-Substituted Stilbenes

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The *cis*-stilbenes (**1a—g**) undergo photocatalysed *cis–trans*-isomerization on CdS; the Hammett plot for the reaction has a sharp break at $\sigma^+ = -0.19$ [$E_{\frac{1}{2}}^{ox} = 1.47$ V vs. standard calomel electrode] and is rationalized in terms of both exergonic and endergonic photocatalysed processes on the semiconductor with different rate-determining steps.

Although the application of semiconductors as photocatalysts for solar energy conversion is one of the most active areas of current photochemical research, much less attention has been focused on the use of these photocatalysts for more general organic transformations.[1—3] We report here an example wherein there is a change of rate-determining step in a series of semiconductor-mediated reactions, the *cis–trans*-isomerization of 4-substituted stilbenes, and rationalize it on the basis of a change of ergonicity.

Recently Fox and Chen reported a quantitative study of substituent effects on a semiconductor photocatalysed reaction.[4] They obtained a linear Hammett plot ($\rho^+ = -0.56$) for the TiO_2 sensitized oxidative cleavage of 4′-substituted 1,1-diphenylethylenes, and suggested that the rate-determining step of the reaction was the formation of the respective cation radicals. We have found that a Hammett plot of the CdS photocatalysed reaction of *cis*-4-substituted stilbenes (**1a—g**) shows a sharp break indicating, we believe, a change in rate-determining step.

Irradiation of a suspension of CdS in methylene chloride containing *cis*-stilbenes (**1b—g**) gave, as does the parent (**1a**),[3] the corresponding *trans*-stilbenes nearly quantitatively. The relative rates for the formation of *trans*-isomers, using (**1a**) as a standard, were determined, together with the oxidation potentials (cyclic voltammetry) and are listed in Table 1.

A Hammet plot for the reaction is shown in Figure 1 and has a sharp break at $\sigma^+ = -0.19$. The oxidative peak potentials of

Table 1. Oxidation potentials of *cis*-4-substituted stilbenes (**1**) and relative rates for production of *trans*-isomers.

Compound	Substituent	$\sigma^{+\,a}$	$E_{\frac{1}{2}}^{ox}$/V *vs.* SCE[b]	$k(\mathbf{1})/k(\mathbf{1a})$
(**1a**)	H	0	1.58	1.00
(**1b**)	NO_2	0.790	1.74	0.22
(**1c**)	CO_2Me	0.484	1.69	0.40
(**1d**)	Cl	0.114	1.58	0.58
(**1e**)	Me	−0.311	1.45	0.96
(**1f**)	MeO	−0.778	1.25	0.67
(**1g**)	NMe_2	−1.7	0.61	0.18

[a] Ref. 5. [b] SCE = standard calomel electrode.

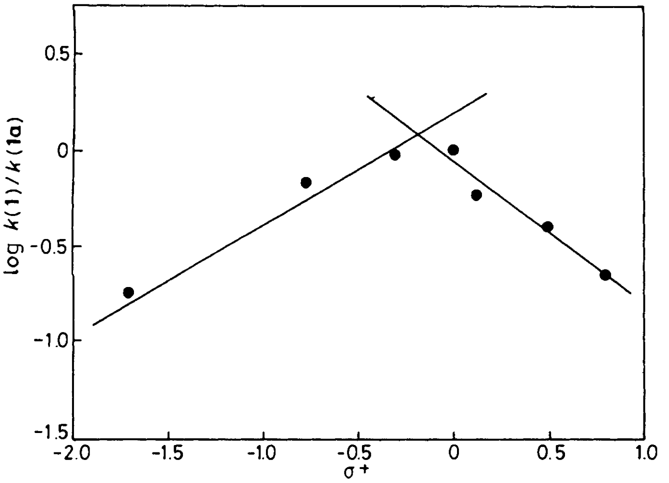

Figure 1. Hammett plot for the production of the *trans*-isomers from (**1a**—**g**).

the stilbenes correlate linearly with the σ^+ values, except for the case of 4-dimethylaminostilbene (**1g**) ($E_{\frac{1}{2}}^{ox} = 0.312\sigma^+ + 1.533$; $r = 0.982$). The rate-determining step can be considered to change, therefore, at $E_{\frac{1}{2}}^{ox} = 1.47$ V. This value is nearly equal to the value of energy level of the valence band of CdS (band gap = 2.45 V; flat band potential = −0.85 V in acetonitrile).[6]

The currently accepted mechanism for photocatalysed reaction on a semiconductor involves the generation of an electron–hole pair in the primary photoprocess. Capture of the photogenerated hole on the valence band of the semiconductor by an adsorbed organic molecule may give rise to a cation radical, which can lead to net chemical change: the hole capture process is usually exergonic. Electron transfer to the hole on the CdS valence band must be endergonic in (**1a**—**d**), and the process may well be the rate-determining step in the isomerization of these compounds. This is consistent with the negative ρ^+ value ($\rho^+ = -0.74$): unfortunately no information about ρ^+ values for endergonic reactions involving the formation of cation radicals is available in the literature. A somewhat larger negative slope than that observed in Figure 1 might have been expected for endergonic electron transfer from the Marcus–Agmon–Levine free-energy relationship (MAL–FER).[7] The observed small ρ^+ value may indicate complex formation between stilbenes and the semiconductor. The formation of π-complexes has been proposed for endergonic electron transfer between an aromatic hydrocarbon cation radical and alkenes.[8] The rate-determining steps of the reactions of (**1e**—**g**) cannot be explained in terms of electron transfer because of the positive ρ^+ value ($\rho^+ = 0.57$). The hole-capture process in (**1e**—**g**) must be exergonic, and the rate constants of the electron transfer are expected to be nearly equal from MAL–FER.[7] A Hammett plot of the rate constants should give, following the decrease in the ease of oxidation, a negative ρ^+ value;[4] however, the reverse is observed. In this case, therefore, the rate-determining step is most probably the rate of bond rotation from the *cis*- to *trans*-cation radical.†

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† The possible role of adsorption as distinct from electron transfer processes will be discussed in detail elsewhere, as will the kinetics.