The Structure and Photochemistry of Formaldazine

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A BRIEF REPORT[1] previously established the existence of formaldazine (I) and suggested that it had the cisoid form, unlike the similar conjugated molecules butadiene, glyoxal, and acraldehyde.[2] A re-examination of the infrared absorption of the gas (corroborated by spectra of the solid) has confirmed, by the activity both of four different fundamentals in the C–H bond-stretching region at 2943, 3007, 3078, and 3235 cm.$^{-1}$ and of the overtone of the intense 1019 cm.$^{-1}$-band at 2033 cm.$^{-1}$, that formaldazine indeed lacks a centre of symmetry. Further evidence is provided by the presence of a series of microwave transitions near 28,000 extending weakly to 29,800 Mc./sec., each

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[1] N. P. Neuriter, *J. Amer. Chem. Soc.*, 1959, **81**, 2910.
[2] R. K. Harris, *Spectrochim. Acta*, 1964, **20**, 1129.

line showing a second-order Stark effect (implying an asymmetric rotor).

Formaldazine has also been discovered to be formed in the reaction of methylene radicals with diazomethane both in solid films of the latter and in argon and nitrogen matrices at 20°K. The formaldazine is itself easily photolysed in both the inert matrix and an initially pure film of solid formaldazine, the products in both cases being methylenimine (III) and hydrogen cyanide, identified by their characteristic infrared absorption spectra. When gaseous formaldazine in a great excess of nitrogen is subjected to flash photolysis, a new transient pair of absorption bands, appearing immediately during the photolysis flash and decaying within 50 microseconds, are observed at 2808 Å (entirely diffuse) and 2847 Å (indications of structure); hydrogen cyanide and ammonia are prominent products (detected by infrared analysis) analogous to the methyl cyanide and ammonia found in the photolysis of acetaldazine.[3] The tentative assignment of these bands to the $H_2C{=}N\cdot$ free-radical can be made, the evidence of electron spin resonance spectra in argon matrices[4] confirming that this radical exists. The mechanism of the formation of the two products in the solids then involves the disproportionation of the methyleniminyl radicals (II) within the cage after severance of the weak N–N bond in the primary photochemical process:

$$\underset{\text{(I)}}{CH_2{=}N{-}N{=}CH_2} + h\nu \rightarrow \underset{\text{(II)}}{2CH_2{=}N\cdot}$$

$$\rightarrow \underset{\text{(III)}}{CH_2{=}NH} + HCN$$

Further details of these studies will be reported later.

I am indebted to Mr. M. C. L. Gerry for making the microwave measurements and to Mr. D. G. Horne for performing the flash photolysis experiments. I also thank Professor R. G. W. Norrish for his continued support and encouragement.

(*Received, July 8th*, 1965; *Com.* 428.)

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[3] R. K. Brinton, *J. Amer. Chem. Soc.*, 1955, **77**, 842.

[4] E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, 1962, **36**, 1938.