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Oxidation of 1,1-Dimethylhydrazine by Oxygen[1]

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The study of the oxidation of 1,1-dimethylhydrazine by molecular oxygen in solutions of diethyl ether or cyclohexane was carried out between 20 and 30 °C. The principal product of this oxidation reaction under these conditions is formaldehyde dimethylhydrazone. Water, 1,1,4,4-tetramethyl-2-tetrazene, nitrogen, methane, ammonia, formaldehyde methylhydrazone, *sym*-hexahydro-1,4-dimethyltetrazine, and *N*-nitrosodimethylamine were also identified products. Fourteen other products were detected by gas chromatography and mass spectral analysis. Mechanisms for the formation of the various products are suggested.

Introduction

The oxidations of 1,1-dimethylhydrazine in air[2-6] at or near room temperature have been reported, but the amount of published data is small. The objective of this study was to investigate the oxidation of 1,1-dimethylhydrazine with elemental oxygen in solution under well-defined conditions to determine if *N*-nitrosodimethylamine is produced in this reaction and also to identify the other oxidation products of this reaction.

Experimental Section and Results

Materials. 1,1-Dimethylhydrazine was obtained from the Rocky Mountain Arsenal and was refluxed and distilled over solid KOH and stored at −4 °C. Formaldehyde 1,1-dimethylhydrazone [$(CH_3)_2N-N{=}CH_2$] was always present as a minor impurity in dimethylhydrazine, so corrections were applied for this impurity in all calculations. 1,1,4,4-Tetramethyl-2-tetrazene,[7] formaldehyde 1,1-dimethylhydrazone,[8] *N*-nitrosodimethylamine,[9] and *sym*-hexahydro-1,1-dimethyltetrazine[10] were prepared by the procedures reported in the literature, and their impurities were checked by ^1H NMR and gas chromatographic analyses. The solvents were reagent grade and were dried by refluxing and distilling over calcium hydride and were stored over calcium hydride. Oxygen was supplied by AIRCO, Inc., Montvale, NJ, and was dried with Drierite.

Apparatus. A combination of a YSI Model 71A and a Sargent Thermonitor temperature controller was used to control the temperature of the reaction bath to within ±0.05 °C. A Brinkman IC-6 cooler was used to cool the bath, and heaters of appropriate capacity were used to heat the bath. The reaction vessel used in this study was a 2.45-L flask with an inlet and outlet for oxygen and a sample-withdrawing port.

Procedure. The reaction vessel was dried at 150 °C for 24 h. The inlet of the vessel was connected to nitrogen and oxygen sources through a three-way stop cock and the outlet vented to the hood. A magnetic stirring bar was added to the vessel, and the sample-withdrawing port was closed with a rubber septum. The vessel was placed over the magnetic stirrer in the temperature-controlled bath and flushed with dry nitrogen to expel air and moisture. After 1 h, the nitrogen flush was replaced by dry oxygen. The oxygen flush was stopped after 30 min. A freshly prepared solution of 1,1-dimethylhydrazine in the desired solvent (containing 4.00 g/L of toluene as the internal standard) was introduced into the reaction vessel. The zero-time reading of the hydrazine:toluene ratio was taken on the chromatograph, and the inlet and outlet of the reaction vessel were closed. The amount of the oxygen was calculated by using the ideal gas law. A similar procedure was used in the oxidation of the pure hydrazine.

Analyses. A Perkin-Elmer 800 gas chromatograph and a Varian Model 3700 gas chromatograph were used to detect and identify the various oxidation products of the hydrazines studied. The former instrument was equipped with a differential thermal conductivity detector and a gas chromatographic 12 ft × $^1/_8$ in. K-20 M Carbowax (15%)-KOH (5%) on Chrom P.A.W. 80/100 mesh size column. A variety of columns and differential thermal conductivity detectors were used with the Varian instrument. Helium was used as a carrier gas. The reaction was followed by analyzing the reaction mixture by gas chromatography and comparing the gas chromatographic peak areas of the various components with that of toluene used as the internal standard. The peak areas were computed by using a manual integrator, by an electronic integrator on the recorder, and by a CDS 111 data analyzer supplied by Varian Associates. Identification of the various reaction products was achieved by comparing their retention times, proton NMR spectra, infrared spectra, and mass spectra with those of known substances.

Reactions of Oxygen with 1,1-Dimethylhydrazine in Diethyl Ether. In each of a series of experiments, 250 mL of a 0.2 M solution of $(CH_3)_2NNH_2$ in diethyl ether containing 1.0 g of toluene was reacted with 91 ± 0.5 mmol of O_2 at 20, 25, or 30 °C in the reaction vessel described earlier. At 20 °C, for more than a 200-h period, no visible change in the color of the solution was observed. The major products identified by gas chromatography were formaldehyde dimethylhydrazone, methane, and nitrogen. In some cases a trace amount of 1,1,4,4-tetramethyl-2-tetrazene was also observed. At 25 and 30 °C, the solution changed to light yellow within a period of 24 h. In the initial stages (48–78 h) the reaction products were formaldehyde 1,1-dimethylhydrazone, methane, and nitrogen. As reaction times were increased, water, 1,1,4,4-tetramethyl-2-tetrazene, and *N*-nitrosodimethylamine began to appear. The rate of oxidation was measured by gas chromatographic analysis, comparing the areas of 1,1-dimethylhydrazine or formaldehyde dimethylhydrazone peaks with the area of the toluene peak as a function of time.

After the rate measurements of 1,1-dimethylhydrazine–oxygen reaction at 25 °C in diethyl ether, the excess ether was evaporated in vacuum. The residual liquid was brown and had an irritating, disagreeable odor. This liquid was only partially soluble in water, carbon tetrachloride, or dimethyl sulfoxide.

(a) Proton NMR Spectrum of the Residual Liquid. The proton NMR spectrum of the portion of the residual liquid which was soluble in deuterated dimethyl sulfoxide showed peaks corresponding to unreacted dimethylhydrazine, the solvent diethyl ether, the internal standard toluene, and the reaction products water, formaldehyde dimethylhydrazone, formaldehyde methylhydrazone and its dimer, and 1,1,4,4-tetramethyl-2-tetrazene. The proton NMR spectrum of the portion of the liquid which was soluble in carbon tetrachloride showed a doublet corresponding precisely to *N*-nitrosodimethylamine[11]

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(1) (a) Mathur, M. A.; Sisler, H. H., paper presented in part at the Congress of American Chemical Society and Chemical Society of Japan, Honolulu, Haw., 1979. (b) Sisler, H. H.; Mathur, M. A., paper presented in part at the Proceedings of the Conference on Environmental Chemistry of Hydrazine Fuels, Tyndall AFB, 1977.

(2) Streim, H. G.; Clark, J. D. "The Vapour Phase Oxidation of Unsymmetrical Dimethylhydrazine", Report LR-6; U.S. Naval Air Rocket Test Station: Dover, N.J., 1955; pp 1-10.

(3) Streim, H. B.; Clark, J. D. "Methylazide Formation in Unsymmetrical Dimethylhydrazine Vapour", Report LR-2; U.S. Naval Air Rocket Test Station: Dover, N.J., 1954; pp 1-3.

(4) Urry, W. H.; Olsen, A. L.; Bens, E. M.; Kruse, H. W.; Ikoku, C.; Gaibel, Z. "Autoxidation of 1,1-Dimethylhydrazine" U.S. Naval Ordinance Test Station Technical Publication 3903; 1965.

(5) Loper, G. L. Proceedings of the Conference on Environmental Chemistry of Hydrazine Fuels; 1977; pp 129-159.

(6) Stone, D. A. Reference 5, pp 161-66.

(7) Bull, W. E.; Seaton, T. A.; Audrieth, L. F. *J. Am. Chem. Soc.* **1958**, *80*, 2516.

(8) Class, J. B.; Aston, J. G.; Oakwood, T. S. *J. Am. Chem. Soc.* **1953**, *75*, 2937.

(9) Scanlan, R. A.; Lohsen, S. M.; Bills, D. D.; Libbey, L. M. *J. Agric. Food Chem.* **1974**, *22*, 149.

(10) Tolles, W. N.; McBride, W. R.; Thun, W. E. *J. Am. Chem. Soc.* **1969**, *91*, 2443.

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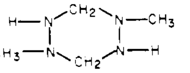
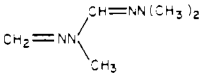
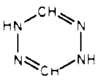
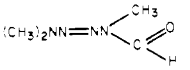
Table I. Products of the Reaction of 1,1-Dimethylhydrazine with Molecular Oxygen

product	basis of identification[a]	mass spectra *m/e* values	remarks
N_2	GC		confirmed
CH_4	GC		confirmed
NH_3	GC		confirmed
H_2O	GC, NMR		confirmed
$(CH_3)_2NN{=}CH_2$	GC, NMR		confirmed
$(CH_3)_2NNO$	GC, NMR, MS	74, 59, 58, 44, 43, 42, 29	confirmed
$CH_3NHN{=}CH_2$	GC, NMR		confirmed
	GC, MS	116, 115, 114, 100, 73, 72, 71, 70, 59, 58, 57, 44, 43, 29	confirmed
$(CH_3)_2NN{=}NN(CH_3)_2$	GC, NMR, MS	116, 72, 58, 44, etc.	confirmed
 $CH_2{=}NN(CH_3)CH{=}NN(CH_3)_2$	GC, MS	114, 84, 71, 70, 58, 44, 42	postulated
$(CH_3)_2NNH(CH_3)$	GC, MS	74, 73, 70, 59, 58, 44, 30, 29	postulated
	GC, MS	83, 56, 44, 42, 30, 29	postulated
 $(CH_3)_2NN{=}NN(CH_3)CHO$	GC, MS	130, 129, 86, 85, 84, 72, 70, 59, 58, 57, 56, 46, 45, 44, 43, 42	postulated

[a] GC = gas chromatographic analysis; MS = mass spectral analysis; NMR = proton nuclear magnetic resonance analysis.

in addition to peaks observed for the portion soluble in deuterated dimethyl sulfoxide but no peak corresponding to water. In addition to these peaks, there were in each solution several other unassigned peaks observed.

(b) Gas Chromatographic Analysis of the Residual Liquid. A gas chromatographic analysis of this liquid on a 10% Carbowax 20 M + 5% KOH column at 80 °C on a Varian 3700 instrument showed 22 substances with retention times between 0.60 and 69.70 min (Figure 1). By comparing the retention times of these substances with those of known substances, some of the substances were shown to be diethyl ether, dimethylhydrazine, formaldehyde dimethylhydrazone, 1,1,4,4-tetramethyl-2-tetrazene, water, formaldehyde methylhydrazone, *sym*-hexahydro-1,4-dimethyltetrazine, toluene, and *N*-nitrosodimethylamine. Diethyl ether was the solvent, and toluene was the internal standard used in the experiment. The Carbowax column is a high-polarity column for basic compounds; therefore, either the substances having higher retention times are highly polar substances or they have higher molecular weights and higher boiling points. Of particular interest was the substance having a retention time of 4.74 min, since a similar retention time has been observed in our laboratory for the oxidation products of methylhydrazine with oxygen.[12]

(c) Mass Spectral Analysis of the Residual Liquid. The gas chromatograph–mass spectral analysis of the residual liquid was done on an AEI MS-30 mass spectrometer and a PYE-Unicam-104 Series gas chromatograph. A 9 ft × $^1/_4$ in. 3% OV 271 column was used between 100 and 250 °C (programmed for 10°/min heating rate). The gas chromatogram of the product showed the presence of 21 substances. The mass spectrum of each of the substances was recorded. The upper *m/e* limit of one of the substances was 280, and there were several substances having upper *m/e* limits above 116. This means that several products having molecular weights higher than that of 1,1,4,4-tetramethyl-2-tetrazene (*m/e* 116) are formed in the oxidation of dimethylhydrazine. The identities of some of the oxidation products were determined or postulated, as listed in Table I.

Reaction of Oxygen with Dimethylhydrazine in Cyclohexane Solutions. In each of another series of experiments using cyclohexane as the solvent, 250 mL of 0.2 M $(CH_3)_2NNH_2$ solution containing 1.0 g of toluene was allowed to react with 91 ± 0.5 mmol of O_2 at 20 and 30 °C. The products identified at 20 °C and at 25 and 30 °C were similar to those observed when the reaction was carried out in diethyl ether. The change of solvent likewise was shown to have little effect on the rate at which dimethylhydrazine is oxidized. The development of yellow color was observed only when the reaction was carried out at 25 and 30 °C.

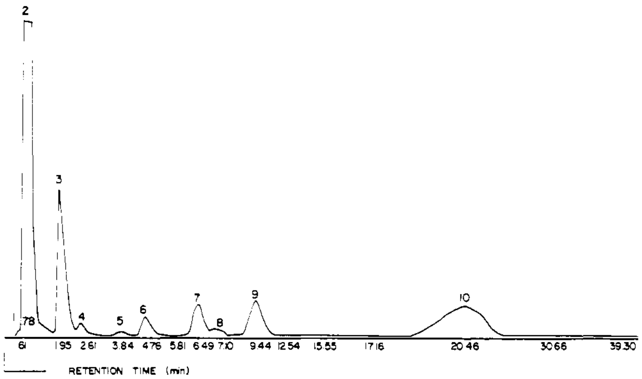


Figure 1. Gas chromatogram of the oxidation products of 1,1-dimethylhydrazine in ether. Key: 1, gas; 2, diethyl ether (solvent); 3, formaldehyde 1,1-dimethylhydrazone; 4, unknown; 5, toluene (reference); 6, formaldehyde methylhydrazone and *sym*-hexahydro-1,4-dimethyltetrazine; 7, water and 1,1,4,4-tetramethyl-2-tetrazene; 8, unknown; 9, unknown; 10, *N*-nitrosodimethylamine.

Reaction of Dimethylhydrazine with Oxygen in the Absence of a Solvent. The reaction between $(CH_3)_2NNH_2$ and O_2 in the absence of a solvent was carried out by allowing 3.0 g of dimethylhydrazine to react with 100 ± 0.5 mmol of dry oxygen at 25 °C. The gas phase was sampled after 85, 285, and 1410 min. In each instance the presence of nitrogen, methane, and formaldehyde dimethylhydrazone, in addition to dimethylhydrazine, was detected. No *N*-nitrosodimethylamine was detected in the gas-phase analysis. The residue which was a brown liquid was partly soluble in dimethyl sulfoxide and the rest in carbon tetrachloride. The proton NMR spectrum of the residue soluble in carbon tetrachloride contained peaks characteristic of the spectrum reported[11] for *N*-nitrosodimethylamine, whereas the portion soluble in dimethyl sulfoxide showed NMR peaks corresponding to unreacted dimethylhydrazine, 1,1,4,4-tetramethyl-2-tetrazene, formaldehyde dimethylhydrazone, and a small amount of water. The presence of water was further confirmed by gas chromatographic analysis of the extract of the residue with methanol.

Reaction of Dimethylhydrazine with a Small Amount of Oxygen in a Nitrogen Atmosphere. In order to show whether or not the formation of the formaldehyde dimethylhydrazone occurs through a disproportionation reaction such as $2(CH_3)_2NNH_2 \rightarrow (CH_3)_2NN{=}CH_2 + CH_4 + N_2$ catalyzed by oxygen molecules, rather than

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(11) Yonezawa, T.; Morishima, I.; Takenchi, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1807.

(12) Sisler, H. H.; Mathur, M. A.; Jain, S. R., unpublished results.

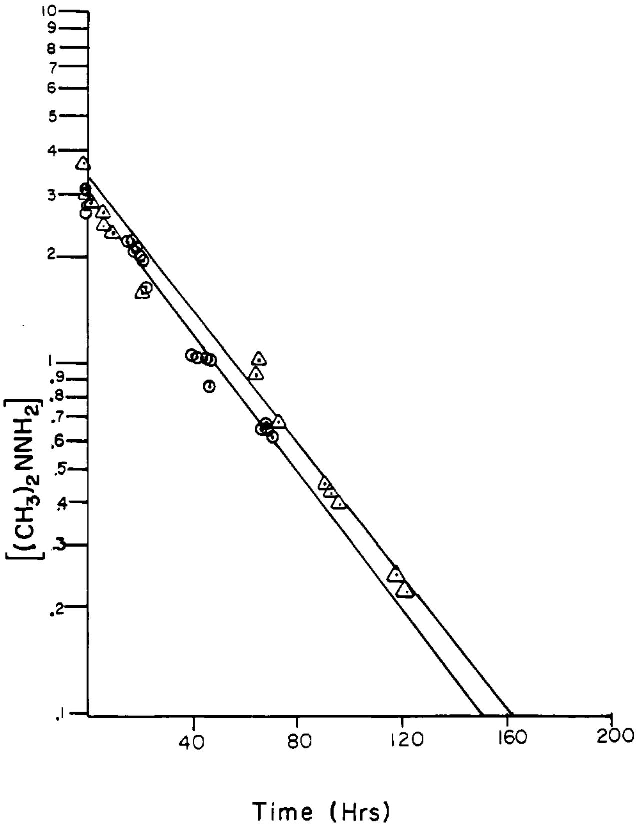


Figure 2. ln $[(CH_3)_2NNH_2]$ vs. time plots for $(CH_3)_2NNH_2$ oxidation at 30 °C in diethyl ether (○) and in cyclohexane (△).

through a straightforward oxidation of dimethylhydrazine by oxygen, the following experiments were carried out.

A reaction vessel containing 250 mL of a 0.2 M solution of dimethylhydrazine in diethyl ether containing 1 g of toluene was filled with dry nitrogen and 25 mL (1.0 mmol) of dry oxygen added through the rubber septum cap. The flask was kept at 25 °C for more than 80 h. The ratio [moles of $(CH_3)_2NNH_2$]/[moles of $(CH_3)_2NN{=}CH_2$] which at time zero equaled 19 dropped to 6 after 3.6 h and then changed no more. Similar results were obtained when cyclohexane was used as solvent. Thus, it is clear that O_2 molecules have a stoichiometric rather than a catalytic role in this reaction.

Discussion

The experiments we have carried out show that the rate of disappearance of the dimethylhydrazine is proportional to the concentration of dimethylhydrazine. The concentration of O_2 in the reaction medium of course changes as the reaction procedes. Urry et al.[4] have reported that the reaction of dimethylhydrazine with molecular oxygen in the gas phase is zero order with respect to oxygen. Pansacker[13] has made a similar report with respect to oxidation of phenylhydrazones. If we make the assumption that the order of the dimethylhydrazine reaction with respect to oxygen in solution is likewise zero, we may presume that reaction is first order with respect to dimethylhydrazine, and we may write eq 1, where k is the

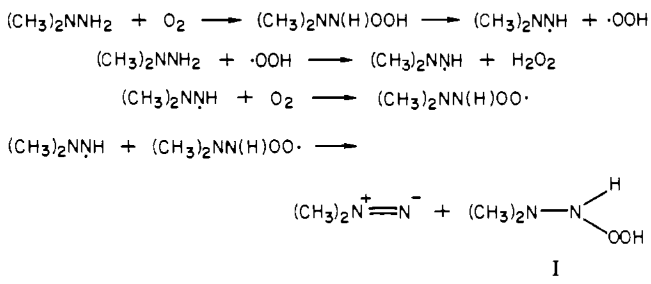
$$-d[(CH_3)_2NNH_2]/dt = k(a - x) \qquad (1)$$

first-order rate constant. The plot of ln $(a - x)$ vs. t should yield a straight line. Such plots of our data confirm this as shown in Figure 2. The values of k at 20, 25, and 30 °C, respectively, as obtained from eq 2 for the reaction in cyclohexane are

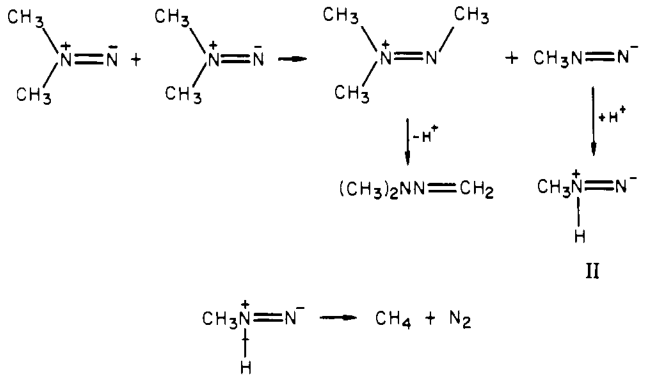
$$k = -[\ln (a - x)]/t \qquad (2)$$

1.8×10^{-6}, 2.2×10^{-6}, and 6.4×10^{-6} s^{-1}. Corresponding values for the reactions in diethyl ether are 1.4×10^{-6}, 3.8×10^{-6}, and 7.0×10^{-6} s^{-1}. These data are insufficiently precise to provide a basis for calculating precise values for activation energies. However, they indicate values in the neighborhood of 100 kJ mol^{-1} in each solvent.

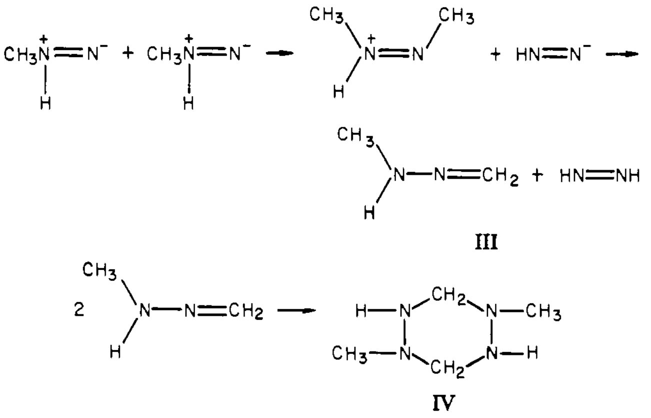
Scheme I



Scheme II

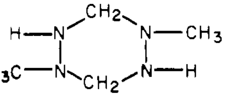


Scheme III



$3HN{=}NH \rightarrow 2N_2 + NH_3$

Products of the Reaction of Dimethylhydrazine with Oxygen. Mechanistic Considerations. The major gaseous products of the oxidation of 1,1-dimethylhydrazine with elemental oxygen are nitrogen, methane, and ammonia. The major liquid products in the reaction mixture are formaldehyde dimethylhydrazone, tetramethyltetrazene, *N*-nitrosodimethylamine, formaldehyde methylhydrazone, and its dimer, *sym*-hexahydro-1,4-dimethyltetrazine



The reaction of oxygen with dimethylhydrazine probably results initially in the formation of dimethyldiazene $[(CH_3)_2N^+{=}N^-]$. It has been suggested that this substance is formed by the steps in Scheme I[4,5] in the gas phase.

If we assume the initial formation of 1,1-dimethyldiazene in the liquid-phase oxidation, the formation of the various observed and postulated products can be easily explained. The

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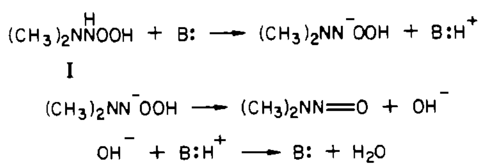
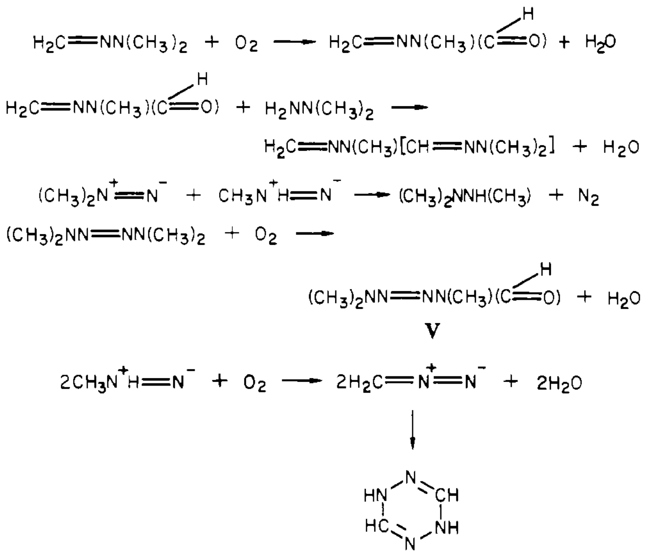
(13) Pansacker, K. H. *J. Chem. Soc.* **1950**, 3478.

Scheme IV



Scheme V



formation of $(CH_3)_2NN{=}CH_2$ can be explained as previously reported by Sisler et al.[1b] (Scheme II).

The formation of 1,1,4,4-tetramethyl-2-tetrazene can readily occur through the dimerization of dimethyldiazene. A reasonable pathway for the formation of formaldehyde methylhydrazone and its dimer, *sym*-hexahydro-1,4-dimethyltetrazine, would begin with the reaction of two molecules of II (Scheme III). Both III and IV are known compounds.[10,14,15]

The presence of III in the reaction product is confirmed by the presence of a typical quartet in the proton NMR spectrum at δ 6.3. The dimer IV is confirmed by the appropriate peaks in the mass spectrum. The retention times of III and IV (in benzene solution) in the gas chromatographic analysis are the same.

Other products confirmed by proton NMR, by mass spectra, and by gas chromatographic analysis include *N*-nitrosodimethylamine and water. The formation of *N*-nitrosodimethylamine and water can occur through the decomposition of I which Urry[4] has indicated might be base catalyzed (Scheme IV). Though Urry[4] and Loper[5] have discussed the possibility of the formation of *N*-nitrosodimethylamine in the gas-phase reaction of dimethylhydrazine and air, no quantitative data concerning the extent of its formation were given. In our studies in the liquid phase, the amount of *N*-nitrosodimethylamine ranges between 1.5% and 13.9% of the reaction product as measured by gas chromatography. The magnitude of these yields combined with the carcinogenic character of *N*-nitrosodimethylamine make these results a basis for concern with respect to the utilization of dimethylhydrazine.

The identities of the remaining four products observed are inferred from gas chromatographic and mass spectral analyses. Scheme V reasonably accounts for the formation of some of these products. The formation of V has been reported as a product of the oxidation of 1,1,4,4-tetramethyl-2-tetrazene by chloramine.[16]

Acknowledgment. The authors gratefully acknowledge the support of the research by the Air Force Office of Scientific Research through a grant to the University of Florida.

Registry No. III, 36214-48-9; IV, 695-20-5; V, 20642-57-3; $(CH_3)_2NNH_2$, 57-14-7; O_2, 7782-44-7; N_2, 7727-37-9; CH_4, 74-82-8; NH_3, 7664-41-7; H_2O, 7732-18-5; $(CH_3)_2NH{=}CH_2$, 2035-89-4; $(CH_3)_2NNO$, 62-75-9; $(CH_3)_2NN{=}NN(CH_3)_2$, 6130-87-6; $CH_2{=}NN(CH_3)CH{=}NN(CH_3)_2$, 75400-49-6; $(CH_3)_2NNH(CH_3)$, 1741-01-1; $(NHCH{=}N)_2$, 61626-05-9.

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(14) Lemal, D. M.; Menger, F.; Coats, E. *J. Am. Chem. Soc.* **1964**, *86*, 2395.

(15) Hammerum, S. *Tetrahedron Lett.* **1972**, 949.

(16) Utvary, K.; Vitovec, G. *Monatsh. Chem.* **1973**, *104*, 908.

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Existence of Stereoselectivity in the Outer-Sphere Redox Reaction between Di-μ-oxo-μ-(propylenediaminetetraacetato)-bis[oxomolybdate(V)] and μ-Amido-μ-hyperoxo-bis[bis(ethylenediamine)cobalt(III)] in Aqueous Solution

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The oxidation of $[\mathrm{Mo^V}_2\mathrm{O_4}(R,S\text{-pdta})]^{2-}$ (1) (pdta = propylenediaminetetraacetate) with Δ,Δ-$[(\mathrm{en})_2\mathrm{Co^{III}}(\mu\text{-NH}_2,\mathrm{O_2}^{(-)})\text{-}\mathrm{Co^{III}}(\mathrm{en})_2]^{4+}$ (2) (en = ethylenediamine) to give molybdenum(VI) species and μ-amido-μ-peroxo-dicobalt(III) complex exhibits stereoselectivity in aqueous solution of pH 3.5 and 4.6 at 25 °C at ionic strengths (I) from 0.2 to 2.0 M. An equimolar (2.69×10^{-3} M; M = mol dm^{-3}) mixture of **1** and **2** undergoes redox reaction (stoichiometry 1:2) to leave the half amount of **1** unreacted, the enantiomeric excess depending on I; ca. 0.15% in favor of R-pdta complex at $I = 0.2$ M and ca. 0.25% in favor of S-pdta complex at $I = 2.0$ M. The pseudo-first-order rate constants (k_{obsd}) determined with racemic oxidant in the presence of an excess of the molybdenum(V) complex at 25 °C are expressed by $k_{\mathrm{obsd}} = 2k_eK_{\mathrm{IP}}[\mathrm{Mo_2}]/(1 + K_{\mathrm{IP}}[\mathrm{Mo_2}])$, where K_{IP} and k_e are the ion-pair formation constant between the redox couple and the electron-transfer rate constant within the ion pair, respectively. K_{IP} (51 ± 7 M^{-1} at $I = 0.2$ M) decreases and k_e (0.76 ± 0.07 s^{-1} at $I = 0.2$ M) increases with increase in ionic strength. The difference in selectivity with ionic strength can be interpreted by assuming different selectivities for K_{IP} and k_e.

Introduction

Existence of stereoselectivity in outer-sphere redox reactions has been discussed by several authors but remains uncertain. Grossman and Wilkins measured the rate of reduction of various optically active iron(III) and cobalt(III) complexes with Δ-$[\mathrm{Fe^{II}}(R\text{-pdta})]^{2-}$ (R-pdta = (R)-propylenediamine-

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