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THE PHOTOFRAGMENTATION OF PHTHALIDE IN LOW-TEMPERATURE MATRICES

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SUMMARY: Phthalide (1) undergoes photofragmentation in N_2 and Ar matrices at 12K, predominantly by loss of CO and 1,3-hydrogen shift, to give benzaldehyde.

In recent communications, we have reported several examples of carbonyl compounds, such as cyclic unsaturated anhydrides, which undergo photofragmentation reactions in low-temperature matrices but not in solution under more normal conditions.[1-3] We now report that phthalide (1) also behaves in this way.

Phthalide (1) was isolated in N_2 and Ar matrices by sublimation on to a CsI window at 12K, with simultaneous deposition of the matrix host gas.[4] The resulting matrices were irradiated for 180-285 minutes with light from a 200W high-pressure Hg-arc equipped with a water-filter. The IR bands of (1) diminished upon photolysis, while those of CO, CO_2 and benzaldehyde (3) grew (Figure).[5] During the photolysis, a blue phosphorescence with a lifetime of several seconds could be observed if the lamp was temporarily extinguished.

The benzaldehyde formed in this reaction presumably arises by loss of CO from (1) followed by a 1,3-hydrogen shift in the intermediate biradical (2) (path a). Comparisons of IR band-intensities for an Ar matrix containing authentic CO and benzaldehyde in a known ratio confirmed that these two compounds were formed in the matrix photolysis of (1), at least approximately, in equimolar amounts.

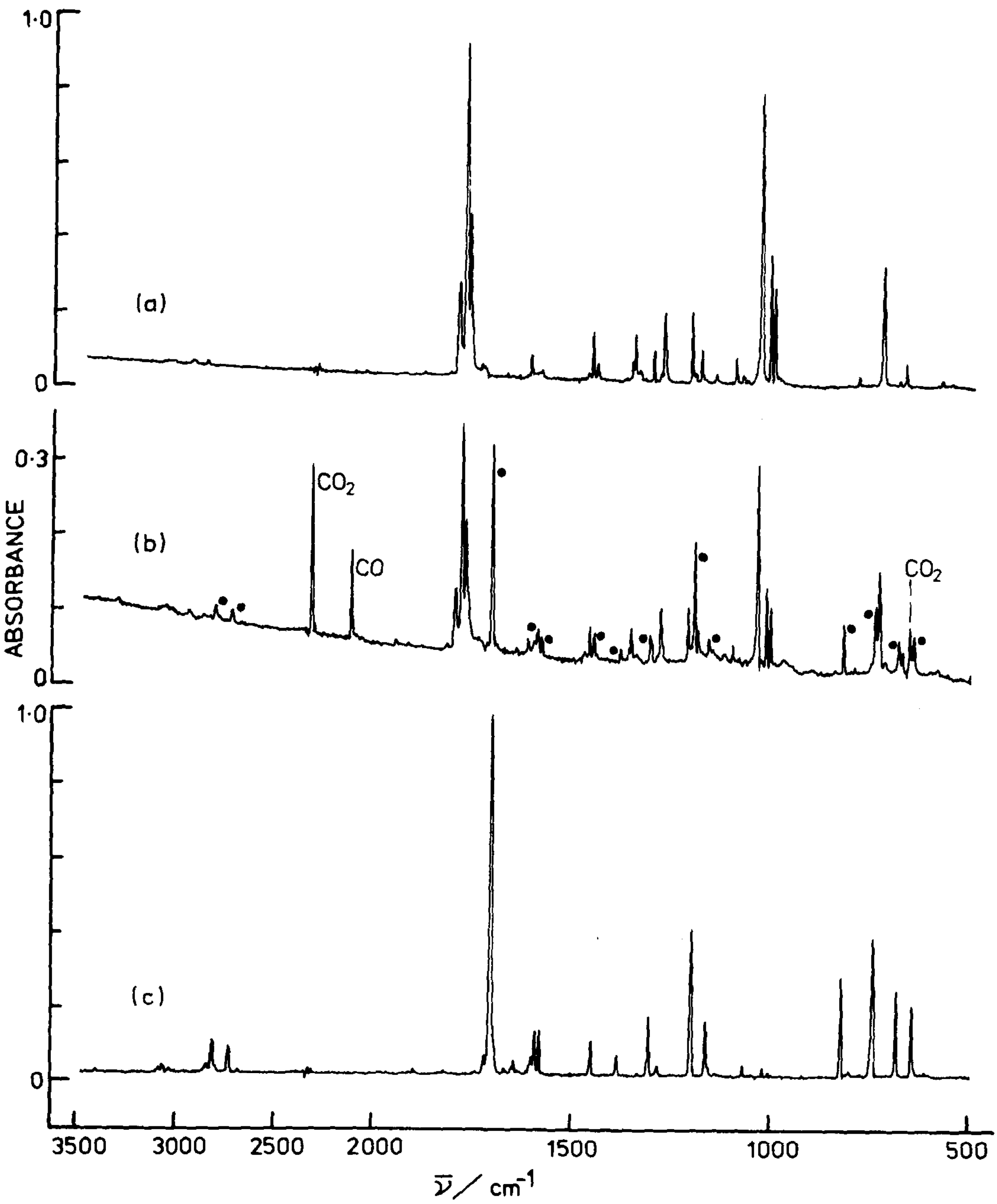
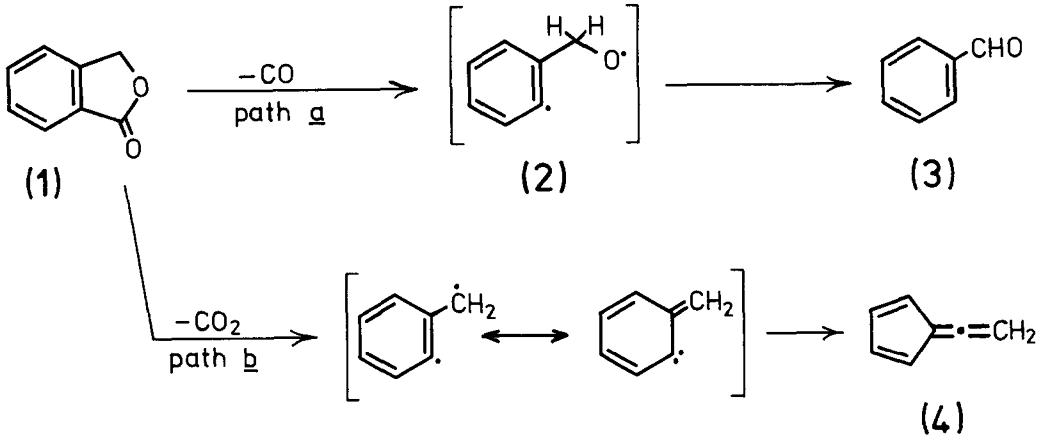


FIGURE. IR spectra of N_2 matrices at 12K: (a) phthalide (1), (b) phthalide after 285 min. Hg-arc photolysis, (c) authentic benzaldehyde (3) (matrix ratio 1:1000). The spectra were subjected to background subtraction. In spectrum (b) the IR bands of CO_2 and CO and the fourteen strongest bands of benzaldehyde (●) are identified.



The CO_2 also observed as a photoproduct arises, therefore, by an alternative pathway. We have, however, been unable to detect any product IR absorptions other than those of (3), CO and CO_2, except for very weak bands. Comparisons of IR band-intensities for CO and CO_2 in matrices of known composition revealed that ν_{asym} for CO_2 (2348 cm^{-1}) gives rise to an absorption that is approximately ten-times as intense as that of ν_{CO} for CO (2142 cm^{-1}). Thus, in the matrix photolysis of (1), where $\nu_{asym}(CO_2)$, appears only about twice as intense as ν_{CO} (CO), molecules of CO_2 and CO are generated in the ratio of about 1:5. Loss of CO (path <u>a</u>) is, therefore, the major fragmentation pathway.

We have been unable to find any previous descriptions of the photochemistry of phthalide. Accordingly, we carried out room-temperature photolysis of (1) in solution (CCl_4 and petroleum-ether), in a PVC film, and in a KCl disc. In solution and in the PVC film, loss of (1) was observed, but no evidence for the formation of benzaldehyde was obtained. In KCl, phthalide appeared unreactive.

It has been reported that flash vacuum thermolysis of (1) at 700-750°C yields fulveneallene (4) by extrusion of CO_2 (path <u>b</u>), and that above 750°C, benzaldehyde appears as an additional thermal product.[6] Thus, as was observed for other carbonyl compounds,[1-3] the matrix photolysis of (1) resembles its gas-phase thermolysis but is quite different from its solution photochemistry. It is likely that matrix photolysis of (1) and similar photofragmentations are two-photon processes. If this is correct, the conditions of matrix isolation will increase the probability of the reaction by prolonging the lifetime of the first excited triplet state and therefore much increasing the probability of second-photon absorption. The observation of a pronounced phosphorescence from matrix-isolated phthalide lends support to this postulate.

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4. Phthalide (m.p. 75-77°) was obtained commercially. Matrix gases were from BOC Ltd., research grade. Cooling was achieved by means of an Air Products Displex model CSA-202. Owing to the sublimation technique used for matrix deposition, matrix ratios could not be estimated.
5. IR spectra were recorded on a Perkin-Elmer 684 spectrometer interfaced with a Perkin Elmer 3600 Data Station. The spectrometer was calibrated regularly with a polystyrene film.
6. U. E. Wiersum and T. Nieuwenhuis, Tetrahedron Lett., (1973) 2581; C. Wentrup and P. Müller, Tetrahedron Lett.,(1973) 2915; C. Wentrup, Tetrahedron Lett., (1973) 2919.

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