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PHOTOLYSIS OF p-BENZOQUINONE IN N_2 MATRICES AT 12K
A NOVEL DECOMPOSITION PATHWAY

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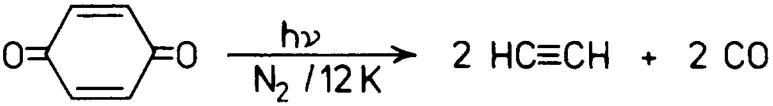
SUMMARY Photolysis of p-benzoquinone in N_2 matrices at 12K has been found to give acetylene and CO, 1,4-naphthoquinone and 9,10-anthraquinone, however, are inert under similar conditions

Photochemical reactions of p-benzoquinone and other quinones have been extensively studied,[1] but the photo-elimination of CO from quinones has rarely been reported p-Benzoquinone appears to react by loss of CO, only when subjected to a glow discharge[2] or flash-vacuum thermolysis.[3,4] The products formed under these conditions are either mixtures of vinylacetylene and other hydrocarbons[4] or dimeric derivatives of cyclopentadienone[2,3] Acetylene has not been found as one of the products, and has been specifically excluded as an intermediate in the formation of vinylacetylene

We now report our findings on the photolysis of p-benzoquinone in N_2 matrices at 12K Matrices were prepared by sublimation of the quinone on to a CsBr window cooled to 20K, with simultaneous deposition of N_2[5] The temperature was lowered to 12K prior to photolysis. Irradiation of the matrices with a 125W medium-pressure Hg arc, fitted with a water filter, led to slow decomposition of the quinone. The reaction was followed by IR spectroscopy[6] During 175 min., the IR bands of p-benzoquinone (ν_{CO} 1662 cm^{-1}) diminished slightly (ca 25% photolysis), while the IR bands of acetylene (3268 and 750 cm^{-1}) and CO (2140 cm^{-1}) appeared[7] Further photolysis (up to 500 min) increased the yield of acetylene and CO, but no other product IR bands were observed. The matrix photolysis of p-benzoquinone is not, therefore, an efficient process, but seems to lead cleanly to acetylene and CO. We have been unable to find a precedent for this mode of decomposition.



Analogous reactions of 1,4-naphthoquinone and 9,10-anthraquinone would yield benzyne as one of the products Both of these quinones, however, were found to be inert when isolated in N_2 matrices at 12K and subjected to UV-irradiation

The facts that (i) the matrix photolysis of *p*-benzoquinone follows a different pathway from that found for solutions at more usual temperatures, (ii) that the reaction seems to have a low quantum efficiency, and (iii) that other quinones do not behave similarly, all suggest the possibility of a two-photon process Further studies may help to decide this point

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REFERENCES

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5 Cooling was achieved by means of an Air Products Displex, Model CSA-202 Nitrogen was from BOC Ltd , research grade Matrix ratios could not be estimated For a further description of the matrix isolation technique, see, for example, I R Dunkin, *Chem Soc Rev* , **9**, 1 (1980).

6 IR spectra were recorded on a JASCO model IRA-2 spectrometer, and frequencies are accurate ± 8 cm^{-1} (above 2000 cm^{-1}) or ± 4 cm^{-1} (below 2000 cm^{-1})

7 The IR bands of C_2H_2 and CO were compared with those of authentic samples in N_2 matrices

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