hydrogen bromide, formed by reaction of the sample with a small amount of adsorbed water in the system (although the system was flamed strongly under high vacuum before bromine was admitted). If one assumes the number of moles of HBr formed by such a reaction is indicated by the increase in total pressure over that expected from the initial pressure of bromine at 700° (973°K.), and that this amount remains constant at higher temperatures, then the measured total pressures, corrected for the contribution from HBr, correspond well with the calculated curve. Even though these experimental difficulties seriously limit the effectiveness of this experiment, the results offer some support to the validity of the interpretation.

Data available concerning $CrCl_4$ may be compared with our results. The heat and entropy changes for the reaction

$$CrX_3(s) + {}^1/_2X_2(g) = CrX_4(g)$$

at 800°K. are 28.0 and 36.4 kcal. and 25.4 and 27.8 e.u., respectively, for X = Cl[7] and X = Br. These entropy changes appear reasonable although a quantitative estimate of the entropy of CrX_4 (g) molecules is difficult to make without spectroscopic data because of the large contribution of vibrational states at this high temperature.

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(7) H. A. Doerner, Bureau of Mines Bulletin, 577, 1937.

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[CONTRIBUTION FROM THE W. A. NOYES LABORATORY, UNIVERSITY OF ILLINOIS]

The Reaction of Nitrogen(II) Oxide with Diethylamine

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The reaction between diethylamine and nitric oxide in ether solution and in the pure amine is described. Infrared and nuclear magnetic resonance spectroscopy indicate that the structure of the product is $Et_2NH_2{}^+Et_2NN_2O_2{}^-$. The sodium salt, $Na^+Et_2NN_2O_2{}^-$ was prepared. A reaction mechanism in which NO behaves as a Lewis acid is proposed to explain this reaction and the one with sulfite ion leading to the formation of $O_3SN_2O_2{}^{=}$.

Introduction

The nature of the reaction between sulfite ion and nitric oxide in basic aqueous solution has been a controversial subject.[2] The structure of the product was eventually established by X-ray diffraction[3] and infrared spectroscopy[4] but the reaction type has not yet been classified. We propose that this reaction and several others reported in the literature furnish evidence that nitric oxide can behave as an electron pair acceptor. In order to establish this reaction mode we are undertaking an investigation of the reactions of nitric oxide with a series of Lewis bases. Reaction conditions for preparing, and evidence for establishing the structure of $Et_2NH_2{}^+Et_2NN_2O^-$ are presented in this article. A general mechanism is tentatively proposed to classify both the amine and sulfite reactions.

Experimental

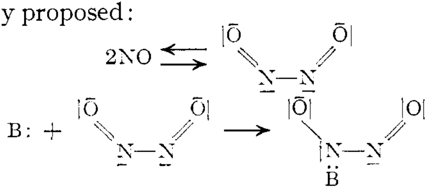
Eastman Kodak "White Label" anhydrous diethylamine (100 ml.) is dissolved in 150 ml. of diethyl ether (Merck, Reagent grade) contained in a dry, three-necked flask. Similar results are obtained from amine freshly distilled from BaO. The relative amounts of amine and ether are not critical. Two of the three necks serve as inlet and outlet, respectively, and the third accommodates a sealed stirrer. The flask is incorporated into a closed system and flushed with nitrogen to remove oxygen. The amine–ether solution is cooled to −78° and nitric oxide gas is slowly added. The commercial grade nitric oxide employed is purified by bubbling through 10 *M* sodium hydroxide and dried by passing through columns containing sodium hydroxide pellets. The product precipitates from solution as the reaction proceeds with stirring for a period of 15 hours. Upon filtration and washing with ether, 10.7 g. of crude product representing a yield of 11% was obtained.

Infrared spectra were obtained with a Perkin–Elmer model 21 infrared spectrometer with sodium chloride optics. The instrument was calibrated using water vapor absorption and the appropriate corrections applied to the reported spectra. The magnetic susceptibility was measured with a modified Curie magnetic balance. Nuclear magnetic resonance spectra were obtained using a Varian high resolution nuclear magnetic resonance spectrometer and associated magnet. Spectra were obtained using a 40 mc. probe.

Results and Discussion

In contrast to the abundance of literature concerning reactions of nitric oxide to produce the nitrosyl ion, there is very little evidence to indicate that nitric oxide is capable of behaving as an electron pair acceptor. The reaction with sulfite ion represents one possible example. The phase diagram for the binary system dimethyl ether–nitric oxide[5] indicates the formation of the compound $(CH_3)_2ON_2O_2$. The proposed existence of the acid $H_2N_2O_3$[6] and the preparation of salts of this acid[7] are further examples.

The following mechanism, consistent with the above observations and with those to be reported on the diethylamine-nitric oxide reaction, is tentatively proposed:



where B is an electron pair donor.

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[1] Abstracted in part from the Senior Thesis of F. E. Paulik, University of Illinois, 1957. Presented at the Fall (1959) Meeting of the American Chemical Society.

[2] J. Pelouz, *Ann. Pharm.*, **15**, 240 (1835); E. Weitz and F. Achterberg, *Ber.*, **66B**, 1718 (1933); F. Raschig, *Ann.*, **241**, 232 (1887); E. Divers and T. Haga, *J. Chem. Soc.*, **67**, 452 (1895); **69**, 1610 (1896); A. Hantzsch, *Ber.*, **27**, 3264 (1894).

[3] E. G. Cox, G. A. Jeffrey and H. P. Stadler, *J. Chem. Soc.*, 1783 (1949); *Nature*, **162**, 770 (1948); G. A. Jeffrey and H. P. Stadler, *J. Chem. Soc.*, 1467 (1951).

[4] R. S. Drago, THIS JOURNAL, **79**, 2049 (1957).

[5] G. Baume and A. F. G. Germann, *J. chim. phys.*, **12**, 244 (1914).

[6] M. L. Nichols and C. W. Morse, *J. Phys. Chem.*, **35**, 1239 (1931).

[7] Angleli, *et al.*, *Gazz. chim. ital.*, **26II**, 17 (1896); **27II**, 357 (1897); **30I**, 593 (1900); **31I**, 15 (1901); **33II**, 245 (1903).

The pi-electron cloud in the product is delocalized throughout the N_2O_2 group as previously reported.[4,8] Low temperature facilitates the dimerization of nitric oxide and results in an increased yield of product. Reactions which occur in fair yield at low temperatures produce only a trace of product when carried out at room temperature.

When B is diethylamine, a white solid product is obtained whose empirical formula is Et_2NHNO. The product is reasonably stable at room temperature. It undergoes slow decomposition over a period of several days in a closed bottle in the presence of air producing a brown oil. The compound has a detectable vapor pressure at room temperature and if left on the desk top will eventually disappear. It can be stored indefinitely at $-78°$ or under ether at room temperature. The crude product is quite pure as indicated by elemental analysis. Found: N, 26.36. Calcd.: N, 27.16. The product is soluble in chloroform and alcohol and can be precipitated from concentrated solutions by the addition of ether. After several fractional precipitations, a purified product is obtained whose infrared spectrum is identical with the crude product. Elemental analysis on this compound are a little closer to the theoretical than the crude. Found: C, 46.24; H, 10.53; N, 26.58. Calcd : C, 46.58; H, 10.66; N, 27.16. In a sealed tube the product melted sharply with decomposition at 107°. In an open tube the product slowly decomposed around 65°. In order to prove that ether functions only as a solvent in this reaction, the product was prepared at $-33°$, using pure diethylamine. The elemental analyses and infrared spectrum of this product are identical with the material prepared in ether. Appreciable quantities of the product are not obtained at room temperature.

The product is diamagnetic indicating that the formula is $(Et_2NHNO)_x$ where x is an even integer. Attempts to obtain an accurate molecular weight were unsuccessful for the product is only slightly soluble at the freezing point of chloroform. A crude value of 170 ± 30 favors $x = 2$.

There are a large number of possible structural formulas that can be written for this compound. Both nuclear magnetic resonance and infrared spectroscopy were utilized to establish the structure.

The complete interpretation of the n.m.r. spectra of chloroform solutions of the product is complicated because of the reactivity of the product in solution. If solutions containing 1 g. of product in 5 ml. of chloroform are made up in the absence of oxygen, placed in a sealed n.m.r. tube and kept cold until the spectra are run, a curve approaching that illustrated by the dotted line in Fig. 1 is obtained. The assignments have been indicated on the spectra. The triplet CH_3 peak and the quadruplet CH_2 peak indicate the ethyl groups are still intact. The N–H resonance occurs at the same place relative to the chloroform peak as the N–H resonance in a saturated chloroform solution of diethylammonium chloride. Structural formulas for the product which place the amine hydrogens on the oxygen are eliminated for this resonance would occur at higher fields. One additional amount of structural information can be obtained from the N–H resonance of the n.m.r. spectrum. The spectrum was obtained at low resolution and the area of the N–H peak compared with that of the methyl peak. The ratio of methyl to N–H hydrogens is 5.9 to 1 as compared to the theoretical ratio 6 to 1 required by the empirical formula. If the spectrum is run in a sealed tube but the other precautions mentioned earlier for running these spectra are not observed, some decomposition occurs and the curve illustrated by the solid line in Fig. 1 is obtained. When the spectrum is run in an open tube, a change is observed with time. There is a gradual and appreciable shift of the N–H resonance to higher fields. Evolution of nitric oxide occurs and an average resonance for the N–H in the compound and the amine is obtained.

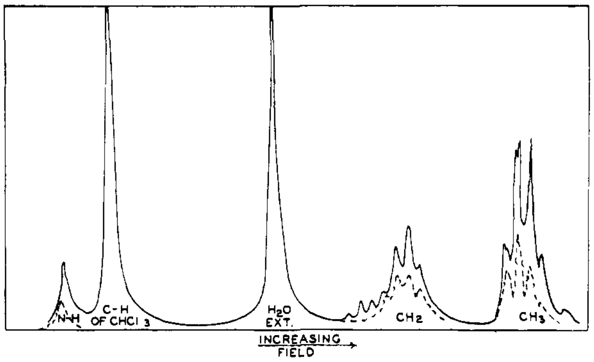

Fig. 1.

In summary, the n.m.r. spectra establish: (1) the ethyl groups are intact; (2) the amine hydrogen is on a quaternary nitrogen in the product; (3) hydrogen is not lost in the reaction.

There is also chemical evidence to indicate that the Et_2N–structure is intact in the molecule. If the product is dissolved in water and hydrochloric acid added, nitric oxide is evolved. Evaporation of the remaining solution to dryness and purification of the resulting solid produces diethylammonium chloride.

The infrared spectra of Nujol mulls of the product and pertinent compounds are summarized in Table I. The number of peaks in common in the spectra of the product and diethylammonium chloride supports a structure $Et_2NH_2^+Et_2NN_2O_2^-$. Most significant are the diethylammonium chloride absorptions in the region 2900 to 2350 cm.$^{-1}$ and that at 1595 cm.$^{-1}$. These have been assigned[9] to $\overset{\oplus}{N}$–H stretches and to $\overset{\oplus}{N}$–H_2 deformation, respectively. In the product these absorptions occur in the 2848 to 2455 cm.$^{-1}$ region and at 1510 cm.$^{-1}$. These lower values are indicative of rather extensive hydrogen bonding. Both the product and diethylammonium chloride exhibit absorption at 807 cm.$^{-1}$ which we attribute to an $\overset{\oplus}{N}$–H_2 rocking mode. A similar mode

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[8] M. G. Evans and J. Gergeley, *Nature*, **162**, 771 (1948).

[9] P. J. Stone, J. C. Craig and H. W. Thompson, *J. Chem. Soc.*, 52 (1958).

TABLE I

INFRARED ABSORPTION FREQUENCIES OF NUJOL MULLS[a]

$Et_2NH_2^+Et_2NN_2O_2^-$	$Et_2NH_2^+Cl^-$	$Na^+Et_2NN_2O_2^-$
2905 i, br[b]	2905 i, br[b]	2900 i, br[b]
2848 i, s	2845 i, br	..
2696 i, s	2702 i, br	..
2455 i, s	2463 i, s	..
..	2376 i, s	..
1571 m, m	1649 wk, m	..
1510 m, s	1595 m, s	..
1451 i, br[b]	1462 i, br[b]	1465 i, m[b]
1404 shoulder	1393 m, s	..
1380 i, m[b]	1378 i, m[b]	1382 i, m[b]
1340 shoulder	1341 m, s	1350 shoulder
1305 wk, s	..	..
1120 m, s	1210 m, s	1225 i, br
1187, 1177, 1170 i, br	..	1210 i, br
1155	1160 i, s	1167 shoulder
1131 m, s		1129 m, s
1075 m, s	1062 m, s	1064 m, s
973 i, s	1050 m, s	965 m, s
932 wk, m	918 wk, s	950 m, s
869 i, s	..	872 i, s
807 i, s	807 i, s	..
..	..	822 wk, m
720 v wk, m	721 wk, m	721 wk, m
		674 wk, m

[a] The first symbol listed refers to the band intensity: i, intense; m, medium; wk, weak; v, very. The second symbol refers to band width: s, sharp; m, medium; br, broad. [b] These broad bands are caused by absorption from the product and from Nujol.

occurs at 878 cm.$^{-1}$ in the spectra of dimethylammonium iodide.[10]

The infrared strongly indicates that the product contains a diethylammonium ion. Further support of this is indicated by the following reaction

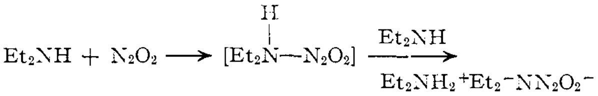
$$Et_2NH_2^+ + Et_2NN_2O_2^- + Na^+ + OEt^- \xrightarrow{\text{alcohol}} Et_2NH + EtOH + NaEt_2NN_2O_2$$

The diethylammonium salt is dissolved in a minimum amount of alcohol and a solution of sodium ethoxide added. A white solid, $Na^+Et_2NN_2O_2^-$ can be precipitated along with the excess diethylammonium salt by adding ether. Excess ethoxide must be avoided. After washing with chloroform, to remove the starting material, elemental analyses obtained are in fair agreement with the formula $Na^+Et_2NN_2O_2^-$. Found: C, 29.04; H, 6.26; N, 25.09. Calcd.: C ,30.47; H, 6.45; N, 27.10. The infrared spectrum of the sodium salt gives added support to the above structure. The absorption in the product attributed to $N^{\oplus}H_2$ vibrations (2800 to 2500, 1571, 1510, 807 cm.$^{-1}$) have disappeared. By comparing the spectra of the three compounds listed in Table I, it can be shown that the absorptions in the anion, $Et_2N\ N_2O_2^-$ (exclusive of the alkyl group absorptions) occur at 1187–1155, 1131, 973 and 809 in the diethyl ammonium salt and at 1225–1210, 1129, 965 and 872 in the sodium salt. The N–O stretching frequencies in these salts occur at 1187 to 1155 cm.$^{-1}$ and at 1225 to 1210 cm.$^{-1}$, being lowered in the diethylammonium salt through hydrogen bonding. The absorption at 1129 and 1131 cm.$^{-1}$ is tentatively assigned to the N–N stretching frequency. This absorption is not affected by hydrogen bonding and occurs at nearly the same place in the nitrosohydroxylamine sulfonates.[4]

Structures for the anion which involve NO_2^- or NO_3^- can be eliminated by comparing the spectra of the anion with reported[11] absorptions for these species.

The infrared spectra of chloroform solutions of the diethylammonium salt were investigated for there is evidence of decomposition when the product is recrystallized from concentrated solutions. The spectra is partly masked by solvent but that which is not is essentially unchanged. The N–O and N–N stretching frequencies are identical with those obtained in Nujol mulls. The absorption in the anion at 973 cm.$^{-1}$ is shifted slightly to 960 cm.$^{-1}$. Concentrations of the product as low as 1% by weight in chloroform were investigated and even in these dilute solutions the anion is intact.

The following scheme is proposed for the reaction leading to the formation of $Et_2NH_2^+Et_2N_2O_2^-$. In the absence of kinetic data this should be regarded as speculative.



$$Et_2NH + N_2O_2 \longrightarrow [Et_2\overset{H}{\overset{|}{N}}—N_2O_2] \xrightarrow{Et_2NH} Et_2NH_2^+Et_2^-NN_2O_2^-$$

The second molecule of amine removes a proton from the proposed intermediate for the hydrogen attached to the quaternary nitrogen is acidic. A compound similar to the proposed intermediate in the above reaction scheme is the product of the reaction when sulfite is the donor, *i.e.*, $O_3SN_2O_2^=$.

The problem of whether the nitric oxide molecule dimer adds base or whether nitric oxide adds base and then reacts with another nitric oxide molecule cannot be rigorously established at this time. The reaction between sulfite ion and nitric oxide is reported to be first order in nitric oxide,[12] however, it appears that the rate-controlling step in this work was the absorption of gaseous nitric oxide by the solution. We have found that the speed of this reaction is greatly dependent upon mixing.[13]

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(10) E. A. V. Ebsworth and N. V. Sheppard, *Spectrochim. Acta*, **13**, 261 (1959).

(11) D. J. Millen and D. Watson, *J. Chem. Soc.*, 1369 (1957).

(12) E. Terres and H. Lichti, *Z. angew. Chem.*, **47**, 511 (1934).

(13) NOTE ADDED IN PROOF.—The reaction of amines with nitric oxide to produce nitrosamines is the subject of two recent patents: Olin Matheson Chemical Corp., Brit., 772,331, April 10, 1957, E. I. du Pont de Nemours and Co., Belg., 1,171,532 Jan. 27, 1959, which have just come to our attention. White solids were obtained as intermediates in nitrosamine formation in the latter patent but the correct structure was not determined for the solids.