[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER]

Photochemical Investigations. VII. The Photolysis of Unsymmetrical Dimethylhydrazine[1]

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The mechanism of the photochemical decomposition of gaseous hydrazine is still in a state of considerable doubt. Two primary processes have been proposed,[3] as represented by the equations

$$N_2H_4 + h\nu \longrightarrow NH_2 + NH_2$$
$$N_2H_4 + h\nu \longrightarrow N_2H_3 + H$$

Reactions subsequent to either of these primary steps may be written which fulfill the requirements of the experimental data. In somewhat more recent work Bamford[4] has compared the photolysis of gaseous hydrazine with that of a mixture of hydrazine and propylene. In the latter he observed the formation of propane and isomeric hexanes and a large decrease in hydrogen production. These facts were interpreted as being conclusive evidence that the primary absorption act yields a hydrogen atom and N_2H_3. However, these experiments were carried out at 100° and hydrazine pressures of 150 mm. or more where the resulting strong absorption of light would bring the absorption zone very close to the cell wall and enhance the importance of secondary, heterogeneous reactions. Furthermore, as far as can be learned from the published details, no consideration appears to have been given to the possibility of a mercury sensitized reaction. The only two photolyses performed were carried out with the full radiation of a mercury arc running hot and with the mercury surface confining the gases in the quartz reaction cell included with the cell in the steam jacket which thermostated the reaction mixture at 100°.

The uncertainty concerning the primary process in the photolysis of hydrazine suggested the study of the photochemistry of unsymmetrical dimethylhydrazine. It was hoped that from an analysis of the decomposition products and from quantum yield measurements it would be possible to establish the initial reaction following the absorption of light by this molecule. It was also hoped that the over-all photochemical decomposition would resemble that of pure hydrazine, so that it would be logical to assume that the primary process for hydrazine is the same as that for the dimethylhydrazine.

Experimental

Materials.—Unsymmetrical dimethylhydrazine was prepared by the method given in "Organic Syntheses."[5] The product was subjected to three distillations in a vacuum-jacketed, 28-cm. column packed with glass helices. The first distillation was made after standing over potassium hydroxide and the second after contact with barium monoxide for several days. After the third distillation the compound was distilled under vacuum into a storage tube which led through a stopcock to the high vacuum system. The storage tube contained pellets of potassium hydroxide above the hydrazine and was of red Pyrex glass, which does not transmit wave lengths shorter than in the red. The distillation temperature was 61.0–61.7°.

On storage in the apparatus over long periods the dimethylhydrazine became somewhat impure as a result of a slow thermal decomposition. To purify the material further for use in a photolysis, the sample was first condensed in a trap immersed in a Dry Ice–alcohol mixture. At this temperature the hydrazine has a small vapor pressure and could be distilled into another trap surrounded by liquid nitrogen. After the desired amount had been condensed, the liquid nitrogen was replaced by acetone mush (−80°) and volatile impurities pumped out of the system. This temperature is sufficiently high to insure the removal of all amines which might be present. Several experiments were made using alcohol mush (−120°) instead of acetone. The results of these experiments were distinctly different in that the percentage of hydrogen in the non-condensable products showed a dependence on pressure of hydrazine just the reverse of that found when acetone mush was used in the purification. This behavior can be attributed only to impurities, undoubtedly amines. From an examination of the physical constants of all the possible amines, it would be expected that they have large enough vapor pressures at −120° to be removed. That they were not removed would indicate that they have an appreciable solubility in dimethylhydrazine at that temperature.

Apparatus.—In the present experiments light of the cadmium 2144 Å. line was used. The system—spark discharge, monochromotor, quartz cell and thermopile—was similar to that used previously[6] in this Laboratory. The cylindrical cell had plane parallel windows and was 25 mm. diameter by 75 mm. long. Irradiation times were of the order of twenty minutes. The thermopile was calibrated each day after a photolysis against a secondary carbon lamp which in turn had been compared with a new (1944) Bureau of Standards primary lamp, C-355. Absorption of light by dimethylhydrazine in a photolysis and calibration of the system against hydrogen bromide were also carried out as earlier.[6]

Analysis of Products.—From an examination of the structure of unsymmetrical dimethylhydrazine, it would seem probable that the decomposition would proceed so as to give products which would be included among hydrogen, nitrogen, methane, ethane, ammonia, methylamine, dimethylamine and substituted hydrazines. The formation of the first four of these products has been established. After the hydrazine had been photolyzed, the trap adjacent to the quartz cell was cooled to −160° by iso-pentane mush, all possible gases except hydrogen, nitrogen, methane and ethane being condensed at this temperature. These latter were then removed with a Toepler pump to a known volume of the system containing the McLeod gage. After determining the pressure (about 0.02 mm. in 370 cc.)

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[3] For detailed discussions see Leighton, "Exposé de Photochimie," Hermann et Cie, Paris, 1938, Chapter III; H. S. Taylor, *J. Phys. Chem.*, **42**, 783 (1938).

[4] Bamford, *Trans. Faraday Soc.*, **35**, 568 (1939).

[5] "Organic Syntheses," Coll. Vol. II, 211 (1932).

[6] Wiig, THIS JOURNAL, **57**, 1559 (1935).

the gases were transferred to a tube of copper oxide at 190° where they remained for six hours. At this temperature the hydrocarbons are unaffected.[7] The water formed was condensed with a Dry Ice–alcohol bath and the gas returned to the McLeod gage, the decrease in pressure indicating the amount of hydrogen. The hydrocarbon analysis was carried out by transferring the remaining gas to a combustion tube containing a known excess of oxygen. The gas was left in this tube in contact with a platinum wire heated to a dull red glow usually overnight. In order to reduce the mercury vapor pressure so that the reaction of oxygen with mercury on the platinum wire would be negligible, traps on both sides of the combustion tube were kept at the temperature of a Dry Ice–alcohol bath. It was found that the most satisfactory results were obtained for the small amount of hydrocarbon present in most of the analyses if about 5 to 6 times the theoretically required amount of oxygen was used. The oxygen was generated by gently heating potassium permanganate and stored in a bulb between mercury cutoffs.

After the combustion, liquid nitrogen was placed about the traps and the uncondensed nitrogen and excess oxygen were returned to the McLeod gage and the pressure determined. Then the liquid nitrogen was replaced by a Dry Ice–alcohol bath and the carbon dioxide formed from the combustion was transferred to the McLeod gage and its pressure determined. From the data obtained, it is possible to calculate the amounts of methane, ethane and nitrogen from a set of three simultaneous equations. In a few experiments hydrogen, nitrogen and methane were separated from ethane and the rest of the products, ethane volatilized later, and the two portions analyzed separately.

Some evidence for the formation of ammonia was obtained. If, after the gaseous products volatile at −160° were removed, the iso-pentane mush around the trap was replaced by acetone mush, additional gas could be removed. The pressure of this gas amounted to about 25–30% of the total gas removed at −160°. A combustion analysis gave a very small amount of carbon dioxide. This behavior was interpreted as meaning that the gas was largely ammonia.

Results and Discussion

The results of the analyses of products and the corresponding quantum measurements are given in the accompanying table. It will be noted that the hydrocarbon analysis is somewhat erratic. In preliminary experiments with the zinc spark at wave length 2100 Å., for which quantum yields were not determined, somewhat larger amounts of decomposition (0.03 mm. pressure compared to less than 0.02 mm. in the table) gave analyses which were more constant. Since the nitrogen is obtained by difference, an error in the hydrocarbon determination is reflected in the nitrogen analysis.

Although the analyses in this work are not reproducible enough to make definite statements, there appear to be certain similarities in the behavior of unsymmetrical dimethylhydrazine to that of pure hydrazine as reported by Wenner and Beckman.[8] For example, the percentage of hydrogen in these experiments appears to decrease slightly with increasing pressure of dimethylhydrazine, while the nitrogen percentage more definitely appears to increase. Wenner and Beckman found a similar dependence with increasing pressure of the unsubstituted hydrazine. Their experiments give an average quantum yield of nitrogen formation of about 0.9, while in this work it is about 0.7–0.8.

TABLE I

QUANTUM YIELDS FOR THE PHOTOCHEMICAL DECOMPOSITION OF UNSYMMETRICAL DIMETHYLHYDRAZINE

Room temp. (25°), λ 2144 Å.

Pressure hydrazine, mm.	Quanta absorbed $\times 10^{-16}$	Per cent. of gases volatile at −160°				Quantum yield for formation of		
		H_2	N_2	CH_4	C_2H_6	H_2	N_2	CH_4
3	9.88 ± 0.3	44.3	32	20.3	2.8	0.71	0.5	0.3
3-4	9.34	38.1	35	26.1	0	.72	.7	.5
3-4	10.10	42.0				.75		
14	10.36	43.6	42	10.8	3.2	.73	.7	.2
23	10.00	38.0	48	14.4	0	.69	.9	.3
30	11.03	40.7	43	14.4	1.7	.64	.7	.2
50	10.89	39.1	47	13.2	0	.75	.9	.3
60	10.56	36.0	44	20.4	0	.61	.8	.4
64	10.78	35.0	55	6.0	4.3	.68	1.0	.1

The quantum yield of hydrogen formation is much smaller for dimethylhydrazine than for hydrazine as might be expected, for the hydrogen content of the molecule which can give rise to the formation of hydrogen molecules is reduced by a factor of two.

Attempts to formulate a mechanism to account for the appreciable amount of methane and yet the small amount of ethane in the products of photolysis lead one to the conclusion that the primary process is the rupture of the hydrogen-nitrogen bond

$$(CH_3)_2NNH_2 + h\nu \longrightarrow (CH_3)_2NNH + H$$

By postulating that the primary process results in the splitting of the nitrogen–nitrogen bond one encounters difficulty in writing reasonable subsequent reactions which will give the experimentally observed percentages and yields of hydrogen, nitrogen and methane. Kay and Taylor[9] have studied the photochemical decomposition of the symmetrical dimethylhydrazine, from which they also conclude that the primary process is the breaking of a nitrogen–hydrogen bond. It is planned to extend the present experiments to a more thorough study of the reaction.

Summary

In a study of the photochemistry of unsymmetrical dimethylhydrazine at wave length 2144 Å., it has been established that hydrogen, nitrogen, methane and ethane are among the products formed. Certain similarities to the photolysis of the unsubstituted hydrazine have been pointed out. Attempts to formulate mechanisms indicate that in order to account for the products formed, it appears necessary to assume that the primary process is the splitting of the hydrogen–nitrogen bond.

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(7) Manning, THIS JOURNAL, **56**, 2589 (1934).

(8) Wenner and Beckman, *ibid.*, **54**, 2787 (1932).

(9) W. L. Kay and H. A. Taylor, *J. Chem. Phys.*, **10**, 497 (1942).