Surface Photochemistry: The Photodimerisation of Acenaphthylene on Dry Silica Gel

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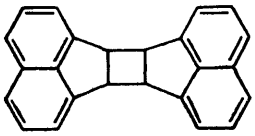
Summary A bimolecular process on dry silica gel, the photodimerisation of acenaphthylene, has been accomplished, both by direct excitation and by sensitisation, and its behaviour compared with that in solution and that expected for a two-dimensional fluid model.

THE study of photochemical reactions of adsorbed molecules is in its infancy. Specifically, investigations of the photochemistry of molecules adsorbed on dry silica gel are limited to two, both homolytic singlet processes; the photo-Fries rearrangement[1] and the decomposition of azocumene.[2†] We report here our preliminary results on a study of a photochemical bimolecular reaction on dry silica gel, the dimerisa-

† A number of unimolecular photoreactions have been described, performed in silica gel–cyclohexane slurries. For a review, see C. H. Nicholls and P. A. Leermakers, *Adv. Photochem.*, 1971, **8**, 315; see also D. Fassler, R. Gade, and W. Guenther, *J. Photochem.*, 1980, **13**, 49.

tion of acenaphthylene,‡ *via* both singlet and triplet pathways, a reaction which has been studied in detail in solution.[3]

By direct irradiation§ in solution in the absence of oxygen, dimerisation leads to both *syn* and *anti* isomers of compound (**1**). It has been shown that the singlet pathway leads essentially to *syn* (**1**) whilst the triplet gives a mixture



(1)

of *syn* and *anti* products. Since increasing time between encounters between the excited acenaphthylene and a ground state molecule increases the likelihood of intersystem crossing, and hence reaction from the triplet, the *syn/anti* ratio obtained from the photochemical dimerisation of adsorbed acenaphthylene should change with surface coverage. Extrapolation to zero coverage may then give the proportion derived from the triplet,¶ provided adsorbed acenaphthylene is moving, intra- and/or inter-particularly, as if in a two-dimensional fluid, and there is no ground-state interaction between adsorbed molecules. A simple plot, which is linear at lower coverage ($r = 0{\cdot}993$—15% coverage), is shown in the Figure. Above *ca.* 40% coverage the uncorrected curve flattens and, presumably, the asymptote indicates the ratio of dimers obtained from the singlet: at 60% coverage the average distance between acenaphthylene molecules is about 3 Å and the singlet reaction should predominate. The *syn/anti* ratio being *ca.* 21, this implies that the singlet affords > 95% *syn* product, as is the case in solution.[3]

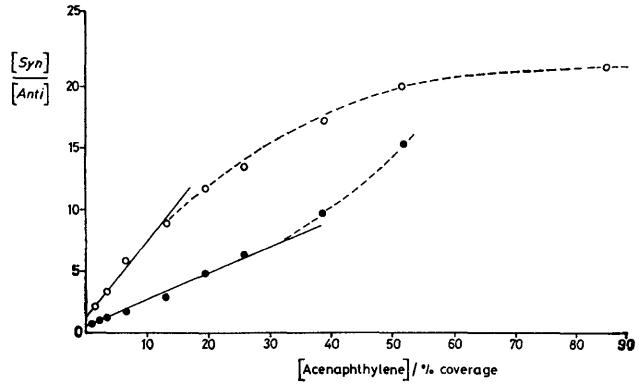


FIGURE. Plot of acenaphthylene percentage coverage against isomer ratio (—○—) (uncorrected) and plot of acenaphthylene + acenaphthene against isomer ratio (total = 60% coverage) (—●—) (corrected).

However, it seems likely that the nature of the surface itself is modified by increasing coverage, and to correct for this a mixture of varying ratios of acenaphthene to acenaphthylene was used [total 1·46 mmol/g; *ca.* 60% coverage ($1{\cdot}7 \times 10^{-8}$ mol/dm^2)] and a similar plot made of dimer ratio *vs.* percentage acenaphthylene coverage. A straight line was also obtained up to *ca.* 25% coverage ($r = 0{\cdot}995$). The value of the *syn/anti* ratio extrapolated to zero acenaphthylene coverage is $0{\cdot}44 \pm 0{\cdot}13$, which should be the ratio of isomers derived from the triplet.

The dimerisation could be sensitised. Adsorption of polar sensitisers (*ca.* 0·1% coverage) (Table) on the silica gel, followed by adsorption of the acenaphthylene (3% coverage plus 57% acenaphthene), with excitation of the translationally immobile sensitiser gave, with all three sensitisers used, a *syn/anti* ratio of *ca.* 0·53. This is in good agreement with the value from the intercept of the corrected curve in the Figure.

TABLE.

Sensitiser	Acenaphthylene (% coverage)[a]	$\frac{[Syn]}{[Anti]}$
Rose Bengal	3·2	0·52
Eosin Y	3·2	0·53
Acridine Orange	3·2	0·53

[a] Acenaphthene covers *ca.* 57% of the surface.

As reported, in solution oxygen quenches the triplet and essentially supresses *anti* dimer formation:[3,5] the same observation has been made on dry silica gel. If silica gel is considered to have a polar surface it is possible to compare values of singlet dimerisation quantum yield** with those found[5] in methanol. In 0·4 M solution $\phi = (3{\cdot}74 \pm 0{\cdot}14) \times 10^{-2}$; with 3, 14, and 27% coverage the values are $1{\cdot}1 \pm 0{\cdot}15$, $4{\cdot}3 \pm 0{\cdot}6$, and $(7{\cdot}9 \pm 1{\cdot}2) \times 10^{-2}$, respectively. If 100% coverage, for purposes of comparison, is taken as equivalent to 100% acenaphthylene in three dimensions, *i.e. ca.* 6 M, then 0·4 M in solution may be compared with 6% coverage; the value found falls between 3 and 14% coverage, compatible with a two-dimensional liquid model. Based on the average separation of molecular centres it is equivalent to 22% coverage.

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‡ The only reports of bimolecular processes of adsorbed molecules of which we are aware are that of the irradiation of vitamin K_3 (H. Werbin and E. T. Strom, *J. Am. Chem. Soc.*, 1968, **90**, 7296) to give a complex mixture including dimers, and a brief mention of the dimerisation of a styrylisoxazole (D. Donati, M. Fiorenza, and P. Sarti-Fantoni, *J. Heterocycl. Chem.*, 1979, **16**, 253).

§ Irradiations were performed in a rotating tube ($\lambda > 350$ nm) after degassing and filling with nitrogen. Silica gel (Merck 35—70 mesh) was dried at 200 °C before use. For direct irradiations conversions were in the range 2—9% for the *syn–anti*-ratios determinations.

¶ This requires that the rate constant for radiationless triplet decay be small with respect to that for intersystem crossing. This appears not to be true in solution.[3,4] We shall discuss the kinetics in our full paper.

** The apparatus and technique will be described elsewhere.

[1] D. Avnir, P. de Mayo, and I. Ono, *J. Chem. Soc., Chem. Commun.*, 1978, 1109.
[2] J. E. Leffler and J. J. Zupancic, *J. Am. Chem. Soc.*, 1980, **102**, 259.
[3] See D. O. Cowan and R. L. Drisko, 'Elements of Organic Photochemistry,' Plenum Press, New York, 1976, pp. 435 *et. seq.*; A. Castellan, G. Dumartin, and H. Bouas-Laurent, *Tetrahedron*, 1980, **36**, 97.
[4] D. O. Cowan and R. L. Drisko, *J. Am. Chem. Soc.*, 1970, **92**, 6268; I.-M. Hartmann, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, 1967, **100**, 3146; see also reference 5.
[5] R. Livingston and K. S. Wei, *J. Phys. Chem.*, 1967, **71**, 541; K. S. Wei, Thesis, Univ. of Minnesota, 1966.