Matrix Photolysis of Unsaturated Cyclic Anhydrides and the Infrared Spectrum of Tetradeuteriobenzyne

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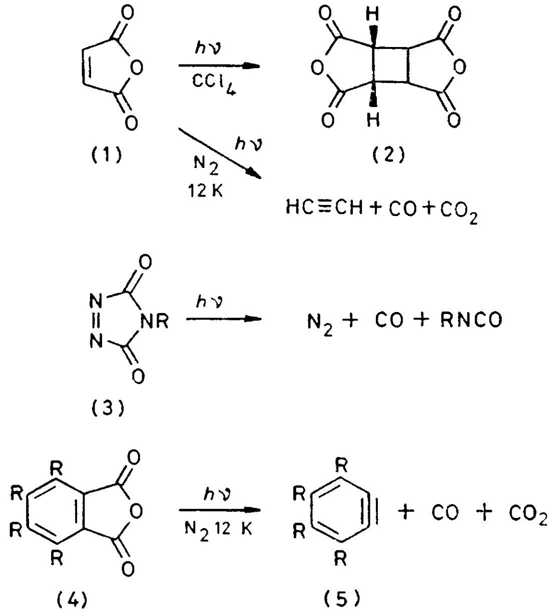
Summary U.v. photolysis of matrix isolated maleic anhydride gives acetylene, CO, and CO_2, while similar reactions of phthalic anhydride and its tetradeuteriated analogue give benzyne and [$^2H_4$]benzyne, respectively.

MALEIC ANHYDRIDE (**1**) and 1,2,4-triazoline-3,5-diones (**3**) have similar electronic structures, yet their solution photochemistry is quite different. Thus, maleic anhydride gives the photodimer (**2**),[1] whereas triazolinediones fragment to N_2, CO, and the corresponding isocyanates (RNCO).[2]

We now report that photolysis (125 W Hg-arc, water filter) of maleic anhydride isolated in N_2 matrices at 12 K proceeds *via* an analogous fragmentation pathway, giving acetylene, CO, and CO_2 as the only observed products. Under the same conditions, 4-methyl-1,2,4-triazoline-3,5-dione[3] (**3**, R = Me) gives CO, methyl isocyanate and, presumably, N_2. Matrices were prepared by direct sublimation of the solid reactant on to a window at 20 K with simultaneous deposition of a stream of nitrogen. Matrix host: guest ratios, therefore, could not be determined. In each case, the reaction was particularly easy to follow, since both reactants and all products except N_2 have strong, characteristic i.r. absorptions.



The photofragmentation of unsaturated cyclic anhydrides potentially offers a convenient means of generating strained triple bonds. Extending the reaction to an aromatic anhydride, we found that u.v. irradiation of phthalic anhydride (**4**, R = H) in N_2 matrices at 12 K proceeded smoothly to give CO, CO_2, and benzyne (**5**, R = H). The i.r. bands of benzyne detected in this reaction are included in the Table. Earlier work has shown that gas-phase pyrolysis[4] and flash photolysis[5] of phthalic anhydride involves benzyne as an intermediate. We have been unable to carry out a similar reaction in solution, however. Phthalic anhydride was recovered quantitatively from CCl_4–$CHCl_3$ or acetone after several hours irradiation (500 W Hg-arc, quartz filter).

Matrix isolated benzyne from other precursors has already been observed by Chapman and his co-workers.[6] The i.r. spectrum of benzyne, obtained from phthalic anhydride agrees closely with the published data, except for a band at 1627 cm^{-1}, which was reported by Chapman but was absent from all our spectra. This band may, therefore, be due to a site effect, and the validity of its assignment to unperturbed benzyne molecules is doubtful.

There have been numerous theoretical studies of the structure of benzyne.[7] On the other hand, relevant experimental data is scant, and the matrix i.r. spectrum of benzyne probably affords the most reliable basis for a discussion of the bonding in this species. Laing and Berry[8] have carried out a normal co-ordinate analysis using this spectrum and achieved a fit for the observed frequencies within 1·1%. These authors concluded that benzyne could be regarded as a true cycloalkyne. From the best-fit force constants, two significant predictions were made. The first was that there should be a band at 2450 cm^{-1} in the i.r. spectrum of benzyne; the second was the complete i.r. spectrum of tetradeuteriobenzyne. The predicted band at 2450 cm^{-1} was not observed by Chapman and we also have failed to detect it. If a band at about this frequency is present, it can have no more than 10% of the intensity of the 2084 cm^{-1} band, which we have now observed at a signal: noise ratio of better than 10 : 1. The first prediction remains unconfirmed, therefore.

TABLE. Vibrational frequencies[a] (cm^{-1}).

Benzyne (**5**, R = H) in N_2 at 12 K	$[^2H_4]$Benzyne (**5**, R = D)		
	In N_2 at 12 K	Predicted[b]	(% difference)
3088		2452	
2084		2380	
1598		2350	
1448	2293		(±2·5)
1056		2243	
1039	2093	2035	(−2·8)
847		1568	
743	1483	1480	(−0·2)
472	1293	1281	(−0·9)
	1108	1112	(0·4)
	1029	1027	(−0·2)
	822	814	(−1·0)
	792	774	(−2·3)
	730	714	(−2·2)
	616	594	(−3·6)
		546	
	471	451	(−4·2)

[a] Spectra in this work were recorded on a JASCO IRA-2 i.r. spectrophotometer. [b] Values from ref. 8.

On photolysis of tetradeuteriophthalic anhydride[9] (**4**, R = D) in N_2 at 12 K, however, we observed i.r. bands due to CO and CO_2, and several bands that we attribute to tetradeuteriobenzyne (**5**, R = D). The frequencies of these bands are presented in the Table with the predicted values. The agreement is reasonable for most bands below 2000 cm^{-1}, but is less satisfactory for the critical bands above 2000 cm^{-1}.

In the light of these new data, a re-examination of the force field for benzyne seems desirable. Studies along these lines are continuing.

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