omissions in the literature. When different valus of the same property were reasonably close, they were averaged. Otherwise a selection was based, if possible, on similar data for similar molecules. For these reasons, the values of Table I must be regarded as approximate, but probably accurate enough to reveal the general effects being studied.

In order to demonstrate the validity of this statement, the bond energies or atomization energies of all gaseous molecules of compounds of these elements in these lower oxidation states for which basic data could be found were calculated according to the theory of polar covalence. This is of course a somewhat circular procedure in that experimental bond energies were used to evaluate the electronegativities. However, there are additional compounds in the table, and in any event, the data are shown to be reasonably self-consistent. Where basic data are accurately known, the theory of polar covalence appears capable of producing calculated bond energies within about 1% of the experimental values. From this viewpoint, the agreement in Table II is not ideally satisfactory. However, if four of the compounds wherein the difference exceeds 10% are omitted, the average difference for the remaining 55 compounds is less than 2.0%. It must be recognized, furthermore, that a difference between calculated and experimental bond energy here may indicate experimental difficulty rather than inadequacy in the method of calculation.

Remember that these electronegativity values are based on the assumption that the inert pair affects only the electronegativity, the homonuclear bond energy and radius remaining unchanged from those of the atom in its maximum oxidation state. This assumption may not be exactly true. When the bond energies for the lower oxidation states were calculated by using the electronegativity corresponding to the highest state, in every example the calculated value was substantially smaller than the experimental value. Assuming no very significant change in nonpolar covalent radius, the larger bond energy in the lower oxidation state must signify either a greatly increased homonuclear bond energy of the metal or a decreased electronegativity. There seems to be no way by which the inert pair could possibly cause an increase in homonuclear energy, assuming its principal effect to be reduction of the effective nuclear charge, on which the homonuclear bond energy largely depends. On the other hand, by nuclear screening, the inert pair could easily reduce the electronegativity, thus causing the bond to be more polar and correspondingly stronger.

The question remaining is whether the homonuclear bond energy might also be reduced, making necessary a still larger decrease in electronegativity to compensate by larger ionic energy for a reduced covalent energy. However, since the homonuclear energy is only one of several factors determining the bond energy and since most of the compounds under study are fairly or highly polar, diminishing the importance of the covalent contribution, it seems reasonable to suppose that the principal effect of the inert pair, aside from its effects both in the molecule and in the solid state, is to reduce the electronegativity. In every example in Table I, this is indeed the result, as reinforced by the data of Table II. The lone-pair effect on electronegativity becomes less as the atomic number within a group increases. The differences in electronegativity between oxidation states III and I are as follows: Ga, 1.56; In, 1.43; Tl, 1.26. The differences between oxidation states IV and II are as follows: Ge, 2.02; Sn, 0.81; Pb, 0.37. In the halides, the partial charges in the lower oxidation states are usually more than doubled as a result of the reduction in electronegativity.

As a consequence of this increase in bond polarity, thallium(I) halides resemble the alkali-metal halides, as thallium hydroxide, TlOH, resembles the alkali-metal hydroxides. Similarly, lead(II) compounds are much more polar and more stable than inorganic lead(IV) compounds. In general, the nuclear screening by inert-pair electrons, largely by reducing the electronegativity, accounts for the notable differences between lower and higher oxidation states.

Registry No. Be, 7440-41-7; Ca, 7440-70-2; B, 7440-42-8; Al, 7429-90-5; Ga, 7440-55-3; In, 7440-74-6; Tl, 7440-28-0; Si, 7440-21-3; Ge, 7440-56-4; Sn, 7440-31-5; Pb, 7439-92-1.

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Reduction of Nitric Oxide by Hydroxylamine. 1. Kinetics and Mechanism[1]

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The reaction of nitric oxide with hydroxylamine conforms to the rate law $-dP_{NO}/dt = k_2[NH_2O^-]P_{NO}$ in the pH range 7.29–13.14, confirming the rate-determining abstraction of an N-bound H atom by NO. Measured kinetic quantities: $k_2 = 6.68 \times 10^{-3}$ M^{-1} s^{-1} at 25 °C; $\Delta H^{\ddagger} = 29.6$ kJ mol^{-1}; $\Delta S^{\ddagger} = -189$ J K^{-1} mol^{-1}. Thermodynamic values have been obtained for the pK_a of NH_2OH at several temperatures; ΔH of dissociation = 55.29 kJ mol^{-1}. The presence of trace amounts of O_2 in the NO–NH_2OH reaction system catalyzes the reaction and leads to a reduced molar product ratio n_{N_2}/n_{N_2O}, effects that are ascribed at least in part to reactive N_2O_3. The difference in reactivity between the NO^- intermediate formed in this reaction and that produced in trioxodinitrate decomposition is discussed.

The reaction between nitric oxide and aqueous alkaline hydroxylamine, first noted by Benson et al.,[2] proceeds in 0.5 M NaOH solution according to the stoichiometry of eq 1.[3] Nitrogen-15 tracer evidence shows that one atom of NO origin appears in each of the product molecules N_2 and N_2O at pH 13.[3,4]

$$2NO + 2NH_2OH = N_2 + N_2O + 3H_2O \qquad (1)$$

The product ratio n_{N_2}/n_{N_2O} declines with decreasing pH, an effect tracer studies have shown to be caused by increasing competition between reduction (eq 4) and dimerization (eq 5) of the intermediate nitrosyl hydride (HNO) in the mechanism of eq 2–5.[4]

$$NO + NH_2OH \rightarrow HNO + NHOH \qquad (2)$$

$$NO + NHOH \rightarrow [ON\text{–}NHOH] \rightarrow N_2O + H_2O \qquad (3)$$

$$HNO + NH_2OH \rightarrow N_2 + 2H_2O \qquad (4)$$

$$HNO + HNO \rightarrow N_2O + H_2O \qquad (5)$$

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

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In particular, reactions conducted with $^{15}N^{18}O$ produce N_2O of masses 45 and 47 (eq 3) at pH ≥ 13, but N_2O of mass 48 (eq 5) appears only at pH <13, in increasing proportions with decreasing pH.[4] While it appears probable that HNO is formed by abstraction of an N-bound H atom (eq 2), it is not known whether the reactive hydroxylamino species is the molecule NH_2OH or the anion NH_2O^-.

Nitrosyl hydride also occurs as intermediate in the reversible self-decomposition of monoprotonated trioxodinitrate[5-7] (eq 6).

$$HN_2O_3^- \rightleftarrows HNO + NO_2^- \tag{6}$$

The HNO from this source exhibits chemical properties different from those observed for the species released in the NO–NH_2OH reaction, with regard to the balance between dimerization (eq 5) and reduction (eq 4) under comparable conditions at pH 8[4] and also to NO^- trapping by tetracyanonickelate[8] (eq 7).

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

Previous kinetic measurements[4] for the nitric oxide–hydroxylamine reaction were valid for comparative purposes only, because the effects of mass transport between gas and solution phases were not eliminated; in this paper we present kinetic results in which a mechanical vibration method[9,10] has been employed to assure elimination of such effects. We also report an apparent catalysis brought about by minor amounts of O_2, associated with changes in the reaction product stoichiometry.

Experimental Section

Reagents. Stock solutions of reagent grade $NH_2OH{\cdot}HCl$ were prepared and stored under a continuous flow of O_2-free He, with EDTA added at the 10^{-4} M level. Concentrations determined by titration[11] at 3-month intervals were invariably found in agreement (±1%) with initial values. Free base NH_2OH was synthesized by the method of Hurd.[12] Commerical NO was purified by repeated distillation from 5-Å molecular sieve at 113 K (2-methylbutane) to 77 K followed by pumping; impurities were reduced below mass spectrometric detection limits. Commercial CF_4 was deoxygenated by repeated passage over a reduced BASF R3-11 catalyst bed.

Kinetic Studies. Solutions were prepared by mixing separately deaerated quantities of KOH and $NH_2OH{\cdot}HCl$ solutions, plus (variously) sodium chloride or phosphate, in proportions designed to provide the desired levels of concentration, pH, and ionic strength (usually 1.5 M). An aliquot of each solution was held for pH measurement, and 10.0 mL was introduced to a reaction vessel by syringe injection at standard taper 1, followed by closing of stopcock B (see ref 9, Figure 1). The solution was outgassed by pumping at 195 K (2×) and at 77 K (1×), and the vessel was then mounted on a Chemapec Model E1 vibromixer and connected to the vacuum line via a flexible glass coil attached at standard taper 2. Constant temperature was maintained by rapid circulation of temperature-controlled water. A CF_4–NO mixture of known composition was introduced through three-way stopcock A,[9] with simultaneous initiation of vibration. The total initial pressure ($P_{CF_4} + P_{NO} + P_{H_2O}$) was then measured manometrically, excess reactant gas returned to storage, and the manifold pumped in preparation for sampling. At measured time intervals the gas phase was sampled by expansion into the side arm at stopcock A[9] during a momentary interruption of vibration. Each sample was transferred via a spiral drying trap (195 K) to a storage bulb by Toepler pump or by condensation at 77 K. (In the latter case no N_2 is collected.) Samples were analyzed by gas chromatography, employing direct vacuum system injection.[13] Partial pressures and molar quantities of NO, N_2, and N_2O, based on CF_4 as reference, were then calculated for each sample.[9]

Table I. pK_a Values for NH_2OH

t, °C	pK_a	t, °C	pK_a
10.0	14.21 ± 0.03	20.0	13.83 ± 0.06
15.0	14.01 ± 0.06	25.0	13.70 ± 0.06

Typical experimental conditions for a kinetic measurement (experiment 4, Table II): $[NH_2OH{\cdot}HCl]_0 = 0.313$ M; $[NaOH]_0 = 0.464$ M; $(P_{NO})_0 = 90.4$ torr; pH 12.45; $t = 25$ °C; $(n_{NH_2OH}/n_{NO})_0 = 6.3$; $I = 1.5$ M; reactant solution volume 10.0 mL; reactant gas volume 108.8 mL; sample volume 3.25 mL.

Acid Dissociation Constant of NH_2OH. Spectrophotometric measurements were carried out over the range 250–220 nm (Cary 14). Two optical cells of identical path length (7.19 cm) were employed, the reference cell containing solvent alone. For each measurement, 5.0 mL of 1.72×10^{-3} M $NH_2OH{\cdot}HCl$ was added anaerobically to 40.0 mL of NaOH solution of known concentration (0.2002–2.423 M). Readings were taken at 2-nm intervals between 240 and 230 nm, and optical densities were determined, with appropriate calibration, at 10, 15, 20, and 25 °C.

Relationship of $[OH^-]$ to pH for Hydroxylamine in Buffer Solution Systems. The salts $NaClO_4$, Na_2SO_4, and $Na_3Fe(CN_6)$ were employed to establish solutions with ionic environments similar to those of the buffers. Solutions containing these salts, plus NaCl (and in some cases NaOH), were prepared in proportions such that the concentrations of Na^+, Cl^-, ClO_4^-, SO_4^{2-}, and $Fe(CN)_6^{3-}$ corresponded to those of Na^+, Cl^-, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} at the pH value measured for each kinetic run. The pH of this solution was measured, an aliquot of NaOH of known concentration added (or HCl if OH^- had already been added), the solution mixed well, and the pH measured again. Further additions and pH measurements were made until the pH value of the buffer of interest was encompassed within the range of measurement. Assuming identical values of γ_{OH^-} for simulated and actual systems, concentrations under the conditions of kinetic measurements were then read from a plot of measured $[OH^-]$ vs. measured pH.

Results

Acid Dissociation Constant of Hydroxylamine. The kinetic study required accurate concentrations for the anion NH_2O^- at several temperatures; hence, the pK_a of NH_2OH was necessary. Hughes et al.[15] provided the value 13.71 for this quantity at 25 °C from kinetic evidence; Ackermann et al.[16] reported kinetic data consistent with it, within substantial experimental error. Hughes et al.[15] also reported the value 13.74 at 25 °C, based on a spectrophotometric measurement. We determined thermodynamic values of the pK_a at four temperatures (Table I), by measurement of optical densities in the range 240–230 nm for solutions at fixed stoichiometric NH_2OH concentration and seven different OH^- concentrations. Complete deprotonation cannot be achieved (estimated degree in 9.7 M OH^- 95%), and high OH^- concentrations cannot be tolerated because of NH_2OH self-decomposition (reported to be third order in $OH^{-\,17}$); therefore, a modification of the Brown and McDaniel successive approximation method[18] was employed.[14] Our value at 25 °C is in agreement with the value of Hughes et al.[15] within experimental error, despite the neglect of incomplete deprotonation in their spectrophotometric method. The data of Table I yield the value 55.29 kJ mol^{-1} for ΔH of dissociation of NH_2OH. For ethanol, isoelectronic with hydroxylamine, pK_a = 15.5[19] at 25 °C and ΔH = 52.30 kJ mol^{-1}.[20]

Kinetics of the Nitric Oxide–Hydroxylamine Reaction at 25 °C and Ionic Strength 1.5 M. Kinetic studies were carried out under pseudo-first-order conditions ($n_{NH_2OH}/n_{NO} \geq 5$) over the pH range 6.02–13.14. A typical first-order kinetic plot is shown in Figure 1, and experimental values for k_{obsd} over the entire pH range are displayed in Table II. All reported values are based upon ob-

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Table II. Observed Pseudo-First-Order Rate Constants (k_{obsd}), Product Mole Ratios (n_{N_2}/n_{N_2O}), Calculated NH_2O^- Concentrations, and Second-Order Rate Constants (k_2) for the NO–NH_2OH Reaction[a]

expt	pH	10^5k_{obsd}, s^{-1}	n_{N_2}/n_{N_2O}	X[b]	$10^3[NH_2O^-]$, M	10^3k_2, M^{-1} s^{-1}
1	13.14	152	1.0	0	206	7.38
2	12.75	69.3	0.967	2.22	89.1	7.78
3	12.58	53.2	0.952	3.25	71.9	7.40
4	12.45	37.3	0.831	11.9	53.2	7.01
5	11.85	9.75	0.691	23.0	15.3	6.37
6	11.67	6.55	0.778	16.0	10.7	6.12
7	11.23	2.55	0.683	23.6	3.66	6.97
8	10.68	1.60	0.665	25.1	2.51	6.37
9	10.75	1.51	0.608	30.1	2.18	6.93
10	10.72	1.38	0.664	25.2	2.09	6.60
11	10.47	0.802	0.682	24.5	1.06	7.57
12	9.82	0.192	0.555	34.8	0.292	6.58
13	8.79	0.0589	0.190	74.0	0.115	5.12
14	8.47	0.121	0.098	86.0	0.0854	14.2[c]
15	7.29	0.0190	0.222	70.0	0.0361	5.26
16	6.02	0.00867	0	100	0.00490	17.7[c]
						6.68 ± 0.62 (av)

[a] Conditions: t = 25.0 °C; $[NH_2OH{\cdot}HCl]_0$ = 0.313 M; I = 1.5 M. [b] X = percent dimerization of HNO. [c] Excluded from average.

Table III. Rate Constants for the NO–NH_2OH Reaction Measured at Various Ionic Strengths and in the Presence and Absence of Chloride[a]

expt	I, M	$[NH_2OH{\cdot}HCl]_0$, M	$[NH_2OH]_0$, M	$[OH^-]_0$, M	$10^2[NH_2O^-]$, M	10^4k_{obsd}, s^{-1}	10^3k_2, M^{-1} s^{-1}
17	1.00	0.0998		0.9989	6.19	4.63	7.48
18	1.00	0.0998		0.4995	4.11	2.88	7.01
19	1.00		0.0419	0.9939	2.74	2.20	8.03
20	1.00		0.0998	0.9989	6.44	4.07	6.32
21	1.00		0.0998	0.4995	4.68	3.10	6.62
							7.09 ± 0.53 (av)
22	0.75	0.115		0.7499	6.07	3.27	5.39
23	0.75	0.115		0.3640	3.40	2.25	6.62
24	0.75		0.110	0.254	3.23	1.82	5.63
25	0.75		0.110	0.0992	1.54	1.00	6.49
							6.03 ± 0.52 (av)
26	0.50	0.0998		0.4995	4.11	2.70	6.57
27	0.50	0.0998		0.3869	3.31	2.22	6.71
28	0.50		0.0998	0.4995	4.68	4.00	8.55
							7.28 ± 0.85 (av)
							6.79 ± 0.66 (overall av)

[a] t = 25.0 °C.

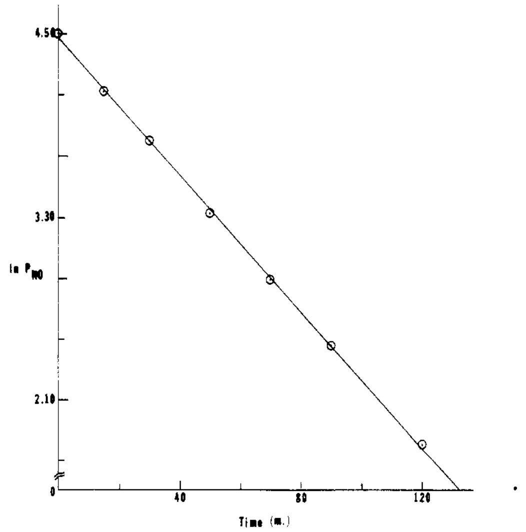

Figure 1. Pseudo-first-order kinetic plot (experiment 4, Table II).

servations made over 2–4 half-lives at higher pH and a minimum of 1 half-life in the lower pH region.

Assuming the reactive form of hydroxylamine to be the anion NH_2O^- and assuming that the reaction step eq 8 is rate-determining, the relationship in eq 9 follows, since [NO] is proportional to P_{NO}.

$$NO + NH_2O^- \xrightarrow{k_2} \text{products} \qquad (8)$$

$$k_{obsd} = k_2[NH_2O^-] \qquad (9)$$

Table IV. Temperature Dependence of the Rate Constant for the Hydroxylamine–Nitric Oxide Reaction[a]

expt	t, °C	pK_a	10^5k_{obsd}, s^{-1}	$10^2[NH_2O^-]$, M	10^3k_2, M^{-1} s^{-1}
29	10.0	14.20	4.77	1.67	2.86
30	18.0	13.92	5.92	1.60	3.70
5	25.0	13.70	9.75	1.53	6.37
31	35.0	13.38	13.8	1.53	9.02
32	45.0	13.08	19.3	1.60	12.1

[a] Conditions: $[NH_2OH{\cdot}HCl]_0$ = 0.313 M; pH 11.85; I = 1.5.

To determine $[NH_2O^-]$, $[OH^-]$ has been calculated directly from the known quantity of OH^- initially added for unbuffered experiments 1–4. For the remaining experiments $[OH^-]$ values have been determined by simulation (see Experimental Section). In calculating $[NH_2O^-]$ thermodynamic values of pK_a and pK_w have been employed; analysis shows that for pH <13 the error from this assumption should be within the range of experimental error.

Rate constants k_2 calculated by eq 9 are shown in column 7 of Table II. The essential constancy of this quantity over such an extended NH_2O^- concentration range confirms the assumption of eq 8 as the rate-determining step. No second term in the rate law in either NH_2OH or NH_3OH^+ is discernible within these data, and there is no doubt that NH_2O^- is the overwhelmingly reactive species in this reaction. (The two values excluded from the reported average value for k_2 are discussed later.)

Nondependence of the Second-Order Rate Constant on Ionic Strength. The choice of the high ionic strength of 1.5 M for the measurements reported in Table II was conditioned in part by the use of $NH_2OH{\cdot}HCl$ stock solutions; for this same reason NaCl

Table V. Kinetic Measurements Carried Out with NO–CF_4 Mixture Contaminated with Trace O_2[a]

expt	pH	n_{N_2}/n_{N_2O}	X[b]	$10^4(k_{obsd})_0$,[c] s^{-1}	10^3k_2,[c] M^{-1} s^{-1}	apparent order
4[d]	12.45	0.831	11.9	3.73	7.01	1.00
7[d]	11.23	0.683	23.6	0.255	6.97	1.00
33	12.24	0.576	32.9	2.64	12.6	1.10
34	12.21	0.394	50.6	2.13	11.3	1.25
35	12.15	0.373	52.8	2.21	13.2	1.15
36	12.12	0.251	66.5	2.59	17.6	1.25
37	12.05	0.123	82.6	2.85	23.4	1.45
38	11.84	0.111	84.2	2.46	24.4	1.35
39	11.82	0.070	89.9	1.81	18.1	0.88
40	11.80	0.047	93.1	1.61	18.0	0.85
41	11.65	0.052	92.4	2.28	29.1	1.08

[a] Conditions: $[NH_2OH{\cdot}HCl]_0 = 0.313$ M; $I = 1.5$ M; $t = 25$ °C. [b] Apparent percent dimerization of HNO. [c] For nonlinear plots, calculated from initial slopes. [d] No O_2 contamination.

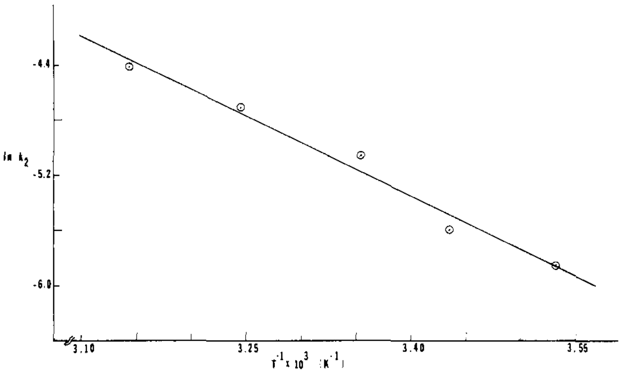

Figure 2. Arrhenius plot for the hydroxylamine–nitric oxide reaction.

was used for ionic strength control. The results of experiments carried out with free base NH_2OH at three lower ionic strengths, in the presence and absence of Cl^- (Table III), show that the value of k_2 is not discernibly affected by either of these factors.

Temperature Dependence of the Rate Constant. Values of k_{obsd} at several temperatures in the range 10–45 °C, all measured for systems at pH 11.85, are listed in Table IV. NH_2O^- concentrations have been calculated from appropriate values of K_a (data of Table I) and K_w at each temperature[21] and the 25 °C value $[OH^-] = 2.64 \times 10^{-2}$ M, the latter justified by the small anticipated variation in activity coefficient. Resultant values of the second-order rate constant, k_2, are shown as an Arrhenius plot in Figure 2. The corresponding activation energy is 32.3 kJ mol^{-1}, and the parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined to be 29.6 kJ mol^{-1} and −189 J K^{-1} mol^{-1}, respectively.

Reaction Product Ratio. The product ratio n_{N_2}/n_{N_2O} decreases with pH, as shown in column 4 of Table II. The quantity X (column 5) is the calculated percentage of dimerization (eq 5) of the intermediate HNO in competition with reduction (eq 4), based upon the applicable stoichiometric relation (eq 7 of ref 4).

Nondetection of Alternate Reaction Pathways. Hyponitrite is a known minor product of NH_2OH disproportionation.[22] Reactant solutions were therefore examined spectrophotometrically for $N_2O_2^{2-}$, with consistently negative results. Complete nitrogen mass balances were obtained in experiments 15 and 16 (Table II) by measuring the partial pressures of NO, N_2O, and N_2 and the concentration of NH_2OH, after extended reaction time. For experiment 15 the measured sum $n_{NH_2OH} + n_{NO} + 2n_{N_2} + 2n_{N_2O}$ after 14 days was 97% of its value at $t = 0$; for experiment 16 after 19 days the comparable figure was 96%. We conclude that there are no significant diversionary reaction paths.

Effects of Small Quantities of O_2. Anomalous results were observed in several kinetic experiments carried out employing CF_4 reference gas that was later found to contain a trace of O_2 impurity. These results are summarized in Table V, in which normal experiments 4 and 7 (Table II) are included for comparison. The following features are observed: (1) initial rates are increased; (2) pseudo-first-order plots become nonlinear (expressed by showing apparent reaction orders derived from best fits to a linear least-squares program); (3) the product ratio n_{N_2}/n_{N_2O} is substantially lower than in "normal" reactions under otherwise comparable conditions.

Table VI. Effects of Nitrite Ion on the NO–NH_2OH Reaction[a]

expt	$10^4[NO_2^-]$, M	n_{N_2}/n_{N_2O}	apparent order	10^4k_{obsd},[b] s^{-1}
5	0	0.691	1.00	0.975
42	3.93	0.686	1.30	1.15
43	33.9	0.763	1.30	1.27

[a] Conditions: $[NH_2OH{\cdot}HCl]_0 = 0.313$ M; pH 11.85; $I = 1.5$ M; $t = 25.0$ °C. [b] Based on initial slopes, for nonlinear plots.

The above observations explain the anomalously high values for k_2 and low product ratios observed in the cases of experiments 14 (pH 8.47) and 16 (pH 6.02) of Table II. Very long reaction periods were involved, and we infer that atmospheric leakage occurred at a level that was very low yet sufficient to perturb these slow reactions without having been otherwise detected. Apparent anomalies of sequence in previously reported results can be explained similarly (Table V of ref 4).

Since it is known that NO reacts rapidly with O_2 to form NO_2 and that NO and NO_2 associate to form N_2O_3, the last species may play a causative role in the observed effects. Experiments were carried out employing a purified NO–CF_4 gas phase and an aqueous phase containing added nitrite as a trace source of N_2O_3, expected because of the anhydride relation shown in eq 10.

$$2NO_2^- + 2H^+ \rightleftarrows N_2O_3 + H_2O \qquad (10)$$

It can be seen in Table VI that added nitrite does cause some increase in initial rates, and loss of linearity in pseudo-first-order plots, but that the product ratio is not altered. Experiments were also carried out with deliberate addition of NO_2: addition of 1 torr of NO_2 at $P_{NO} = 48$ torr (pH 12, $[NH_2OH]_0 = 0.303$) increased k_{obsd} by 19%; addition of 1.9 torr of NO_2 increased k_{obsd} a total of 31%. Product ratios were 0.25 and 0.20, compared with 0.57 in absence of NO_2, and apparent reaction orders were 1.2 and 1.6.

Discussion

The kinetic measurements reported here establish that the rate law of eq 11 applies to the entire investigated pH range of

$$-dP_{NO}/dt = k_2[NH_2O^-]P_{NO} \qquad (11)$$

7.29–13.14. The result is consistent with evidence that deprotonated hydroxylamines tend to be more reactive than their corresponding free bases in alkaline solution, as shown in previous autoxidation studies.[15,23,24] The reaction is confirmed to proceed via abstraction of N-bound hydrogen by NO. Inability of NO to abstract amino hydrogen atoms has been cited as a reason for

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its poor nitrosation power,[25] yet it has been shown that organic pyrolyses can be inhibited by NO, presumably because of H atom abstraction.[26] The value observed here for the activation energy of the NO–NH_2O^- reaction, 32.3 kJ mol^{-1}, is comparable to the activation energies observed for a number of radical–molecule H atom abstractions. (For isopropyl radical H atom abstraction from cyclohexadiene, for example, E_a = 29.7 kJ mol^{-1}.)[27]

The neutral radical species ·NHOH reacts predominantly with itself in acid solution to produce N_2.[28] By contrast, the radical anion ·NHO^- produced in the nitric oxide–hydroxylamine reaction combines preferentially with a second NO radical, a conclusion that is reinforced by studies of the *N*-alkylhydroxylamines (see accompanying paper).

The observed effects of O_2 on the NO–NH_2OH reaction may be plausibly ascribed at least in part to the expected presence of N_2O_3, which, unlike NO_2, is an effective agent of nitrosation.[29] Equilibrium data indicate that N_2O_3 should be fully dissociated in the gas phase under the conditions employed in this study but that NO and NO_2 will have a strong recombination tendency in solution.[30,31] It has been reported that N_2O_3 introduced to solution directly from the gas phase is capable of reacting readily with even weakly basic amines,[32] whereas N-nitrosation by HNO_2 along the established N_2O_3 pathway is restricted to acidic conditions.[33] It has been suggested that recombination of NO with NO_2 in solution produces the symmetrical isomer ONONO and that this species is much more reactive than the more stable unsymmetric isomer ON–NO_2 formed by self-reaction of aqueous HNO_2.[32]

In the presence of N_2O_3, the observed initial rate of the NO–NH_2OH reaction is in every case faster than the normal rate-determining step (eq 12). While a simple nitrosation reaction

$$NH_2O^- + NO \rightarrow HNO + HNO^- \qquad (12)$$

(eq 13) could account for an increased initial rate and decreased

$$NH_2O^- + N_2O_3 \rightarrow N_2O + NO_2^- + H_2O \qquad (13)$$

product ratio, the rate should return to its normal value upon exhaustion of the impurity if only parallel reactions were involved, whereas in the majority of cases a continuous decrease in rate was observed. Thus, while reactions 12 and 13 occurring in parallel could in principle account for the observed effects, the actual mechanism must be considerably more complex. In view of this complexity and the limitations of our observations, further work will be necessary before a detailed mechanistic hypothesis can be advanced. The difference between the effects of N_2O_3 added directly in solution via NO_2^- on one hand and of N_2O_3 formed from the gas phase on the other does strongly suggest a contributing role on the part of reactive, symmetric N_2O_3. The effect of contaminant carried initially as O_2 in CF_4 appears to be greater than that of NO_2 added as such, suggesting the possibility that traces of unreacted O_2 may unexpectedly perservere into the reaction system, in which case its reactions with the intermediates (e.g. NO^- and HNO^-) could play an important part. The evidence of apparent kinetic order and the erratic nature of the measurements pertaining to it (including values less than unity in two cases) suggest the involvement of one or more chain processes.

Evidence previously reported suggests that the reactivity of HNO derived from $HN_2O_3^-$ toward NH_2OH is much greater than that of the HNO derived from the NO–NH_2O^- reaction.[4] This difference may have its origin in isomerism of the intermediate, HNO being formed in one case and NOH in the other, leading to NO^- in different electronic states upon rapid deprotonation (expected since pK_a = 4.7 for HNO[34] and NOH should be more acidic). The species formed in $HN_2O_3^-$ decomposition is probably HNO,[35] and since this molecule is known to have a singlet ground state,[36] it should form singlet NO^-. Calculations show that the molecule NOH (which has not been experimentally observed) should have a triplet ground state[37–39] and should therefore lead to triplet NO^-. Singlet NO^- is known to be excited relative to its triplet ground state,[40] in an energy level spacing similar to that of the isoelectronic molecule O_2.[41] Since the species we assume to be singlet NO^- is the more reactive one, the case is fully analogous to that of singlet/triplet O_2. The lifetime of singlet O_2 in water is about 2 μs.[42] If singlet NO^- exhibits a similar decay constant of the order of 10^6 s^{-1} and if its reduction by NH_2OH is diffusion-controlled, we estimate that the rate of decay cannot compete with reduction as long as [NH_2OH] ≥ 10^{-2} M. Unfortunately, direct spectroscopic verification appears to be virtually precluded by the fact that the ionization potential of NO^- (0.24 eV) is very small in relation to its $^3\Sigma^-$–$^1\Delta$ excitation energy (0.75 eV).[43]

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Registry No. NO, 10102-43-9; $HONH_2$, 7803-49-8.

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