Journal of Photochemistry, 5 (1976) 311 - 315

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PHOTOLYSIS OF 3-CHLORO-3-METHYLDIAZIRINE

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(Received November 24, 1975)

Summary

Photolysis of 3-chloro-3-methyldiazirine through glass gives vinyl chloride, acetylene, hydrogen chloride and nitrogen as products. The mechanism proposed is that of Frey and Stevens for photolysis of 3-methyldiazirine. In addition 1,1-dichloroethane is formed. Photolysis with added hydrogen bromide leads to the formation of 1-bromo-1-chloroethane.

Introduction

The sole products of the thermal decomposition of 3-chloro-3-methyldiazirine (CMD) have been reported to be vinyl chloride and nitrogen [1]. The photolysis of CMD has been shown to lead to a singlet carbene which rearranges to vinyl chloride [2]. However, in the photolysis of 3-methyldiazirine Frey and Stevens [3] reported acetylene and hydrogen as products in addition to ethylene and nitrogen. We have investigated the photolysis of CMD to determine if products analogous to those reported by Frey and Stevens for 3-methyldiazirine are formed.

Experimental

3-Chloro-3-methyldiazirine [4] was photolyzed with a 275 W sun lamp through glass in a 425 cm^3 water-cooled cell for 3 to 6 hours with from 5 to 15% conversion at pressures from 1 to 13 Torr. The gaseous photolyte was trapped in a 17.2 cm^3 U-tube with liquid nitrogen. Vinyl chloride and acetylene were analyzed with Porapak Q in a 3 ft. × 1/4 in. copper tube at 68 °C, 20 lb/in^2 (gauge) He using n-propane as an internal standard. Hydrogen chloride was detected in the mass spectrum of the photolyte under ionizing conditions such that only undetectable amounts of hydrogen chloride were produced from vinyl chloride.

Flash photolysis of CMD and mixtures of this diazirine with excess HCl and HBr was undertaken in apparatus described previously [5]. Flash photolysis was followed by mass spectral analysis. Steady photolysis of CMD through glass with excess HBr gave the same products as flash photolysis through quartz.

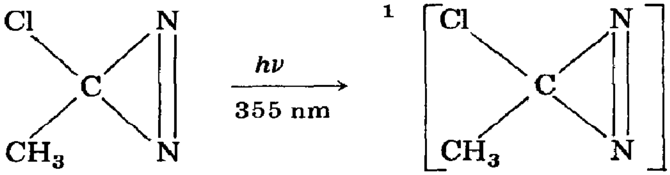
We should like to add a word of caution that CMD may explode if subjected to liquid nitrogen temperatures or if shocked (by vibrations on glass carrier lines, for example). On the other hand, storage at dry ice temperatures for indefinite periods gave no problems.

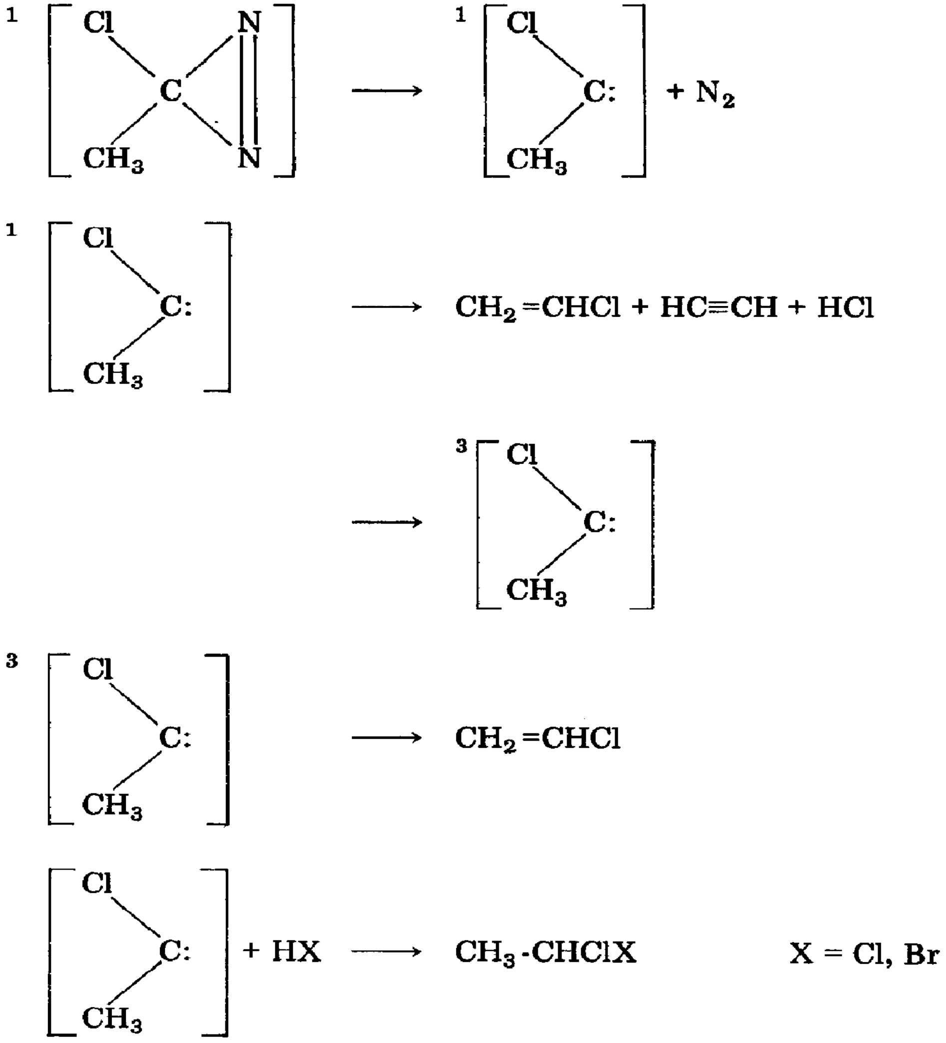
Results

Gas phase photolysis of CMD produces vinyl chloride, acetylene, hydrogen chloride, nitrogen and 1,1-dichloroethane. A reasonable mechanism for formation of 1,1-dichloroethane is by insertion of the intermediate carbene into hydrogen chloride. We tested this hypothesis by photolyzing CMD (5 - 15 Torr) in the presence of excess HBr (100 Torr). Mass spectral analysis shows that 1-bromo-1-chloroethane is a new product.

Flash photolysis of CMD through quartz gave the same products as steady photolysis through glass. In addition a product with a persistent, strong absorption continuum from 240 nm to shorter wavelengths was formed at higher pressures (greater than 10 Torr). These observations are consistent with the formation of an azine [6] by bimolecular reaction of the carbene with unphotolyzed diazirine. Azines are well-known decomposition products of diazirines [7].

We propose a mechanism for the photolysis of CMD following that of Frey and Stevens [3] for 3-methyldiazirine. Photolysis of CMD through glass leads to the $^1n\pi^*$ state [8] followed by elimination of nitrogen. The photo-isomerization of 3H-diazirine to diazomethane has been reported [9] but Frey favours direct elimination of nitrogen [10]. This leads to a high energy singlet species which forms vinyl chloride, acetylene and hydrogen chloride. A fraction of the high energy species decays to a low energy carbene which rearranges to vinyl chloride. One or both of the reactive intermediates inserts into hydrogen halide present as a product or added in excess to produce a 1,1-dihaloethane. These steps are summarized in the following scheme:





It is the high energy path leading to acetylene and hydrogen chloride that distinguishes the photolysis from the thermal reaction. Apparently new potential surfaces are reached by photolysis. Investigation of the energetics is hampered by lack of reliable thermochemical data. Three popular estimates of the heat of formation of 3H-diazirine itself, ΔH_1, are 79 [11] and 61 or 101 kcal/mol [12]. Theoretical or semi-empirical estimates do not narrow the choice. An STO–SCF calculation using semi-empirical correlation energy favours the high value [13]. A GTF–SCF calculation has been used to derive an estimate in close agreement with the intermediate value [14]. A MINDO/3 calculation [15] using the experimental, unoptimized geometry [16] gives a low value of 48 kcal/mol [17].

The bond energies of the exocyclic bonds in 3H-diazirine and 3, 3-dimethyldiazirine have been estimated [18]. Using these values, standard bond energies for the ring, and assuming the ring strain is a

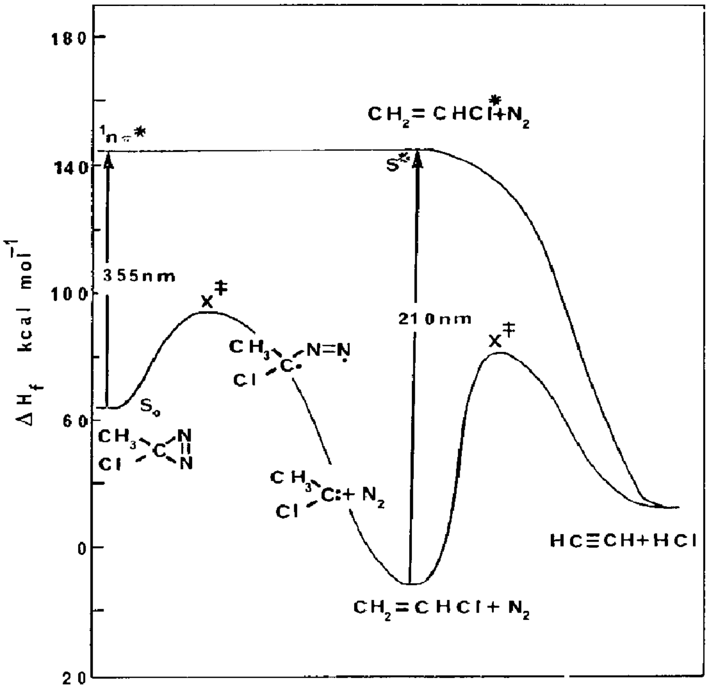


Fig. 1. Schematic diagram illustrating the relationship of the photochemistry of 3-chloro-3-methyldiazirine and the photochemistry of vinyl chloride.

constant for diazirines the heat of formation of 3, 3-dimethyldiazirine, ΔH_2, may be related to ΔH_1 by the formula $\Delta H_2 = \Delta H_1 - 15$ kcal/mol. In normal, unstrained compounds the Franklin group values for methyl and chloro are the same [19]. Thus ΔH_2 may also be taken as the heat of formation of CMD. To be specific we shall assume $\Delta H_1 = 79$ kcal/mol; then $\Delta H_2 = 64$ kcal/mol.

If we accept the value of 64 kcal/mol as the heat of formation of CMD we are in a position to speculate on the nature of the new potential surfaces in the photolysis. It is known that direct photolysis of vinyl chloride effects elimination of HCl with wavelengths as low as 210 nm [20]. As can be seen in Fig. 1, it is just possible energetically to reach the same spectroscopic states of vinyl chloride by photolysis of CMD at the 0 – 0 band, 355 nm [8], even if the heat of formation of CMD is as low as 64 kcal/mol. We suggest, therefore, that photolysis of CMD at 355 nm provides a method of entering the potential surfaces of excited vinyl chloride which effect elimination of HCl. The HCl produced by flash photolysis of chloroethylenes has a vibrational population inversion sufficient to support lasing [21].

The latter possibility for CMD and the pressure dependence of product composition are being investigated.

Acknowledgements

The research for this paper was supported by the Defence Research Board of Canada through Grant number 9530-115 to W. E. Jones and Grant number 9530-137 to M. T. H. Liu.

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