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AN ENVIRONMENTAL EFFECT IN A PHOTOCHEMICAL REACTION: PHOTOLYSIS OF MATRIX-ISOLATED 4-PHENYL-1,3,2-OXATHIAZOLYLIO-5-OXIDE

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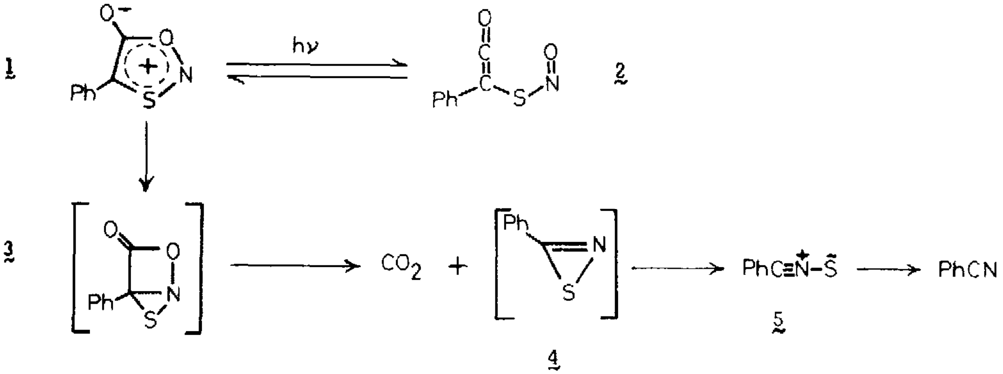
We wish to report an example of a solid phase photochemical reaction in which the reaction pathway is totally altered by a change in the immediate molecular environment of the reactant.

Irradiation ($\lambda \simeq 420$ nm) of mesoionic 4-phenyl-1,3,2-oxathiazolylio-5-oxide (1) in an EPA glass at 85K has been shown to follow two routes a reversible ring-opening to give the keten (2), and elimination of CO_2 (possibly *via* intermediates (3) and (4)) to give benzonitrile sulfide (5) and ultimately benzonitrile[1,2].



Mesoion (**1**) was isolated at 10K in rigid N_2 matrices[3] and exhibited a strong i.r. absorption at 1750 cm^{-1} ($\nu_{C=O}$), shown in Fig. 1(a). When the matrix containing (**1**) was annealed (warmed and re-cooled), the band at 1750 cm^{-1} decreased in intensity and a strong band at 1710 cm^{-1} ($\nu_{C=O}$) appeared Prolonged annealing resulted in the complete disappearance of the 1750 cm^{-1} band, leaving only the 1710 cm^{-1} band (Fig. 2(a)). Thereafter, the spectrum remained unchanged on further warming, even when all the nitrogen was boiled off Thus we assign the band at 1710 cm^{-1} to molecular aggregates.[4]

A similar shift of the carbonyl absorption of the mesoion in tetrachloroethylene solution (1750 cm^{-1}) compared with a KBr disc (1700 cm^{-1}) has been reported and attributed to the difference in polarity of these two media.[5] The matrix experiments demonstrate that the shift was probably due to the presence of crystals in the KBr sample.

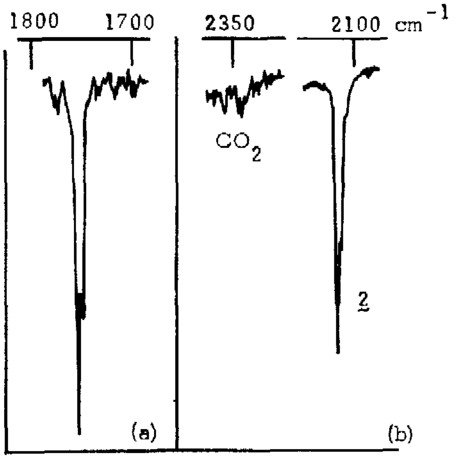


Fig. 1

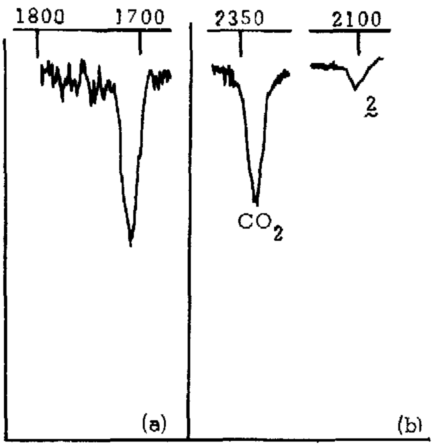


Fig 2

I r spectra of Fig 1, isolated mesoion (**1**); Fig 2, aggregates
(a) Before, and (b) after photolysis ($\lambda \simeq 367$ nm)

In the N_2 matrix at 10K, the isolated and aggregated forms showed strikingly different photochemical behaviour. Irradiation of isolated (1) ($\lambda \simeq 367$ nm, 2 min.) led to the formation of keten (2) ($\nu_{C=C=O}$ 2120 cm^{-1}, ν_{N-O} 1595, 1575 cm^{-1}),[6] with only a trace of CO_2 (Fig. 1(b)). On the other hand, irradiation of aggregates of (1) ($\lambda \simeq 367$ nm, 160 min.) gave very little keten, but a substantial amount of CO_2 ($\nu_{C=O}$ 2330 cm^{-1}) (Fig. 2(b)), as well as a weak band at 2220 cm^{-1}, attributed to benzonitrile Thus the molecular environment of the mesoion appears to dictate which of the two reaction paths is followed

The difference in reaction pathway between isolated and aggregated molecules might be attributed to (i) a change in the rigidity of the medium, (ii) selective self-quenching in the aggregates, permitting otherwise unfavourable primary processes to occur, or (iii) a bimolecular reaction in the aggregates. Support for the first of these alternatives results from the photolysis of (1), existing largely as isolated molecules, in a PVC[7] film at 10K. In this very rigid medium, the principal photoproducts are CO_2, (5) and benzonitrile, with very little keten (2) being formed. The photolysis in PVC is, however, much more efficient than with the aggregates in N_2. Thus it appears that the rigidity of the immediate molecular environment is the decisive factor, and the self-quenching, which inevitably occurs with aggregated molecules, results only in a severe reduction in quantum yield.

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References

1. A Holm, N. Harrit, K. Bechgaard, O. Buchardt, and S.E. Harnung, J.C.S.Chem.Comm., 1125 (1972).
2. A. Holm, N. Harrit and N.H. Toubro, J.Amer.Chem.Soc., <u>97</u>, 6197 (1975).
3. Essentially by a short path-length evaporation from a copper surface at a controlled temperature, with simultaneous deposition of the matrix gas.

4. Deposition of (1) with N_2 generally resulted in the formation of both isolated molecules and aggregates, the latter being favoured by faster rates of evaporation of (1), higher temperatures, and prolonged standing (e.g. overnight) even at 20K. With care, however, (1) could be obtained, for practical purposes, exclusively in either the isolated or the aggregated form.

5. H. Gotthardt, Chem.Ber., 105, 188, (1972).

6.(a) cf. keten in Ar at 20K, $\nu_{C=C=O}$ 2133 cm^{-1}.

B. Meyer, Low Temperature Spectroscopy, Elsevier, New York (1971), p. 372.

(b) cf. CH_3SNO, ν_{N-O} 1534 cm^{-1} (gas phase), and $(C_6H_5)_3CSNO$, ν_{N-O} 1480-1500 cm^{-1}

R.J. Philippe, J.Mol.Spectroscopy, 6, 492 (1961), R.J. Philippe and H. More, Spectrochimica Acta, 17, 1004 (1961), G. Kresze, U Uhlich, Chem.Ber. 92, 1048 (1959)

7. Poly(vinyl chloride).