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FINAL REPORT TO THE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

ON

LEVEL II

STUDIES RELATING TO THE SYNTHESIS OF MONOMETHYLHYDRAZINE

BY CHLORAMINATION

AFOSR-80-0007

AND

PROBLEM RELATING TO THE PROTECTION OF THE ENVIRONMENT

FROM THE VAPORS OF 1,1-DIMETHYLHYDRAZINE,

MONOMETHYLHYDRAZINE AND HYDRAZINE

For Period of October 1, 1979 to June 30, 1981

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The synthesis of monomethylhydrazine was successfully achieved by reacting solutions of hydroxylamine-O-sulfonic acid with methylamine in diglyme. The synthesis of 1,1-dimethylhydrazine was carried out in a similar manner with dimethylhydrazine. A mechanism for the formation of formaldehyde dimethylhydrazone by the reaction of dimethylamine and chloramine was proposed. A study was conducted on the oxidation of monomethylhydrazine and 1,1-dimethylhydrazine by oxygen.			

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INTRODUCTION

This progress report summarizes the results obtained on the project entitled "Studies Relating to the Synthesis of Monomethylhydrazine by Chloramination and Problems Relating to the Protection of the Environment from the Vapors of 1,1-Dimethylhydrazine, Monomethylhydrazine and Hydrazine", a proposal approved by the Air Force Office of Scientific Research in 1979. The starting date of the proposed research was October 1, 1979. This project was, in fact, the continuation of the on-going project entitled "Basic Studies Relating to the Synthesis of Unsymmetrical Dimethylhydrazine, and Monomethylhydrazine by Chloramination". A final report relating to the results obtained on the original project from the period September 1, 1975 to September 30, 1979 at the University of Florida was submitted to the Air Force Office of Scientific Research on December 7, 1979. Since these two projects were interrelated, some remaining work of the original project was also completed between the period of October 1, 1979 and June 30, 1981. These results are included in this report.

1. Syntheses of Monomethylhydrazine.

(a) By the Reaction of Methylamine and Hydroxylamine-O-Sulfonic Acid.

The synthesis of monomethylhydrazine was successfully achieved by reacting solutions of $\text{NH}_2\text{OSO}_3\text{H}$ with CH_3NH_2 in diglyme. For example, 0.37 mol of $\text{NH}_2\text{OSO}_3\text{H}$ was mixed with 1.7 mol of CH_3NH_2 in dry diglyme at -10°C . The total yield of N-N bonded material, based on $\text{NH}_2\text{OSO}_3\text{H}$ taken, was 55%. On fractional distillation of the reaction mixture

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on a spinning bond column a mixture containing 84.3% monomethylhydrazine, 11.5% methanol and a small amount of methylamine, water and solvent was obtained. The products of this mixture were identified by gas chromatographic analysis as well as by ^1H nuclear magnetic resonance spectroscopy. The complete results of this study were reported in Inorg. Chem., 1980, 19, 2846. A reprint is included in Appendix I.

(b) By the Chloramination of Methylamine by Chloramine.

The study relating to the synthesis of monomethylhydrazine by the chloramination of methylamine begun earlier was completed during this project period. The reaction between CH_3NH_2 and NH_2Cl was studied under the following conditions: (1) In presence of KOH and NH_3 , (2) in presence of CH_3ONa and NH_3 , and (3) in absence of NH_3 and fixed base. Monomethylhydrazine formation was observed in (1) and (2) and a yield of total hydrazine content up to 84% was observed. It is therefore evident that a permanent base like KOH or CH_3ONa is favorable for formation of monomethylhydrazine in the chloramination of methylamine. The details of this study are reported in the Inorg. Chem., 1980, 19, 2192. A reprint is included in Appendix II.

2. Syntheses of Unsymmetrical Dimethylhydrazine.

(a) By the Reaction of Dimethylamine with Hydroxylamine-O-Sulfonic Acid.

The synthesis of 1,1-dimethylhydrazine was successfully carried out by the treating solutions of $\text{NH}_2\text{OSO}_3\text{H}$ with $(\text{CH}_3)_2\text{NH}$ in diglyme.

For example, 0.15 mol of $\text{NH}_2\text{OSO}_3\text{H}$ was mixed with 1.78 mol of $(\text{CH}_3)_2\text{NH}$ in diglyme at -78°C . After the reactants were mixed the reaction mixture was brought to 25°C . The reaction mixture was filtered to remove $[(\text{CH}_3)_2\text{NH}_2]_2\text{SO}_4$ and was then distilled over KOH. The fraction distilling between $60-64^\circ\text{C}$ was collected. The gas chromatographic analysis of this distillate showed 81.5% of 1,1-dimethylhydrazine. The other products were dimethylamine 9.1%, 1,1,4,4-tetramethyl-2-tetrazene 1.44%, and diglyme 1.63%. No formaldehyde dimethylhydrazone was detected. The complete results of this study are reported in *Inorg. Chem.*, 1980, 19, 2846. (Appendix I).

(b) By the Reaction of a Chloramine-Ammonia Mixture with Dimethylamine in the Presence of KOH.

For example, a solution containing 0.5 mol of $(\text{CH}_3)_2\text{NH}$ and 0.2 mol of KOH in *n*-butanol was treated with the $\text{NH}_2\text{Cl}-\text{NH}_3$ effluent (.1 mol NH_2Cl) of the chloramine generator at -78°C . The volatile gases were allowed to escape. The solid formed was removed by filtration and the solution was fractionally distilled. The 1,1-dimethylhydrazine obtained was estimated by ^1H NMR analysis. The yield of the 1,1-dimethylhydrazine based on NH_2Cl used was 30%. The details of this study are reported in *Ind. and Eng. Chem. Prod. Res. Dev.*, 1981, 20 181-5 (Appendix III).

3. Studies of the Mechanism of the Formation of Formaldehyde Dimethylhydrazone.

The study of the formation of formaldehyde dimethylhydrazone was

completed and a mechanism for the formation of formaldehyde dimethylhydrazone by the reaction of dimethylamine and chloramine was proposed. The results of this study have been published in Ind. and Eng. Chem. Prod. Res. Dev., 1981, 20, 181-5. It is worthwhile to note that the reaction between $(\text{CH}_3)_2\text{NNH}_2$ and NH_2Cl is very fast and, therefore, that NH_2Cl could be used to remove $(\text{CH}_3)_2\text{NNH}_2$ vapors from the atmosphere using a NH_2Cl solution in the scrubbers. A reprint is included in Appendix III.

4. Studies Relating to the Oxidation of 1,1-Dimethylhydrazine by Oxygen.

The original paper on the "Oxidation of 1,1-Dimethylhydrazine by Oxygen" was submitted in early 1979. A revised version of this study was prepared in compliance with the referee's comments and has been published in Inorg. Chem., 1981, 20, 426-429. A reprint is included in Appendix IV. This study was conducted to examine the problems relating to the protection of the environment from the vapors of 1,1-dimethylhydrazine and its oxidation products.

5. Oxidation of Monomethylhydrazine.

The interaction of monomethylhydrazine with oxygen was investigated. The results may be summarized as follows:

(a) Reaction of Monomethylhydrazine with Oxygen without Solvent.

This study was conducted before the current project period and the results are summarized in the "Final Report to the Air Force Office of the Scientific Research on the 'Basic Studies Relating to the

Synthesis of Unsymmetrical Dimethylhydrazine and Monomethylhydrazine by Chloramination'" submitted on December 7, 1979.

(b) Oxidation of Monomethylhydrazine by Oxygen in Ether Solution at 25°C.

For example, monomethylhydrazine (2.3 g, .050 mol) and 1 g benzene were dissolved in 100 mL of ether solution, and were transferred into a 2.45-liter reaction vessel containing pure oxygen at 25°C and 761 mm of Hg pressure. The zero time of the reaction was recorded. The zero reading of the methylhydrazine concentration was determined by comparing the chromatographic peak areas of methylhydrazine and benzene before mixing with oxygen. The progress of the reaction was followed by observing the ratio of the areas of the gas chromatographic peaks of CH_3NHNH_2 and C_6H_6 as a function of time. Typical results are summarized in the following table:

Time in minutes	$\frac{\text{CH}_3\text{NHNH}_2 \text{ peak area}}{\text{C}_6\text{H}_6 \text{ peak area}}$
	0
9	0.16
17	0.11
26	0.0
40	0.0

The other products detected by gas chromatographic analysis were formaldehyde monomethylhydrazone or its dimer, methanol, and water. In conclusion, monomethylhydrazine is quickly oxidized by the oxygen and, therefore, quickly removed from the atmosphere.

A spinoff from this research was the discovery that the oxidation of methylhydrazine by mercuric oxide yields appreciable amounts of the highly toxic mercury dimethyl. This was reported in the J. Org. Chem., 45, 1329 (1980). A reprint is included in Appendix V.

6. Synthesis of Unsymmetrical Di-isopropyl Hydrazine by the Chloramination of Di-isopropylamine.

The chloramination of di-isopropylamine was carried out in ethylether and also in diglyme. No hydrazine was obtained in either instance. The chloramination reaction was also carried using the pure amine without dilution. In this case $(i-C_3H_7)_2NNH_2$ was obtained in 75% yields. No evidence of the formation of $(CH_3)_2NN=C(CH_3)_2$ was obtained. This supports our previously reported mechanism for the formation of $(CH_3)_2NN=CH_2$ in the chloramination of dimethylamine since $[(CH_3)_2CH]_2N=N^+$ would be less likely to undergo the nucleophilic reaction analogous to that postulated for $(CH_3)_2N=N^+$ (Appendix III). These results have been accepted for publication in the J. Inorg. Nucl. Chem. (Appendix VI).