

The Flash Photolysis of Ethenetetracarbonitrile

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Abstract

The flash photolysis of ethenetetracarbonitrile gives rise to two short-lived diffuse absorption bands at 299.0 and 321.2 nm which are tentatively attributed to the dicyanocarbene radical. Flash photolysis of ethenetetracarbonitrile which has been photolysed or heated for a prolonged period yields a similar pair of bands with a lifetime of many minutes. The identity of the carrier of these bands is not known, but some possibilities are discussed.

We report some work on the flash photolysis of ethenetetracarbonitrile which although incomplete has yielded a number of results which we feel are of interest.

The pyrolysis of ethenetetracarbonitrile in a tube packed with quartz chips has been shown to yield cyanogen and dicyanoacetylene at temperatures between 700 and 800°C.¹ The products are consistent with a mechanism based on the molecular elimination of cyanogen whereas, by analogy to tetrafluorethene in which double-bond cleavage to yield difluorocarbene is the major mode of decomposition in both pyrolysis² and photolysis,³ it might be expected that dicyanocarbene formation would occur and that this would be reflected in the products. The gas-phase photolysis of ethenetetracarbonitrile is therefore of some interest but does not appear to have been reported in the literature. Accordingly such a study was undertaken, and since the compound exhibits a spectrum comprising strong continuous absorption below 200 nm with a number of overlapping bands at longer wavelengths up to 261.7 nm, where ϵ is 10540,⁴ flash photolysis in the near ultraviolet was used.

Flash photolysis was carried out in the gas phase under isothermal conditions (with nitrogen as diluent), and what is believed to be a new transient spectrum, consisting of two diffuse bands (λ_{\max} 299.0 and 321.2 nm), was recorded. The spectrum appeared with maximum intensity immediately after the flash, then decayed over the next 500 μ s. The spectrum of the CN radical was not detected, so it is suggested that the observed spectrum is that of dicyanocarbene or of an excited state of ethenetetracarbonitrile. Both of these may react by addition across the double bond of the parent compound as shown in reactions (1) and (2) since it has been shown that somewhat analogous reactions leading to substituted cyclopropane formation occur between

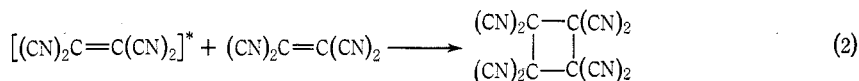
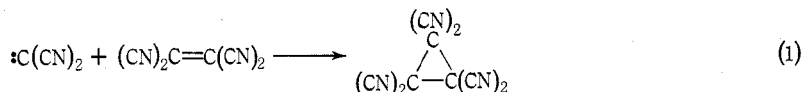
¹ Ciganek, E., and Krespan, C. G., *J. Org. Chem.*, 1968, **33**, 541.

² Modica, A. P., and LaGraff, J. E., *J. Chem. Phys.*, 1966, **45**, 4729.

³ Dalby, F. W., *J. Chem. Phys.*, 1964, **41**, 2297.

⁴ Prochorow, J., and Tramer, A., *Bull. Acad. Pol. Sci., Ser. Sci., Math. Astron. Phys.*, 1964, **12**, 429.

diazomethane and ethenetetracarbonitrile⁵ and between dicyanocarbene and cyclohexene,⁶ while substituted cyclobutanes are formed during the thermal dimerization of fluoro olefins.⁷



On subsequent flashing of the same mixture, the bands were seen as before (with the CN spectrum again absent) but this time absorption was still detectable 20 min after the flash. Careful measurement of the band positions at long time delays showed them to be different (λ_{max} 298.7 and 320.5 nm) to those at short delay so we conclude that this second new spectrum arises from photolysis of a product of the first flash.

Confirmation of this was sought in flashing a mixture of ethenetetracarbonitrile/diethyl fumarate/nitrogen (1.5/7/400). In this case, although the short-lived bands appeared as before, the long-lived bands were completely suppressed. The double bond of diethyl fumarate, by virtue of the electron-withdrawing nature of the ester groups, is expected to exhibit similar reactivity to that of ethenetetracarbonitrile so the result is interpreted in terms of the carrier of the short-lived bands being removed principally by reaction with the fumarate. It is noted however that the absorption spectrum of diethyl fumarate consists principally of a strong band at 209.8 nm (ϵ_{max} 17000)⁸ so some photolysis can be expected and this could complicate the issue.

The effect of prolonged heating was the same as that of a single photolysis flash. In this experiment a sealed reaction vessel filled with ethenetetracarbonitrile/nitrogen (1.5/400) was heated for 5 days at 96°C (in the dark). Subsequently a single flash yielded both the short-lived and the long-lived bands. These results are consistent with the long-lived bands being attributed to a very stable radical perhaps such as is shown in reactions (3) or (4). Alternatively the spectrum and its slow decay may be associated merely with condensation of a stable compound of low vapour pressure, perhaps the cyclic compounds proposed in reactions (5) and (6). Other possibilities involving the photolytic elimination of cyanogen can also be proposed. Such suggested mechanisms imply that pyrolysis occurred during heating for 5 days at 96°C. However, it is noted that other workers reported no pyrolysis in a packed tube at or below 600°C,¹ so there is clearly an area here to be explored further.

The rate of decay of the long-lived bands was followed with a continuous source and a photomultiplier, but since there was a considerable scatter between the results of separate experiments it was not possible to determine the order of the decay process. However, it was noted that the rate decreased with repeated flashing of the same mixture; typical half-lives for consecutive flashes (subsequent to a preliminary flash)

⁵ Scribner, R. M., Sausen, G. N., and Pritchard, W. W., *J. Org. Chem.*, 1960, **25**, 1440.

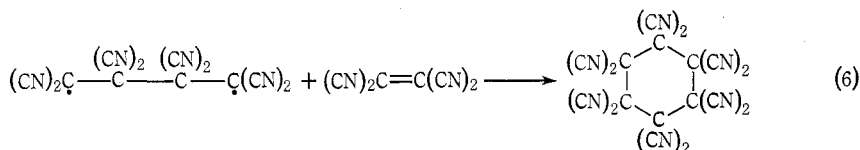
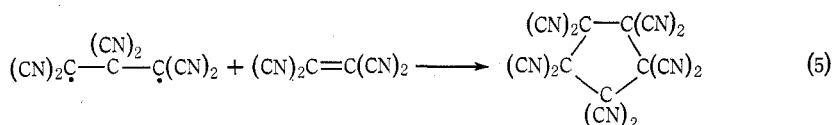
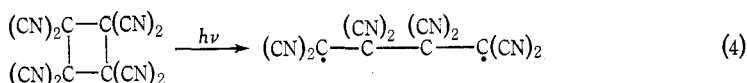
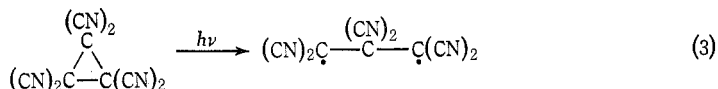
⁶ Ciganek, E., *J. Amer. Chem. Soc.*, 1966, **88**, 1979.

⁷ Sharkey, W. H., *Fluorine Chem. Revs.*, 1968, **2**, 1.

⁸ Closson, W. D., Brody, S. F., Kosower, E. M., and Huang, P. C., *J. Org. Chem.*, 1963, **28**, 1161.

were 480, 720 and 840 s. This change may possibly be interpreted in terms of depletion of ethenetetracarbonitrile leading to a lower rate of reactions such as (5) and (6).

We offer the foregoing as quite speculative explanations of the experimental results. Further work is obviously required to satisfactorily complete the study but it is not intended that it will be pursued further in this laboratory.



Experimental

A photolysis flash of 2000 J (half-life of 8 μs), and a capillary type spectroscopic flash of 100 J (half-life duration of 6 μs) were used. The photolysis lamp (50 cm long) was of Spectrosil quartz. The reaction vessel was of Vitreosil quartz (50 cm long) and this was jacketed by a Spectrosil tube through which distilled water at 96°C was pumped continuously.

Spectra were recorded on Ilford HP3 plates, a Hilger medium quartz spectrograph being used. Time delays referred to are from the beginning of the photolysis flash to the beginning of the spectroscopic flash; the shortest delay obtainable was 7 μs .

Continuous monitoring of transient spectra was carried out with a Xenon arc (150 w) and a Bausch & Lomb grating monochromator (2,700 lines/mm) fitted with a photomultiplier (E.M.I. 9526B). The response of the photomultiplier was linear over the range of light intensities used.

Ethenetetetracarbonitrile (Aldrich) was purified by vacuum sublimation followed by recrystallization from benzene then by drying under vacuum. A stock solution (0.1%) in methylene chloride was made up and the ethenetetracarbonitrile was transferred to the vessel by injecting 2 ml of this solution through a side arm. The solvent was removed under vacuum, with care taken to ensure that the solute was deposited uniformly over the length of the vessel. A diluent gas was then added (400 Torr of dry, oxygen-free nitrogen) and the side arm sealed off. The vessel was then placed in the jacket and heated at 96°C for 1 h before flashing. At this temperature ethenetetracarbonitrile has a vapour pressure of 1.5 Torr.⁹

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⁹ Boyd, R. H., *J. Chem. Phys.*, 1963, **38**, 2529.