Electronic Energy Transfer at the Gas–Solid Interface

By RICHARD L. DAUBENDIEK, HILLEL MAGID, and G. R. MCMILLAN*
(*Department of Chemistry, Case Western Reserve University, Cleveland, Ohio* 44106)

THE correlations obtained by Hammond and his co-workers[1,2] between product distributions in photosensitized *cis*→*trans*-isomerizations and the triplet excitation energy of the sensitizer have been used by Weis, Bowen, and Leermakers[3] to study sensitizer molecules adsorbed on silica gel. The approach may be extended to yield information about surface states of molecular crystals. We find that irradiation of certain organic, crystalline compounds, established as photosensitizers in solution, in the presence of *cis*- or *trans*-penta-1,3-diene vapour leads to isomerization of the penta-1,3-diene.

The sensitizers chosen were several of those studied in solution,[1,2] including benzophenone, naphthalene, 9,10-anthraquinone, Michler's ketone, 2-acetonaphthone, and 9-fluorenone. The solid, polycrystalline samples, used in most cases without special purification, were typically degassed in small spherical flasks, *cis*-penta-1,3-diene was added to a pressure of 5 mm. and the system irradiated with that part of the emission from a medium-pressure mercury arc transmitted by a Corning 0-54 filter ($\lambda > 2900$ Å). After 15—24 hr. at $\sim 27°$, partial *cis*→*trans*-isomerization was observed in every case. The conversion was only 3% when 9-fluorenone was used as the sensitizer, but 14—60% for the other compounds. Irradiation of *cis*-penta-1,3-diene in the absence of a sensitizer gave 1·3% isomerization in 18 hr. When a mixture of *cis*-penta-1,3-diene at 5 mm. pressure and sensitizer at the equilibrium vapour pressure is irradiated at room temperature considerable isomerization may result; for example, 2-acetonaphthone gave 9·5% isomerization compared with 60% in the same time upon irradiation in the presence of the solid sensitizer. For the relatively involatile 9,10-anthraquinone (vapour pressure[4] $\sim 10^{-6}$ mm. at 25°), the extent of isomerization upon irradiation of the vapour mixture was not greater than that observed on irradiation of pure penta-1,3-diene.

In the Table is compared the composition of the mixture of penta-1,3-diene isomers at the photostationary state for three sensitizers with compositions reported in benzene solution[2] and in a benzene–silica gel matrix.[3] The compositions observed in the solid–gas experiments are not very different from those observed otherwise and show no unique direction of shift. It appears that triplet–triplet energy transfer can occur at the gas–solid interface, but with a purely gas-phase transfer competing in some cases under the present experimental conditions. Accepting the correlation published by Hammond and his co-workers,[1,2] the present results indicate energy differences of about a kilocalorie between triplet states in solution and on the surface of organic crystals.

TABLE

Composition of mixture of penta-1,3-diene isomers at the photostationary state for different sensitizers

	% *trans*		
Sensitizer	Solid–gas	Solution	Silica gel–benzene
Naphthalene	62·2[a] 61·2[b]	69[c]	
9,10-Anthraquinone	65·2[a] 64·7[b]	57[c]	
2-Acetonaphthone	72·7[a] 72·6[b]	72[c], 75[d]	71[d]

[a] The initial mixture was *trans*-rich compared to the photostationary state; [b] the initial mixture was *cis*-rich compared to the photostationary state; [c] reference 2; [d] reference 3.

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