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Reduction of Nitric Oxide by Hydroxylamine. 2. Reactions of the Alkylated Hydroxylamines[1,2]

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Received September 19, 1985

The reactions between NO and the hydroxylamines CH_3NHOH, NH_2OCH_3, and CH_3NHOCH_3 proceed by N-bound H atom abstraction to form HNO. In the case of the dialkyl compounds $(CH_3)_2NOH$ and $(C_2H_5)_2NOH$, abstraction occurs at the α-carbon. The reaction is inhibited by O-methylation since no reactive anion can form. The ratio of reactivities of NH_2O^- to NH_2OH is determined to be at least 3.38×10^5. In the reaction between NO and CH_3NHOH, unlike that with NH_2OH, a stable nitrosohydroxylamine product remains in solution and does not release N_2O. Release of N_2 product in this case is delayed, an observation that is interpreted in terms of an intermediate *N*-nitrosomethylamine species on the pathway of reduction of HNO. Release of N_2 from this species is facilitated by Cl^- with formation of CH_3Cl. The N_2O product of reaction with the *N,O*- and *N,N*-dialkyl compounds arises largely from HNO dimerization, even at very high pH, indicating formation of stable nitrosohydroxylamine products. In the latter case an apparent competition with a nitrone-forming reaction occurs, leading to further reduction of NO to NO^-.

In an accompanying paper[2] we have reported kinetic studies of the reduction of nitric oxide by hydroxylamine, in which the active reductant species has been shown to be the anion NH_2O^- and the rate-determining step to be N-bound hydrogen atom abstraction by NO. In this paper we present the results of studies of the reaction between nitric oxide and several alkylated hydroxylamines, carried out in an effort to achieve further elucidation of the underlying mechanistic processes at work in this reaction system.

Experimental Section

N-Methyl-, *O*-methyl-, *N,N*-dimethyl-, *N,O*-dimethyl-, and *N,N*-diethylhydroxylamine hydrochloride salts (Aldrich) were employed without further purification. Kinetic studies were carried out as described in the accompanying paper;[2] alkylhydroxylamine concentrations were determined by weight. Nitrogen atom mass balances for the *N*-methylhydroxylamine–NO reaction were carried out by using a combination of GC analysis and UV spectrophotometry (Cary 14). $K_2Ni(CN)_4$ for use as a diagnostic for NO^-[3] was synthesized by the reaction of $NiSO_4$ with KCN and twice recrystallized from water.[4] The concentration of $NiNO(CN)_3^{2-}$ in solution was determined by optical density measurement at $\lambda = 498$ nm, employing the value $\epsilon = 427$ M^{-1} cm^{-1}.[5]

Tracer experiments were conducted employing ^{15}NO (99% ^{15}N, Stohler); isotopic analyses were carried out on an AEI MS-30 mass spectrometer.[6] Separation of N_2–N_2O–NO gas mixtures for mass spectrometric analysis was carried out by first holding N_2O and NO at 77 K while N_2 was collected by Toepler pump, followed by repeated bulb-to-bulb distillations through a spiral trap held at 113 K (2-methylbutane).

Results

N-Methylhydroxylamine. The kinetics of this reaction were followed under pseudo-first-order conditions, by measurement of the rate of disappearance of NO at 25.0 °C and ionic strength $I = 1.5$ M. Good linear first-order plots were obtained. As seen in Table I and Figure 1, only a very small amount of N_2O is observed among the products, and N_2 product is released slowly at pH 12.7. Further experiments at this pH showed that the yield of N_2 at a fixed time (45 min) is virtually independent of the initial reactant ratio. Table II and Figure 2 show that at the lower pH of 11.4 the rate of release of N_2 is more comparable to the rate of consumption of NO. In these cases and all others observed, no more than half of the nitrogen atoms consumed from NO can be accounted for among the gas products at reaction completion. However, the UV spectra of the reactant solutions revealed an absorption at $\lambda_{max} = 247$ nm, indicating formation of *N*-methyl-*N*-nitrosohydroxylamine (molar absorption coefficient 5600 M^{-1} cm^{-1}.)[7] Unlike the case of unsubstituted hydroxylamine, in which a nitrosohydroxylamine intermediate decays rapidly to form N_2O, the nitrogen of NO consumed by nitrosylation of the *N*-methyl compound does not return to the gas phase. Since N_2O appears in increasing amounts with decreasing pH, we assume its origin to lie entirely in the HNO dimerization reaction (eq 4).

Table I. Reaction of *N*-Methylhydroxylamine with NO, Experiment 1[a]

time, min	P_{NO}, torr	P_{N_2}, torr	P_{N_2O}, torr	"yield"[b]
0	69.0	0	0	0
10	27.3	2.95	0.026	0.072
20	10.3	4.33	0.065	0.076
30	4.21	5.36	0.063	0.085
45	0	7.60	0.074	0.113
60	0	8.09	0.076	0.120
400	0	21.9	0.079	0.321
1850	0	30.3		0.442
4140	0	31.4	0.085	0.458

[a] Conditions: $[CH_3NHOH\cdot HCl]_0 = 0.313$ M; $[OH^-]_0 = 0.609$ M; pH 12.7; $(n_{CH_3NHOH\cdot HCl}/n_{NO})_0 = 7.8$; $I = 1.5$ M; $t = 25.0$ °C. [b] "Yield" = $(n_{N_2} + 2n_{N_2O})/\Delta n_{NO}$.

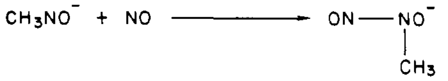
Table II. Reaction of CH_3NHOH with NO, Experiment 4[a]

time, min	P_{NO}, torr	P_{N_2}, torr	P_{N_2O}, torr	"yield"[b]
0	73.0	0	0	0
15	55.2	3.23	0.346	0.221
30	38.9	10.6	0.646	0.349
45	34.3	12.6	0.865	0.371
75	22.2	19.2	1.20	0.426
120	10.6	25.3	1.50	0.454
180	0	32.0	1.62	0.484
1200	0	32.0	1.67	0.485

[a] Conditions: $[CH_3NHOH\cdot HCl]_0 = 0.313$ M; $[OH^-]_0 = 0.344$ M; pH 11.4; $(n_{CH_3NHOH\cdot HCl}/n_{NO})_0 = 7.3$; $I = 1.5$ M; $t = 25$ °C. [b] "Yield" = $(n_{N_2} + 2n_{N_2O})/\Delta n_{NO}$.

The observations described above are consistent with the overall mechanism shown in eq 1–4. Major differences from the NO–NH₂OH reaction are that (1) no N_2O is released at step 2 and

$$NO + CH_3NHO^- \longrightarrow HNO + CH_3NO^- \quad (1)$$



$$CH_3NO^- + NO \longrightarrow ON{-}\underset{\displaystyle CH_3}{\underset{|}{N}}O^- \quad (2)$$

$$HNO + CH_3NHO^- \rightarrow N_2 + CH_3OH + OH^- \quad (3)$$

$$HNO + HNO \longrightarrow N_2O + H_2O \quad (4)$$

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[1] Research supported by the National Science Foundation, Grant No. 78-24176.

[2] Part 1: Bonner, F. T.; Wang, N.-Y. *Inorg. Chem.*, companion paper in this issue.

[3] Bonner, F. T.; Akhtar, M. J. *Inorg. Chem.* **1981**, *20*, 3155.

[4] Fernelius, W. C., Ed. *Inorganic Synthesis II*; McGraw Hill: New York, 1946, p 227.

[5] Veprek-Siska, J.; Lunak, S. *Collect. Czech. Chem. Commun.* **1972**, *37*, 3846.

[6] Stony Brook Mass Spectrometry Facility.

[7] Kortüm, G.; Finck, B. *Z. Phys. Chem., Abt. B* **1940**, *48*, 32.

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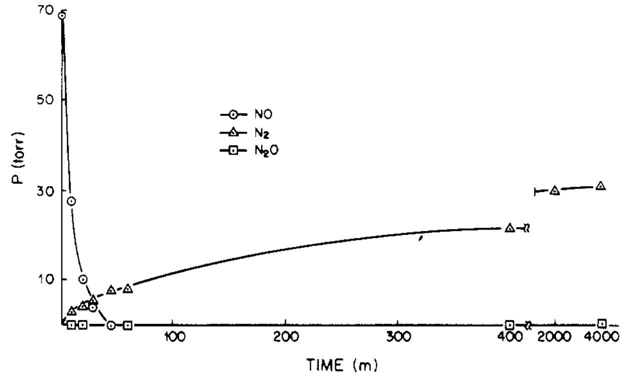


Figure 1. Pressures of NO, N_2, and N_2O at various times, experiment 1 (Table I).

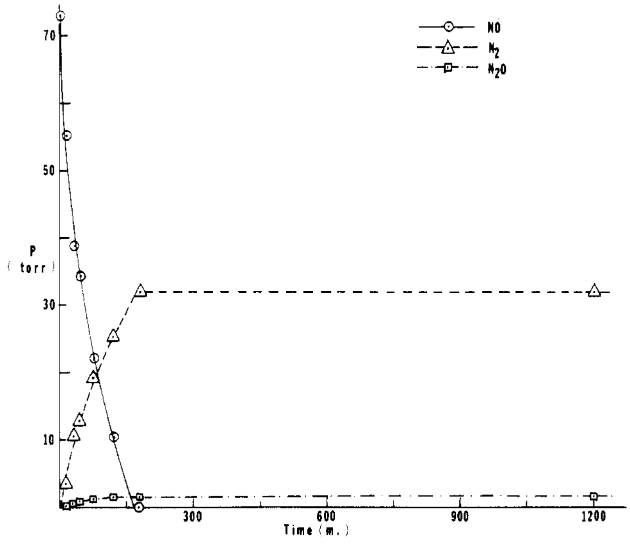


Figure 2. Pressures of NO, N_2, and N_2O at various times, experiment 4 (Table II).

Table III. Reaction of CH_3NHOH with NO[a]

expt no.	$[OH^-]_0$, M	pH	10^4k_{obsd}, s^{-1}	n_{N_2}/n_{N_2O}	X,[b] %
1	0.609	12.7	15.6	370	0.54
2	0.402		4.38	530	0.38
3	0.360		2.85	37.4	5.08
4	0.344	11.4	2.60	19.1	9.46
5[c]		11.0	1.77	74.6	2.61
6[c]		10.6	1.19	57.5	3.36
7[c]		10.5	1.02	23.6	7.80

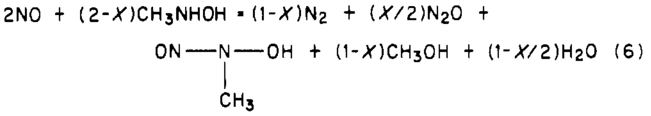
[a] Conditions: $[CH_3NHOH{\cdot}HCl]_0 = 0.313$ M; $I = 1.5$ M; $t = 25.0$ °C. [b] Percent dimerization of HNO. [c] Phosphate buffer.

(2) N_2 is released slowly, from some additional intermediate species, at step 3. The quantity designated "yield" in Tables I and II, a measure of the extent of conversion of reactant NO to gas products, is defined in relation to the mechanism in eq 1–4.

Additional kinetic runs are reported in Table III. The steep dependence of rate upon pH is reminiscent of the behavior of NH_2OH[2] and suggests that the O-deprotonated form CH_3HNO^- is the active reductant as postulated in eq 1. The values of pK_a for NH_3OH^+ and $CH_3NH_2OH^+$ are almost identical (5.97 and 5.96 at 25 °C);[8] hence, we assume that pK_a for CH_3NHOH is closely similar to the value of 13.70 observed for NH_2OH at 25 °C.[2] On this assumption, $[CH_3NHO^-]$ concentrations for experiments 1–4, and corresponding values of k_2 for the rate law (eq 5) have been calculated, as shown in Table IV. The level of consistency of k_2 values obtained in this way shows that the value employed for pK_a is reasonable and substantiates our assumption that reaction 1 is rate-determining. This reaction is also seen to be substantially faster ($k_2 = 1.75 \times 10^{-2}\ M^{-1}\ s^{-1}$) than that between NO and NH_2O^- ($k_2 = 6.68 \times 10^{-3}\ M^{-1}\ s^{-1}$)[2] at 25 °C.

$$-dP_{NO}/dt = k_2[CH_3NHO^-]P_{NO} \qquad (5)$$

The quantity X in Table III is the percentage of HNO formed in reaction 1 that is diverted to N_2O by dimerization, calculated from observed product ratios n_{N_2}/n_{N_2O} at reaction completion in the overall stoichiometry for eq 1–4, as expressed in eq 6. As



$$2NO + (2-X)CH_3NHOH = (1-X)N_2 + (X/2)N_2O + ON{-}N(CH_3){-}OH + (1-X)CH_3OH + (1-X/2)H_2O \qquad (6)$$

in the case of NH_2OH, X increases with decreasing pH; the reason for the apparent discontinuity between unbuffered and phosphate-buffered systems is not known. The percentage of dimerization in the presence of the *N*-methyl derivative is generally smaller than in the case of hydroxylamine under corresponding conditions (e.g. 0.54 vs. 2.2% at pH 12.7). When these values of X (Table III) were used to calculate the distribution of products at reaction completion, the results were reasonably consistent with experimental values, including the yields of *N*-methyl-*N*-nitrosohydroxylamine determined by spectrophotometry.

An experiment at pH ca. 11.0 (unbuffered) was carried out with $Ni(CN)_4^{2-}$ added to confirm the presence of HNO intermediate by means of the known displacement reaction, eq 7.[3] The

$$Ni(CN)_4^{2-} + NO^- \rightarrow NiNO(CN)_3^{2-} + CN^- \qquad (7)$$

violet color of $NiNO(CN)_3^{2-}$ was observed, and the concentration of this species was determined spectrophotometrically at λ = 498 nm. Since this pH is well below the level at which detectable nitrosyl complex forms by NH_2OH insertion,[3] we interpret this as a conclusively positive test for HNO. Product distribution measurements at completion showed that 9.8% of the intermediate was trapped by $Ni(CN)_4^{2-}$, 29.7% dimerized to N_2O, and 60.5% was reduced to N_2. An anomalously high value for the concentration of *N*-methyl-*N*-nitrosohydroxylamine was obtained by absorption measurement at λ = 247 nm, probably due to the presence of the nickel complex. In a similar experiment at the higher pH of 12.7 no N_2O was detected, and the quantity of N_2 produced corresponded to just 67% of expected HNO, presumably indicating 33% trapping by $Ni(CN)_4^{2-}$. However, in this case the expected violet color of the nitrosyl complex did not appear, for reasons not clear to us. (A transient appearance of violet color was observed in one qualitative preliminary experiment.) Anomalously high absorption at 247 nm was also observed at pH 12.7, to a significantly greater extent than at pH 11.

As a final, additional check on the proposed mechanism of eq 1–4, tracer experiments were carried out, employing 99% ^{15}NO gas, at conditions similar to those of experiments 1 and 3. The mechanism predicts that the products should consist largely of $^{15}N^{14}N$ (mass 29) and $^{15}N^{15}N^{16}O$ (mass 46), and these expectations were realized. The mass spectrometer also revealed strong peaks in our separated N_2O samples at masses 50 and 52, in approximately 3 to 1 ratio, which we have identified to be due to CH_3Cl. This new gas product, which had not been detected by gas chromatography, was formed in greater amount at the lower of the two pH conditions examined.

***O*-Methylhydroxylamine.** The reaction between NH_2OCH_3 and NO was found to be extremely slow: at pH ca. 15.2 ($[NH_2OCH_3{\cdot}HCl]_0 = 0.313$ M, $[OH^-]_0 = 1.82$ M) and 25 °C under pseudo-first-order conditions ($n_{CH_3ONH_2}/n_{NO} = 7.4$), a linear first-order plot was obtained over 1.5 half-lives, with $k_{obsd} = 1.86 \times 10^{-6}\ s^{-1}$. The gas products are N_2 and N_2O in a ratio of 1.08, similar to the case of unsubstituted hydroxylamine. The mechanism shown in eq 8–10 is proposed.

$$NH_2OCH_3 + NO \rightarrow NHOCH_3 + HNO \qquad (8)$$

$$NHOCH_3 + NO \rightarrow ON\text{-}NHOCH_3 \rightarrow N_2O + CH_3OH \qquad (9)$$

$$HNO + NH_2OCH_3 \rightarrow N_2 + CH_3OH + H_2O \qquad (10)$$

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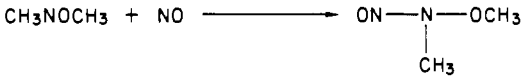
[8] Bissot, T. C.; Parry, R. W.; Campbell, D. H. *J. Am. Chem. Soc.* **1957**, *79*, 796.

Table IV. Second-Order Rate Constants, Experiments 1–4

expt no.	$[OH^-]_0$, M	10^4k_{obsd}, s^{-1}	$10^2[CH_3NHO^-]$, M	10^2k_2, $M^{-1}\ s^{-1}$
1	0.609	15.6	8.98	1.74
2	0.402	4.38	3.15	1.39
3	0.360	2.85	1.70	1.68
4	0.344	2.53	1.15	2.20
				1.75 ± 0.34 (av)

***N,O*-Dimethylhydroxylamine.** The reaction of CH_3NHOCH_3 with NO was found to be much slower than that of either NH_2OH or CH_3NHOH but faster than that of NH_2OCH_3: at pH ca. 14.8 ($[CH_3NHOCH_3{\cdot}HCl]_0 = 0.313$ M, $[OH^-]_0 = 1.01$ M) at 25 °C, with an initial reactant ratio of 7.2, a linear pseudo-first-order plot was obtained over 4 half-lives, with $k_{obsd} = 3.32 \times 10^{-5}\ s^{-1}$. The product gases consisted of N_2 and N_2O in approximately equal proportions; CH_3Cl was identified as an additional gas product by mass spectrometry, and the gas phase included a substantial vapor pressure of the reactant CH_3NHOCH_3. A ^{15}N tracer experiment showed that in product N_2 one nitrogen comes from each reactant source but that both nitrogen atoms in N_2O come from NO. As in the case of CH_3NHOH, HNO dimerization thus appears to be the sole source of N_2O. Dimerization accounts for 66% of HNO at surprisingly high pH in this case, compared with only 0.54% at pH 12.7 in the case of CH_3NHOH. The mechanism proposed for the overall reaction is as follows:

$$CH_3NHOCH_3 + NO \longrightarrow CH_3NOCH_3 + HNO \qquad (11)$$



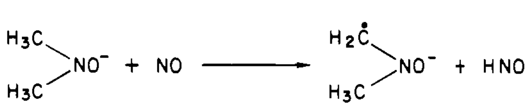
$$CH_3NOCH_3 + NO \longrightarrow ON{-}\underset{\displaystyle CH_3}{\underset{|}{N}}{-}OCH_3 \qquad (12)$$

$$HNO + CH_3NHOCH_3 \longrightarrow N_2 + 2CH_3OH \qquad (13)$$

$$HNO + HNO \longrightarrow N_2O + H_2O \qquad (4)$$

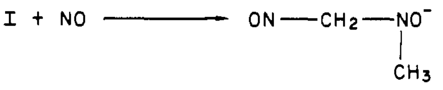
***N,N*-Dimethylhydroxylamine.** The reaction between $(CH_3)_2NOH$ and NO was studied at two different pH levels, as shown in Table V. Pseudo-first-order plots displayed upward curvature in all cases (apparent reaction orders with respect to NO lying in the range 1.30–1.45). The values of k_{obsd} given in Table V are based upon initial slopes. The observed decrease in rate with pH suggests that the reactive species involved is the anion $(CH_3)_2NO^-$. N_2 is a minor product relative to N_2O even at the higher pH level. The fact that only half of the nitrogen atoms from NO appear in the gas products at pH 13.4, and slightly more than half at the lower pH, suggests that a stable nitrosyl compound remains in solution. In the presence of $Ni(CN)_4^{2-}$ (experiment 9) the complex $NiNO(CN)_3^{2-}$ was observed, confirming the intermediacy of HNO;[3] the results of this experiment (including absorption at λ = 498 nm) show that 9.15% of HNO released is trapped by $Ni(CN)_4^{2-}$, 87.6% dimerized to N_2O, and 3.25% reduced to N_2, compared with 17.2% reduction in the absence of complex (experiment 8). Tracer experiments with ^{15}NO showed that $^{15}N^{15}NO$ (mass 46) is the exclusive form of N_2O produced at both pH levels and that the N_2 product at high pH contains one N atom from each reactant (mass 29). At the lower pH an abnormally high proportion of N_2 at mass 28 was observed and may indicate that some self-decomposition of $(CH_3)_2NOH$ occurred during the relatively long reaction time employed.

The results described above leave no doubt that HNO is intermediate, and in this case the only hydrogen atom available for abstraction by NO is at the α-carbon position:



(14)

I



$$I + NO \longrightarrow ON{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{N}}O^- \qquad (15)$$

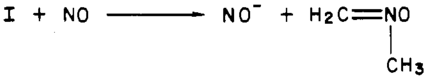
$$HNO + (CH_3)_2NOH \longrightarrow N_2 + 2CH_3OH \qquad (16)$$

$$HNO + HNO \longrightarrow N_2O + H_2O \qquad (4)$$

On the basis of this mechanism, the overall stoichiometry of the reaction will be given by eq 17, in which X represents the fraction

$$2NO + (2 - X)(CH_3)_2NOH = (1 - X)N_2 + (X/2)N_2O + ONCH_2N(CH_3)OH + 2(1 - X)CH_3OH + (X/2)H_2O \qquad (17)$$

of HNO molecules formed (eq 14) that undergo dimerization (eq 4). However, when values of X based on observed product ratios are used to calculate the molar quantities of N_2 and N_2O expected on the basis of eq 17, the calculated values are smaller than observed values (Table V) in all but one instance. To account for additional N_2 and N_2O, an additional source of HNO must be sought. Radical ion I, in addition to its ability to form a stable species by combining with NO (eq 15), may be subject to further electron loss to form a nitrone (II; eq 18) and additional NO^-,



$$I + NO \longrightarrow NO^- + H_2C{=}\underset{\displaystyle CH_3}{\underset{|}{N}}O \qquad (18)$$

II

the latter leading to additional N_2 and N_2O. If reactions 18 and 15 are assumed to compete in a 1 to 2 ratio, the overall stoichiometry of eq 19 is obtained. As shown in Table V, molar

$$3NO + (^7/_2 - X)(CH_3)_2NOH = XN_2O + 2(1 - X)N_2 + I + {}^1/_2II + 4(1 - X)CH_3OH + XH_2O \qquad (19)$$

quantities of gas products calculated on the basis of eq 19 are in close agreement with observed values at the lower pH level, lending plausibility to the assumption of a competition. If this interpretation is correct, the results indicate that reaction 18 becomes less competitive, in relation to eq 15, with increasing pH.

***N,N*-Diethylhydroxylamine.** A kinetic run was carried out for the reaction between $(C_2H_5)_2NOH$ and NO at pH ca. 14.0 and conditions otherwise similar to those of experiment 8 (Table V). The observed reaction behavior of the diethyl compound is closely similar to that of dimethylhydroxylamine on the basis of initial slope, although slower ($k_{obsd} = 1.87 \times 10^{-4}\ s^{-1}$). The mechanisms of these reactions are probably identical. The diethyl derivative shows 83% dimerization of HNO at pH ~14.0. Calculations similar to those described above support an assumption of competition between a radical association reaction and nitrone formation, as in eq 15 and 18, in somewhat less than a 2:1 ratio at pH 14.

Discussion

In extension of our studies of hydroxylamine,[2] these results confirm the generally greater reactivity of deprotonated hydroxylamines in comparison with their corresponding free bases.[9–11]

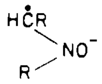
Table V. Reaction of $(CH_3)_2NOH$ with NO[a]

						$10^4\Delta n_{N_2}$[d]			$10^4\Delta n_{N_2O}$[d]		
							calcd			calcd	
expt no.	pH	10^4k_{obsd}, s^{-1}	n_{N_2}/n_{N_2O}	X,[b] %	$10^4\Delta n_{NO}$[c]	obsd	eq 17	eq 19	obsd	eq 17	eq 19
8	13.4	4.33	0.415	82.8	4.00	0.335	0.344	0.459	0.794	0.828	1.10
9[e]	13.4	4.32	0.074	87.6	4.84	0.091	0.079	0.105	1.23	1.06	1.41
10	12.0	1.62	0.061	97.0	3.93	0.075	0.059	0.079	1.24	0.95	1.27
11	11.8	1.03	0.020	99.0	4.25	0.028	0.021	0.028	1.38	1.05	1.40

[a] Conditions: $[(CH_3)_2NOH]_0 = 0.313$ M; $(n_{(CH_3)_2NOH}/n_{NO})_0 > 7$; $I = 1.5$ M; $t = 25.0$ °C. [b] Percent dimerization of HNO. [c] Moles of reactant consumed, at time ∞. [d] Moles of product produced, at time ∞. [e] $Ni(CN)_4^{2-} = 2.57 \times 10^{-3}$ M; 9.15% NO^- trapping observed.

In the case of *O*-methylhydroxylamine, no O-deprotonated form is available, and we assume that the measured value of k_{obsd}, 1.86 × 10^{-6} s^{-1} at $[NH_2OCH_3]$ = 0.313 M, pertains to reaction with free base. The second-order rate constant is thus 5.94 × 10^{-6} M^{-1} s^{-1} at 25 °C. The corresponding second-order rate constant for NH_2O^- is 6.68 × 10^{-3} M^{-1} s^{-1},[2] and the ratio of the reactivities of NH_2O^- and NH_2OCH_3 is therefore calculated to be 1125 to 1. Substitution by a methoxy group on nitrogen has been reported to weaken the N–H bond by nearly 42 kJ mol^{-1} and consequently to increase the reactivity of the H atom by a factor of more than 300.[12] We conclude that NH_2O^- is at least 3.38 × 10^5 times more reactive than NH_2OH toward NO. Although free base NH_2OH is presumably subject to oxidation by NO, the rate is too insignificant to be observed as a second term in the rate law, even at the lowest pH levels explored (ref 2). Introduction of a methyl group at nitrogen weakens the remaining N–H bond by about 46.0 kJ mol^{-1},[12] consistent with our observation that the reactivity of CH_3NHO^- (k_2 = 1.75 × 10^{-2} M^{-1} s^{-1}) is substantially greater than that of NH_2O^- toward NO.

In the case of the *N*,*N*-dialkylhydroxylamines, our results strongly suggest that NO reacts by C-bound H atom abstraction. In the reaction of amines containing both C–H and N–H bonds with *tert*-butoxy radicals, it has been suggested that C–H abstraction is the dominant process.[13,14] Radical ions of the type postulated here

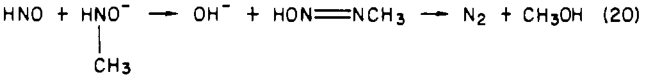


would exhibit properties different from those of type $R\dot{N}O^-$, and the dialkylhydroxylamines are unique in reaction product stoichiometry and in the nonlinearity of their pseudo-first-order kinetic plots. The stoichiometric feature can be explained by our assumption of a competition between combination of the radical with NO to form a stable molecule and its reaction with NO to form NO^-. That is, the observed increase of N_2 and N_2O products requires more than one HNO molecule to be formed per two NO molecules consumed (contrast eq 1–4 with eq 14–18).

As observed in the case of the radical ion $\cdot NHO^-$,[2] the radical ions produced in reactions of NO with *N*-alkylhydroxylamines combine preferentially with NO rather than with one another. In the cases of *N*-methylhydroxylamine and *N*,*N*-dimethylhydroxylamine stable molecules result, in contrast to *N*-nitrosohydroxylamine, which undergoes rapid dehydration to form N_2O.

Competition between reduction and dimerization of the reactive intermediate species HNO is dependent upon several factors. Not surprisingly, it has been observed that a greater percentage of HNO goes to form N_2O when the hydroxylamine concentration is reduced under otherwise identical conditions. The competition also depends upon the reducing power of the reductant species present. Substitution of an alkyl group at nitrogen and O-deprotonation should both enhance the availability of the nitrogen lone pair and increase the reactivity of the reducing agent. Our observations of a percentage of dimerization at pH 12.7 that is lower in the presence of *N*-methylhydroxylamine than of hydroxylamine, and of generally increasing percentages of dimerization with decreasing pH, are consistent with this expectation. Although the reducing powers of *N*,*N*-dialkyl derivatives should be stronger than those of *N*-alkylhydroxylamines, very high dimerization percentages (ca. 83%) were observed for both the *N*,*N*-dimethyl and *N*,*N*-diethyl compounds at high pH. In these cases the values of pK_a are unknown to us, and the degrees of O-deprotonation under the conditions of observation are uncertain; steric effects around the nitrogen center may also be an important factor.

The production of N_2 in the reaction between CH_3NHOH and NO has been observed to occur very slowly at elevated pH (see e.g. Figure 1), although N_2 is predominant over N_2O product at reaction completion. This can be interpreted in terms of an HNO reduction pathway involving an additional intermediate species, the tautomeric form of *N*-nitrosomethylamine, as shown in eq 20.



$$HNO + \underset{\displaystyle CH_3}{\underset{|}{HNO^-}} \rightarrow OH^- + HON{=}NCH_3 \rightarrow N_2 + CH_3OH \quad (20)$$

In the case of hydroxylamine itself, in which prompt N_2 release is observed, the final step is characterized by the ease of release of OH^- or H_2O (eq 21). The apparent stabilization of the

$$HNO + NH_2O^- \rightarrow OH^- + HON{=}NH \rightarrow N_2 + H_2O \quad (21)$$

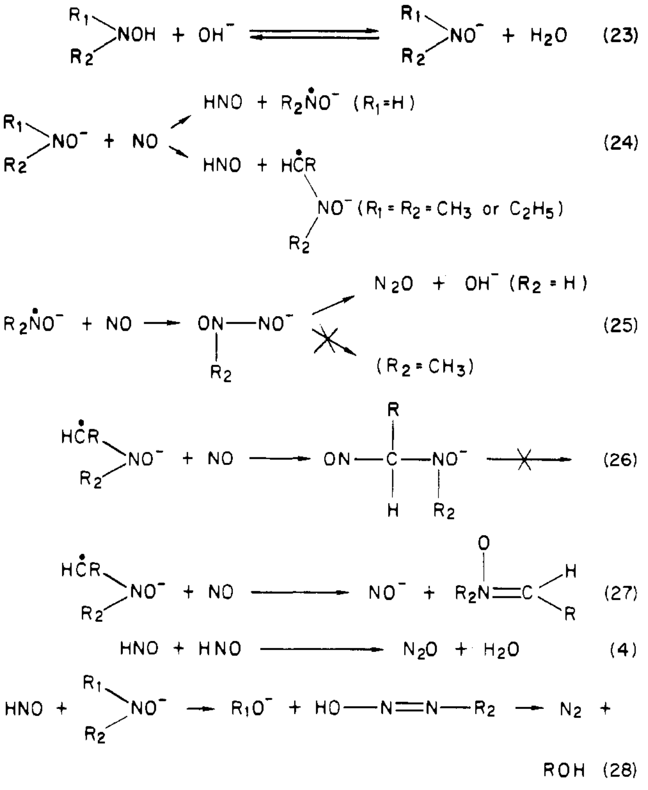
intermediate in the case of *N*-methylhydroxylamine is most probably due to the relative difficulty of release of CH_3OH (eq 20). For the *N*,*N*-dialkyl compounds, release of CH_3O^- would be required in the first step of this mechanism, and we assume that the difficulty of this process, in combination with steric hindrance, may inhibit formation of the intermediate, accounting for the overwhelming predominance of dimerization.

Finally, the release of N_2 from the intermediate proposed in eq 20 can be assisted by the presence of chloride, as shown in eq 22. This appears to be the most plausible explanation for our

$$HON{=}NCH_3 + Cl^- \rightarrow CH_3Cl + N_2 + OH^- \quad (22)$$

observation of CH_3Cl as product in the reactions of NO with *N*-methyl and *N*,*O*-dimethyl compounds and its absence in the *N*,*N*-dialkyl cases. In a series of experiments with CH_3NHOH, Cl^- concentration was increased with decreasing pH to maintain ionic strength, and increasing quantities of CH_3Cl product were observed. Similarly, our observation of slower release of N_2 at higher than at lower pH (Figures 1 and 2) can be explained as reflecting Cl^- catalysis, since a greater Cl^- concentration was present at the lower pH level.

In summary, the results of this study support the following general mechanistic scheme for the reaction between nitric oxide and the hydroxylamines:



Acknowledgment. We are grateful to Dr. Mohammad Javaid Akhtar for assistance with mass spectrometry.

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