toward BF_3 than DMF or DMSO must be considered as not reliable at the present time.

An extension of these ligand preference studies to a wide variety of organic bases, including compounds of biological importance, is now in progress. These boron trihalide complexes are also being studied using boron-11, fluorine-19, and nitrogen-14 nmr, as well as the chemical shift and peak intensity methods described here and in previous reports.[13-15]

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The Stoichiometry and Kinetics of Manganese(III) Reactions with Hydroxylamine, O-Methylhydroxylamine, and Nitrous Acid in Acid Perchlorate Solution[1]

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The stopped-flow apparatus has been used to determine the kinetics of reaction between manganese(III) and the reductants NH_3OH^+, $NH_3OCH_3^+$, and HNO_2 at 25° in acid (0.50–3.70 *M*) perchlorate media. Nitrate was determined as a product of oxidation of hydroxylamine. Stoichiometric measurements with Mn(III) in excess were used to analyze the kinetic data with excess of substrate in terms of the reactions

$$6Mn(III) + NH_3OH^+ + 2H_2O \longrightarrow 6Mn(II) + NO_3^- + 8H^+$$

$$2Mn(III) + 2NH_3OCH_3^+ \longrightarrow 2Mn(II) + N_2H_3(OCH_3)_2^+ + 3H^+$$

$$2Mn(III) + HNO_2 + H_2O \longrightarrow 2Mn(II) + NO_3^- + 3H^+$$

All reactions were second order over-all, and first order in each reactant. The reactions were also independent of initial concentration of reactants, $[Mn^{2+}]$, $[NaClO_4]$, $[NaNO_3]$, ionic strength, and wavelength. The observed rate constant was dependent on acidity. A mechanism consistent with these results was postulated, in which the rate-determining steps involve the formation of the $NH_2O\cdot$, $\cdot NHOCH_3$, and $\cdot NO_2$ radicals for the reactions with NH_3OH^+, $NH_3OCH_3^+$, and HNO_2, respectively. The acidity dependence arises from reaction with Mn^{3+} and $MnOH^{2+}$. With the primed rate constant designating $MnOH^{2+}$ reaction, the rate constants for the rate-determining steps are: NH_3OH^+, $k_1 = (1.4 \pm 0.1) \times 10^3\ M^{-1}\ sec^{-1}$, $k_1' = (3.1 \pm 0.3) \times 10^3\ M^{-1}\ sec^{-1}$; $NH_3OCH_3^+$, $k_3' = 6.1 \pm 0.4\ M^{-1}\ sec^{-1}$, $k_3 < 0.5\ M^{-1}\ sec^{-1}$; HNO_2, $k_5 = (2.2 \pm 0.2) \times 10^4\ M^{-1}\ sec^{-1}$, $k_5' = (4.9 \pm 0.4) \times 10^4\ M^{-1}\ sec^{-1}$. The relative slowness of the reaction with $NH_3OCH_3^+$ is ascribed to the lack of hydrogen bonding in this system.

Introduction

In this paper we report a study of the stoichiometry and kinetics of the reactions between manganese(III) and hydroxylamine, O-methylhydroxylamine, and nitrous acid in aqueous perchloric acid. The reactions were studied by standard analytical methods, and the kinetics have been investigated using a stopped-flow apparatus. Relevant equilibrium data for these reactants are summarized in Table I.

Many examples of metal ion oxidations of nitrogen bases such as those considered here may be found in the literature.[2] The reactions are often characterized by large and complex over-all stoichiometries.[2,3] As a result, relatively few kinetic studies have been attempted on these systems. Interpretation of kinetic data is simplified by the use of the well-characterized[4] Mn(III)–Mn(II) system in the presence of a large excess of Mn(II). The formation of radicals in these systems has been demonstrated by esr, as in the oxidation of hydroxylamine.[5,6] Comparison with the oxidation of O-methylhydroxylamine[5] provides further insight into the nature of the primary steps. It will also be shown that a knowledge of the kinetics of oxidation of nitrous acid is useful in understanding the reaction with hydroxylamine.

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(1) This investigation was supported in part by Public Health Service Research Grant GM-08893-07 from the National Institute of General Medical Sciences, Public Health Service, and in part by National Science Foundation Grant GP-4277.

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TABLE I

EQUILIBRIUM DATA AT 25°

Reaction	Ionic strength[a] of medium	Constant[a]
$NH_3OH^+ \rightleftarrows NH_2OH + H^+$	$\mu = 0$ (cor)	1.1×10^{-6} [b,c]
$NH_3OCH_3^+ \rightleftarrows NH_2OCH_3 + H^+$	$\mu = 0$ (cor)	2.5×10^{-5} [c]
$HNO_2 \rightleftarrows NO_2^- + H^+$	$\mu = 1$ ($NaClO_4$)	1.6×10^{-3} [d]
$Mn^{3+} \rightleftarrows MnOH^{2+} + H^+$	$\mu = 4.0$ (ClO_4^-)	0.93[e]

[a] Units are *M*. [b] R. A. Robinson and V. E. Bower, *J. Phys. Chem.*, **65,** 1279 (1961). [c] T. C. Bissot, R. W. Parry, and D. H. Campbell, *J. Am. Chem. Soc.*, **79,** 796 (1957). [d] E. G. Vassian and W. H. Eberhardt, *J. Phys. Chem.*, **62,** 84 (1958). [e] C. F. Wells and G. Davies, *J. Chem. Soc., A*, 1858 (1967).

TABLE II

EXTINCTION COEFFICIENTS[a] FOR NITRITE AND NITRATE IN WATER AND ACID PERCHLORATE SOLUTIONS[b] AT 25°

Wave-length, nm	Extinction coefficient $\times 10^{-3}$			
	Nitrite		Nitrate	
	Water	Acid soln[b]	Water	Acid soln[b]
200	4.88	...	8.34	...
205	5.42	...	11.57[c]	...
210	5.59	2.86	6.90	6.50
215	5.18	2.36	5.12	4.70
220	4.20	1.75	3.16	2.90
225	2.95	1.19	1.58	1.46
230	1.83	0.75	0.72	0.68

[a] All extinction coefficients are in M^{-1} cm^{-1}. [b] [$HClO_4$] = 2.16 *M*, [Mn(II)] = 0.54 *M*. [c] At 204 nm: M. A. Hussain, G. Stedman, and M. N. Hughes, *J. Chem. Soc., B*, 1703 (1968).

TABLE III

ANALYSIS OF THE SPECTRUM OF PRODUCT NITRATE IN THE REACTION WITH HYDROXYLAMINE AT 25°[a]

Wave-length, nm	Absorbance[b]	$10^4[HNO_2]$, *M*	$10^4[NO_3^-]$,[c] *M*
210	1.36	4.76	2.03
215	0.99	4.19	2.02
220	0.600	3.43	1.98
225	0.295	2.48	1.94
230[c]	0.120	1.60	1.71
		Av	1.99 ± 0.03

[a] [$HClO_4$] = 2.16 *M*, [Mn(II)] = 0.54 *M*, $[Mn(III)]_0 = 13.48 \times 10^{-4}$ *M*, $[NH_3OH^+]_0 = 2.80 \times 10^{-4}$ *M*. [b] Measured in matched 2-mm quartz cells and corrected for $[Mn(III)]_\infty$. [c] Measurements at 230 nm have been neglected in computing the average.

Experimental Section

Reagents.—Preparation and standardization procedures for perchloric acid, manganese(III) solutions, and the perchlorates of manganese(II), iron(II), sodium, and barium were as described previously.[7] Sodium nitrate (Baker Analyzed reagent grade) and sodium nitrite (Fisher Chemical Co.) were used, without further purification, to make up stock solutions. Nitrite solutions were made up daily and estimated iodometrically in the absence of oxygen.[8]

Reagent grade hydroxylamine sulfate ($(NH_2OH)_2H_2SO_4$) from Baker and Adamson was used without further purification. We have found that hydrazine and $N_2H_4 \cdot H_2SO_4$ are oxidized at the same rate under the present conditions.[9] Presumably, the large excess of Mn(II) and the high acidity greatly reduce the concentration of free SO_4^{2-}.[10] O-Methylhydroxylamine was obtained as the free base by distillation of the hydrochloride (Eastman) from 50% w/v aqueous NaOH. The distillate was collected up to 55°, twice redistilled from solid NaOH, refluxed over calcium hydride for 3 hr, and finally fractionally distilled (bp 48.1° (757 mm)). The base was stored at low temperature under nitrogen. Stock solutions are moderately unstable and were made up by weight immediately before use. Attempts to prepare a pure sample of N-methylhydroxylamine as the free base from the hydrochloride were unsuccessful.

Stoichiometry.—Spectrophotometric measurements of [Mn(III)] were made directly at 250 or 260 nm and by estimation of Fe(III) formed by sampling into excess acidic Fe(II). The Fe(II) sampling method is inapplicable in the presence of nitrate, which absorbs strongly at the wavelengths used. Any product gases were collected, measured quantitatively, and identified using a high-vacuum gas chromatography system, as described previously.[7,11] A modified gas-line stoichiometry vessel was used to avoid possible prereaction due to substrate distillation during preliminary degassing of the solutions. Glass beads were found to be effective in reducing the time required for degassing.

Nitrate was estimated quantitatively as a product of oxidation of hydroxylamine by comparison with spectra of nitrite and nitrate in the region 210–230 nm under the same conditions as those used for the stoichiometry measurements.

The spectrum of nitrite was investigated in the region 210–230 nm in water and in a solution with [$HClO_4$] = 2.16 *M* and [Mn(II)] = 0.54 *M*. With [NO_2^-] = 1.65×10^{-4} *M* we obtained the extinction coefficients shown in column 1 of Table II. Beer's law is obeyed for nitrite in the range [HNO_2] = 0–12.80×10^{-4} *M*. The extinction coefficient for HNO_2 in this region is seen to be smaller than that of NO_2^- (columns 1 and 2). Nitrite solutions were found to decompose slowly in acid perchlorate solution, the rate increasing with increasing [HNO_2]. The decomposition is accompanied by an increase in absorbance in the region 210–230 nm, which is greater than that expected for NO_3^- formation.

The nitrate ion has an absorption maximum in the uv region at 301 nm (ϵ 6.83), and Beer's law is obeyed in the range [NO_3^-] = 0–6.00×10^{-4} *M*. The extinction coefficients obtained in water and the same medium as used for stoichiometry measurements are shown in columns 3 and 4 of Table II. The species present have the same extinction coefficient in the different media. The extinction coefficient of nitrate is unaffected by a 600-fold excess of hydroxylamine in this wavelength range. Since the extinction coefficient of hydroxylamine is no greater than unity in this wavelength range, the observed absorbance at the end of a reaction could be corrected for any remaining Mn(III) (concentration known from sampling into Fe(II)) and shown to be due to nitrate, and not nitrite, at each wavelength. An example of this treatment of absorbance data is shown in Table III. Agreement between product concentration and reactant consumption was generally satisfactory.

Kinetics.—The reactions which are reported here are rapid and a stopped-flow apparatus (constructed of quartz and glass) was used for quantitative study.[7,12] An excess of reductant was employed so that no Mn(III) remained at the end of a reaction. Kinetic studies in the presence of excess Mn(III) are much less precise because of low extinction coefficients ($\epsilon \lesssim 100$) in the region 350–600 nm and the low concentrations ([Mn(III)] $\lesssim 10^{-3}$ *M*) which are available.[4] Variation of ionic strength, μ, in the range μ = 2.10–4.20 *M*, was achieved by adjustment of the concentrations of sodium or manganese(II) perchlorates or sodium nitrate.

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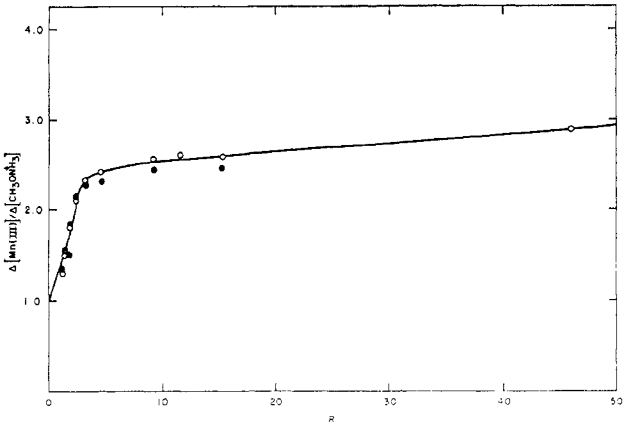

Figure 1.—Variations in the stoichiometry of reaction with O-methylhydroxylamine. The conditions are: $[HClO_4]$ = 2.16 *M*, [Mn(II)] = 0.54 *M*, μ = 3.78 *M*, temperature 25°; ○, direct spectrophotometry; ●, sampling method.

The temperature was maintained at 25 ± 1°. The kinetic procedure has already been described,[7,11] the disappearance of manganese(III) being followed at 470 or 510 nm. None of the reductants or products absorbs appreciably in the visible region. Manganese(III) was always freshly prepared by electrolysis of an excess of acidic Mn(II), and the reductant was added to the solution to be mixed with Mn(III) immediately before reaction. (This latter precaution was taken to avoid any possibility of substrate decomposition prior to reaction with Mn(III).) At least three reaction traces were recorded for each set of concentrations, results of duplicate runs usually agreeing to within ±5%. The rates of reaction showed no detectable oxygen dependence. In most cases the apparent extinction coefficient of Mn(III) could be estimated by extrapolation of kinetic plots to zero time.

Table IV

Stoichiometry of Reaction with Hydroxylamine by Spectrophotometric Analysis at $[HClO_4]$ = 2.14 *M*, [Mn(II)] = 0.54 *M*, μ = 3.80 *M*, and 25°[a,b]

10^4[Mn(III)]$_0$	10^4[Mn(III)]$_\infty$	10^4-$[NH_3OH^+]_0$	10^4-$[NO_3^-]$[c]	% yield[d]	R[e]
13.48	8.96	0.80	0.80	17.7	16.9
13.48	3.39	2.00	1.62	16.0	6.74
13.48	0.33	2.80	1.99	15.1	4.82
13.48	0.24	4.00	2.36	17.8	3.37
14.48	10.81	0.90	0.60	14.6	16.1
14.48	9.58	1.20	0.61	16.3	12.1
14.48	0	4.00	2.27	15.7	3.62
14.48	0	13.50	1.86	12.8	1.07
15.54	0	28.0	1.33	8.6	0.56
15.54	0	100	0.73	4.7	0.16
15.54	0	200	0.97	6.2	0.08
15.54	0	400	0.63	4.0	0.04
1.08	0	955	0	0	0.001

[a] All concentrations are molar. [b] Extinction coefficients used for Mn(III) are ϵ_{260} 1.35 × 10^3 M^{-1} cm^{-1} and ϵ_{250} 1.92 × 10^3 M^{-1} cm^{-1}: G. Davies, Ph.D. Thesis, Birmingham, England, 1966. [c] Extinction coefficients used are those in Table II. [d] % yield = $[NO_3^-]_\infty$/([Mn(III)]$_0$ − [Mn(III)]$_\infty$) × 100. [e] R = [Mn(III)]$_0$/$[NH_3OH^+]_0$.

Table V

Gaseous Products from Oxidation of Hydroxylamine and O-Methylhydroxylamine

Substrate	Mn(III) consumed, mol	Initial substrate, mol	Product gas, mol
Hydroxylamine	1.73 × 10^{-5}	5.02 × 10^{-4}	N_2, 2.71 × 10^{-6}
	3.46 × 10^{-6}	5.02 × 10^{-4}	N_2, 2.2 × 10^{-7}
	1.73 × 10^{-5}	5.02 × 10^{-5}	No gaseous product detected
O-Methylhydroxylamine	5.92 × 10^{-6}	5.20 × 10^{-5}	No gaseous product detected
	2.12 × 10^{-5}	5.20 × 10^{-5}	

Results

Stoichiometry. (A) Spectrophotometric Analysis. (a) Hydroxylamine.—The results in Table IV show that the oxidation of hydroxylamine to nitrate is quantitative when the ratio $R = [Mn(III)]_0/[NH_3OH^+]_0$ is in the range 16.9–3.6, the average molar nitrate yield of 16.2 ± 0.4% agreeing well with the theoretical value of 16.7%. The nitrate yield falls off as *R* decreases, however, and is negligible when $R \lesssim 10^{-3}$ (Table IV). From this data we estimate that nitrate is the primary product of oxidation in the kinetic range (see Kinetics section).

(b) O-Methylhydroxylamine.—The stoichiometry of the reaction between Mn(III) and O-methylhydroxylamine is also a function of $R = [Mn(III)]_0/[NH_3OCH_3^+]_0$ (Figure 1). At low *R*, where all of the kinetic runs were made, the stoichiometric consumption ratio is close to unity. We have assumed a stoichiometry of unity in analyzing our kinetic data in the range $6 \times 10^{-3} < R < 5 \times 10^{-2}$.

(c) Nitrous Acid.—The stoichiometry in the presence of excess Mn(III) with $[HClO_4]$ = 2.15 *M* and [Mn(II)] = 0.54 *M* at 25° was found to be $\Delta[Mn(III)]/\Delta[HNO_2]$ = 1.97 ± 0.06 (14 determinations) in the range *R* = 10.8–2.7. Agreement between spectrophotometric and sampling methods was satisfactory. This stoichiometry was also found for the reaction with nitrite in pyrophosphate media.[13] Stoichiometric measurements were much less precise in excess nitrous acid, where mixtures of nitrous acid and nitrate had to be analyzed. As a result, we have assumed that the stoichiometric ratio is unchanged in the range *R* = 1.6–0.2 used for kinetic measurements (see Kinetics section).

(B) Analysis of Gaseous Products.—The results of an examination of the gaseous products from the oxidation of hydroxylamine and O-methylhydroxylamine at low *R* are summarized in Table V. Nitrogen is found as a product only at very low values of *R* in the oxidation of hydroxylamine, supporting the results of the previous section. The observation that no nitrogen is produced in the oxidation of the methoxy compound eliminates the reaction

$$2Mn(III) + 2CH_3ONH_3^+ \longrightarrow N_2 + 2CH_3OH + 2H^+ + 2Mn(II)$$

from consideration.

Kinetics.—Although the relative error associated with the evaluation of individual reaction traces did not exceed ±5% (*vide supra*), uncertainties in solution

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(13) R. Belcher and T. S. West, *Anal. Chim. Acta*, **6**, 322 (1952).

composition and stoichiometry over the entire concentration range studied are reflected in the greater relative error (approximately 8%, *vide infra*) associated with individual second-order rate constants. These values will be given explicitly as we turn again to a consideration of the substrates taken individually.

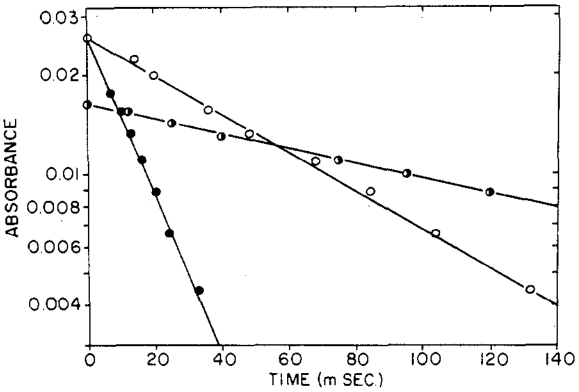

Figure 2.—Pseudo-first-order plots for the disappearance of Mn(III) in the presence of hydroxylamine. The ordinate is logarithmic and the abscissa is in milliseconds. The conditions are: ○, $[HClO_4] = 0.60\ M$, $[Mn(II)] = 1.10\ M$, $[Mn(III)]_0 = 4.73 \times 10^{-4}\ M$, $[NH_3OH^+]_0 = 10.0 \times 10^{-3}\ M$; ◑, $[HClO_4] = 1.80\ M$, $[Mn(II)] = 0.15\ M$, $[NaClO_4] = 1.65\ M$, $[Mn(III)]_0 = 2.08 \times 10^{-4}\ M$, $[NH_3OH^+]_0 = 5.0 \times 10^{-4}\ M$; ●, $[HClO_4] = 3.50\ M$, $[Mn(II)] = 0.13\ M$, $[Mn(III)]_0 = 4.56 \times 10^{-4}\ M$, $[NH_3OH^+]_0 = 45.0 \times 10^{-4}\ M$. Ionic strength 3.90 *M*; temperature 25° throughout.

TABLE VI

KINETIC DATA FOR REACTION WITH HYDROXYLAMINE[a] AT 25° AND $\mu = 3.90\ M^b$

$[HClO_4]$	10^4-$[NH_3OH^+]_0$	$10^{-3}k_A{}^c$	$[HClO_4]$	10^4-$[NH_3OH^+]_0$	$10^{-3}k_A{}^c$
3.50	15.0	1.6	1.20	10.0	1.9_5
	35.0	1.8		15.0	2.3
	45.0	1.7		15.0^g	2.1_5
	10.0^d	1.5		5.0^h	1.8
	20.0^d	1.7		10.0^h	1.9
	40.0^d	1.9		15.0^h	2.4
	Av	1.7 ± 0.1		20.0^h	1.9
2.40	40.0	2.0		5.0^i	1.7
	50.0	2.0		10.0^i	2.1
	70.0	2.1		20.0^i	1.8
	15.0^e	1.9		Av	2.0 ± 0.2
	25.0^e	1.8	0.60	10.0	2.3
	30.0^e	1.9		15.0	2.5
	35.0^e	2.0		25.0	2.6
	Av	2.0 ± 0.1		5.0^j	2.3
1.80	10.0	1.7		10.0^j	2.7
	15.0	1.8		15.0^j	2.6
	20.0	2.0			
	25.0	2.2		Av	2.5 ± 0.1
	5.0^f	1.9			
	10.0^f	1.8			
	15.0^f	1.9			
	Av	1.9 ± 0.1			

[a] All concentrations are molar; $[Mn(III)]_0 = 1.09\text{–}5.19 \times 10^{-4}\ M$. [b] Ionic strength adjusted with Mn(II) except where noted otherwise. [c] Units are $M^{-1}\ sec^{-1}$. [d] $[Mn(II)] = 0.05\ M$, $[NaClO_4] = 0.267\ M$. [e] $[Mn(II)] = 0.18\ M$, $[NaClO_4] = 1.12\ M$, $\mu = 4.06\ M$. [f] $[Mn(II)] = 0.15\ M$, $[NaClO_4] = 1.65\ M$. [g] Measured at 510 nm. [h] $[Mn(II)] = 0.30\ M$, $\mu = 2.10\ M$. [i] $[Mn(II)] = 0.15\ M$, $[NaNO_3] = 2.25\ M$; $[Mn(III)]_0$ was estimated from initial absorbance using the extinction coefficient in perchlorate media.[4] [j] $[Mn(II)] = 0.60\ M$, $[NaClO_4] = 1.50\ M$.

(a) **Hydroxylamine.**—Examples of plots of log [Mn(III)] *vs.* time in the presence of excess hydroxylamine are shown in Figure 2. The observed linearity shows that the reaction is first order in [Mn(III)]. Moreover, the linearity at only moderate excesses of NH_3OH^+ suggests that the stoichiometry of the reaction is high, consistent with the stoichiometric determination. The invariance of the derived second-order rate constant with $[NH_3OH^+]_0$ (Table VI) supports the assignment of the stoichiometry of the reaction, namely, $\Delta[Mn(III)]/\Delta[NH_3OH^+] = 6$, within the range of kinetic measurements. We thus define

$$(\text{rate})_A \equiv -\left(\frac{1}{6}\right)\frac{d[Mn(III)]}{dt} = k_A[Mn(III)][NH_3OH^+] \quad (I)$$

where the equality represents the empirical rate law. The results in Table VI show that k_A is independent of $[Mn(III)]_0$, $[NH_3OH^+]_0$, μ, [Mn(II)], $[NaClO_4]$, $[NaNO_3]$, and wavelength. The rate constant is, however, acidity dependent, increasing with decreasing $[HClO_4]$. Calculations of extinction coefficients for manganese(III) at 470 and 510 nm and zero time give values in good agreement with those in the absence of hydroxylamine.

(b) **O-Methylhydroxylamine.**—Graphs of log [Mn(III)] *vs.* time are linear for reaction in the presence of excess substrate; the second-order rate constants, at different acidities, obtained from Figure 3 are collected in Table VII. For reaction with $NH_3OCH_3{}^+$ we may therefore define

$$(\text{rate})_B \equiv -\frac{d[Mn(III)]}{dt} = k_B[Mn(III)][NH_3OCH_3{}^+] \quad (II)$$

(c) **Nitrous Acid.**—The rate law, with a stoichiometric consumption ratio of 2 over the kinetic concen-

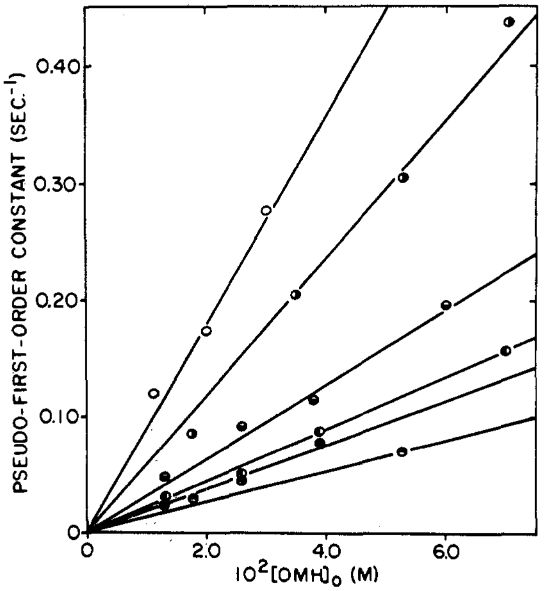

Figure 3.—Plot of pseudo-first-order rate constant *vs.* initial concentration of reductant for reaction with O-methylhydroxylamine at various acidities: ○, $[HClO_4] = 0.60\ M$; ◑, $[HClO_4] = 1.20\ M$; ◒, $[HClO_4] = 1.80\ M$; ◐, $[HClO_4] = 2.40\ M$; ●, $[HClO_4] = 3.00\ M$; ◓, $[HClO_4] = 3.60\ M$ (*cf.* Table VII).

Table VII

Second-Order Rate Constants for Reaction with O-Methylhydroxylamine at $\mu = 3.90\ M^a$ and 25°[b]

[$HClO_4$]	$10^4[Mn(III)]_0$	$k_B{}^c$
3.60	5.29	1.4 ± 0.1
3.00	6.81	2.0 ± 0.1
2.40	5.35	2.3 ± 0.1
1.80	4.19	3.3 ± 0.2
1.20	4.00	5.5 ± 0.4
0.60^d	2.88	8.8 ± 1.0

[a] Ionic strength adjusted with Mn(II). [b] All concentrations are molar. [c] Units are M^{-1} sec^{-1} (*cf.* Figure 3). [d] $\mu = 4.20\ M$.

tration range, is

$$(\text{rate})_C \equiv -\left(\frac{1}{2}\right)\frac{d[\text{Mn(III)}]}{dt} = k_C[\text{Mn(III)}][\text{HNO}_2] \quad \text{(III)}$$

The kinetic data were analyzed in terms of the appropriate second-order function[7] for this reaction, and examples of plots under various conditions are shown in Figure 4. The general linearity supports the stoichiometric assignment with excess of reductant. Kinetic data for this substrate are collected in Table VIII.

Mechanism

Table VIII

Kinetic Data for Reaction with Nitrous Acid at 25°[a] and $\mu = 3.90\ M^b$

[$HClO_4$]	$10^4[HNO_2]_0$	$10^{-4}k_C{}^c$	[$HClO_4$]	$10^4[HNO_2]_0$	$10^{-4}k_C{}^c$
3.60	5.0	3.0	1.40	5.0	2.8
	10.0	3.1		10.0	2.8
	15.0	2.6		15.0	3.5
	20.0^d	2.6		10.0^f	3.5
	5.0^d	2.7		15.0^f	3.3
	10.0^d	3.2		20.0^f	3.0
	15.0^d	2.8		Av	3.1 ± 0.3
	25.0^d	2.5			
	Av	2.8 ± 0.2	0.50	1.25	3.9
				10.0	4.2
3.00	5.0	2.6		3.75^g	3.9
	12.5	3.0		5.0^g	3.9
	15.0	2.7		7.5^g	4.5
	Av	2.6 ± 0.2		10.0^g	4.3
				3.75^h	4.4
2.16	5.0	2.6		5.0^h	4.4
	10.0	3.0		7.5^h	4.3
	15.0	3.0		Av	4.2 ± 0.2
	20.0	3.1			
	5.0^e	2.5			
	12.5^e	3.0			
	15.0^e	2.6			
	Av	2.8 ± 0.2			

[a] All concentrations are molar; $[Mn(III)]_0 = 1.96–6.55 \times 10^{-4}\ M$. [b] Ionic strength adjusted with Mn(II), except where noted otherwise. [c] Units are M^{-1} sec^{-1}. [d] $[Mn(II)] = 0.06\ M$, $[NaClO_4] = 0.12\ M$. [e] $[Mn(II)] = 0.18\ M$, $[NaClO_4] = 1.2\ M$. [f] $[Mn(II)] = 0.30\ M$, $\mu = 2.30\ M$. [g] $[Mn(II)] = 0.60\ M$, $\mu = 2.30\ M$. [h] $[Mn(II)] = 0.60\ M$, $[NaNO_3] = 1.60\ M$; $[Mn(III)]_0$ was estimated from initial absorbance using extinction coefficient in perchlorate media.[4]

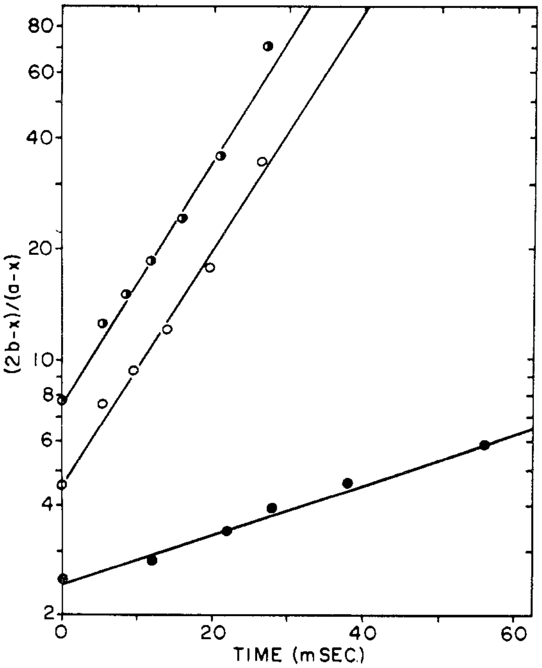

Figure 4.—Typical second-order plots for reaction with HNO_2. The conditions are: ◑, $[HClO_4] = 0.50\ M$, $[Mn(II)] = 0.60\ M$, $[NaNO_3] = 1.60\ M$, $[Mn(III)]_0 = a = 2.55 \times 10^{-4}\ M$, $[HNO_2]_0 = b = 10.0 \times 10^{-4}\ M$; ○, $[HClO_4] = 2.16\ M$, $[Mn(II)] = 0.56\ M$, $a = 6.55 \times 10^{-4}\ M$, $b = 15.0 \times 10^{-4}\ M$; ●, $[HClO_4] = 3.60\ M$, $[Mn(II)] = 0.10\ M$, $a = 4.13 \times 10^{-4}\ M$, $b = 5.0 \times 10^{-4}\ M$.

Two assumptions are fundamental to mechanistic descriptions of the reactions we have studied. These are (1) that all protolytic equilibria are rapid in comparison to the rate-determining steps and (2) that a radical mechanism operates for each reaction. The first assumption is germane to all three reductants, whereas the involvement of free radicals has to be discussed in the special context of each reaction. We shall therefore follow the pattern of the previous section and consider assumption 1 in general and then treat the individual reactions in detail.

Acid–base equilibria of the type involved with Mn^{3+}–$MnOH^{2+}$ and each of the reductants studied are generally very rapidly established—in times of the order of microseconds for the concentrations employed here.[14] It is well known that when both partners in a reaction participate in a rapid protolytic preequilibrium, it is not possible to establish the true molecular identity of the activated complex.[15] When, however, the acidity range covered is very far from the region $[H^+] \approx 1/K_{\text{acid}}$, it is often possible to rule out one of the species in the conjugate acid–base pair, as in the oxidation of hydrogen peroxide by manganese(III) in acid (1–4 M) perchlorate.[7]

For O-methyl- and hydroxylamine the acid dissociation constant is of the magnitude $K_a = [H^+] \cdot [\text{base}]/[\text{acid}] \sim 10^{-6}\ M$. Therefore, if we assume that the contribution from the inverse (base) pathway is within the experimental limit of ±10%, then the rate constant for this reaction would be given by $k_{NH_2OH} \simeq$

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[14] M. Eigen, W. Kruse, G. Maass, and L. De Maeyer, *Progr. Reaction Kinetics*, **2**, 287 (1964).

[15] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1961, p 307.

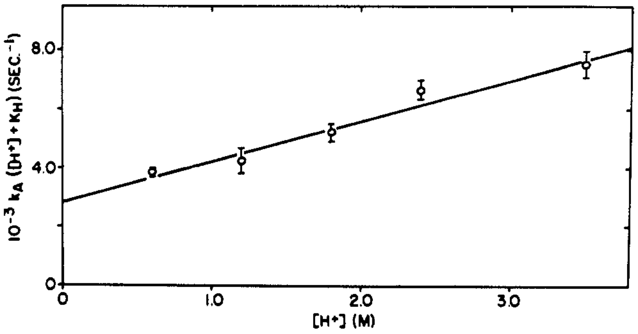

Figure 5.—Plot of $10^{-3}k_A([H^+] + K_H)$ vs. $[H^+]$ for reaction with hydroxylamine, using the value $K_H = 0.93\ M$ at 25°.

$10^{-1}([H^+]k_A/K_a)$ (for hydroxylamine) and similarly for the O-methyl derivative. At $[H^+] \simeq 1\ M$ we calculate $k_{NH_2OH} \approx 10^9\ M^{-1}\ sec^{-1}$, which is close to the diffusion-controlled limit for a reaction of this charge type. Consequently, for the two hydroxylamine substrates, the reducing species will be assumed to be unequivocally NH_3OH^+ and $NH_3OCH_3^+$. Since the nitrite ion is too weak a base to apply the foregoing assumptions, a somewhat more circumspect treatment will be used. This type of analysis will be provided as we consider each reaction separately.

Hydroxylamine.—With [Mn(III)] representing the concentration of total oxidized manganese and NH_3OH^+ the reducing species, the following mechanism may be applied to the disappearance of manganese(III) to obtain the empirical rate equation (I)

$$Mn^{3+} + NH_3OH^+ \xrightarrow{k_1} Mn^{2+} + NH_2O\cdot + 2H^+ \quad (1)$$

$$MnOH^{2+} + NH_3OH^+ \xrightarrow{k_1'} Mn^{2+} + NH_2O\cdot + H_3O^+ \quad (1')$$

$$2H_2O + 5Mn(III) + NH_2O\cdot \xrightarrow{k_2} 5Mn(II) + NO_3^- + 6H^+ \quad (2)$$

In this mechanism only reactions 1 and 1′ are meant to represent single-step processes. However, it is postulated that, for the composite process (2), $k_2 \gg k_1, k_1'$. Assuming that all protolytic equilibria are rapidly established with respect to reactions 1 and 2 it may be shown that

$$k_A = \frac{k_1[H^+] + k_1'K_H}{[H^+] + K_H} \quad (IV)$$

In Figure 5 the function $k_A([H^+] + K_H)$ is plotted against $[H^+]$ from which the values $k_1 = (1.2 \pm 0.2) \times 10^3\ M^{-1}\ sec^{-1}$ and $k_1' = (3.4 \pm 0.3) \times 10^3\ M^{-1}\ sec^{-1}$ are obtained.

O-Methylhydroxylamine.—With $NH_3OCH_3^+$ as the reducing species and applying the same assumptions as for the hydroxylamine reaction, a mechanism consistent with (II) is

$$Mn^{3+} + NH_3OCH_3^+ \xrightarrow{k_3} Mn^{2+} + \cdot NHOCH_3 + 2H^+ \quad (3)$$

$$MnOH^{2+} + NH_3OCH_3^+ \xrightarrow{k_3'} Mn^{2+} + \cdot NHOCH_3 + H_3O^+ \quad (3')$$

$$2(\cdot NHOCH_3) \xrightarrow{k_4} N_2H_2(OCH_3)_2 \quad (4)$$

with $k_4 \gg k_3, k_3'$.

An initial treatment of the data according to the equation analogous to (IV) indicated that $k_3[H^+] \ll k_3'K_H$. Consequently, a plot of $1/k_B$ vs. $[H^+]$ should be linear, as shown in Figure 6. From this plot we have determined $k_3' = 6.3 \pm 0.4\ M^{-1}\ sec^{-1}$; we also estimate $k_3 < 0.5\ M^{-1}\ sec^{-1}$ in the range 0.5–3.0 M $HClO_4$.

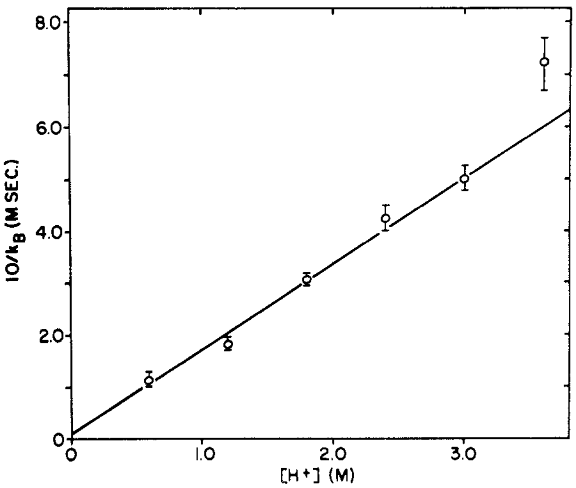

Figure 6.—Plot of $10/k_B$ vs. $[H^+]$ for reaction with O-methylhydroxylamine at 25°.

Nitrous Acid.—Since the nitrite ion is the weakest base of the series, it is necessary to consider a more complete mechanism for the rate-determining steps. Thus, the reaction with nitrite in strong acid solution should be written as

$$Mn^{3+} + HNO_2 \xrightarrow{k_5} Mn^{2+} + H^+ + \cdot NO_2 \quad (5)$$

$$MnOH^{2+} + HNO_2 \xrightarrow{k_5'} Mn^{2+} + H_2O + \cdot NO_2 \quad (5')$$

$$Mn^{3+} + NO_2^- \xrightarrow{k_6} Mn^{2+} + \cdot NO_2 \quad (6)$$

$$MnOH^{2+} + NO_2^- \xrightarrow{k_6'} Mn^{2+} + \cdot NO_2 + OH^- \quad (6')$$

$$H_2O + Mn(III) + \cdot NO_2 \xrightarrow{\text{very fast}} Mn^{2+} + NO_3^- + 2H^+ \quad (7)$$

with (7) as the fastest process. Under these conditions one may derive an expression identical with the empirical rate law (eq III) where

$$k_C = \frac{k_5[H^+] + k_5'K_H + k_6K_a + (k_6'K_aK_H/[H^+])}{[H^+] + K_H} \quad (V)$$

and $K_a = [NO_2^-][H^+]/[HNO_2] \approx 10^{-3}\ M$.

As a starting hypothesis, we assumed that the last term in the numerator would be smaller than any of the other three terms (on the grounds that this term contains the quotient $K_aK_H/[H^+] \ll 1$). We therefore plotted $k_C([H^+] + K_H)$ vs. $[H^+]$, which should then be linear, as is indeed the case (Figure 7). This treatment yields the rate constant k_5 from the slope, but the intercept is $k_5'K_H + k_6K_a$, representing the two kinetically indistinguishable pathways, as discussed above. However, we may draw upon two observations to make an assignment. First, other studies[9] suggest that $k_6' \approx k_6$. If this condition also holds for the reaction with manganese(III), then it follows that $k_6K_a \approx k_6'K_aK_H/[H^+]$; therefore, since omission of the k_6' term was justifiable, so too is neglect of k_6K_a with

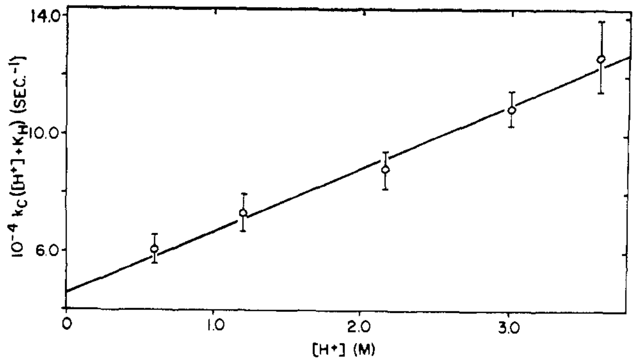

Figure 7.—Plot of $10^{-4}k_C([H^+] + K_H)$ *vs.* $[H^+]$ for reaction with nitrous acid, using the value $K_H = 0.93$ *M* at 25°.

respect to $k_5'K_H$. From Figure 7 and the foregoing argument we obtain $k_5 = (2.2 \pm 0.3) \times 10^4$ M^{-1} sec^{-1}, intercept $= (k_5'K_H + k_6K_a) = (4.6 \pm 0.4) \times 10^4$ M^{-1} sec^{-1}, and $k_5' \simeq (4.9 \pm 0.4) \times 10^4$ M^{-1} sec^{-1}.

Discussion

The kinetic results of this study, with those obtained from an investigation of the reaction between Mn(III) and H_2O_2, are collected together in Table IX. It is apparent from this grouping that, whereas the differences among the first three substrates are slight, $NH_3OCH_3^+$ is appreciably less reactive than the others. The differences in hydrogen bonding in these systems may be an important factor in determining the relative rates of these reactions, being favored for the first three substrates in Table IX but less likely for O-methylhydroxylamine.

Table IX

Rate Constants for Reactions of Mn^{3+} and $MnOH^{2+}$ with Selected Substrates in Perchlorate Media at 25°

Substrate	*k*, M^{-1} sec^{-1}	
	Mn^{3+}	$MnOH^{2+}$
H_2O_2[a]	7.3×10^4	3.2×10^4
HNO_2	2.2×10^4	4.9×10^3
NH_3OH^+	1.2×10^3	3.4×10^3
$NH_3OCH_3^+$	<0.5	6.1

[a] Reference 7.

Electron transfer to Mn^{3+} (the only mode of attack reasonable for this species) and H atom transfer to $MnOH^{2+}$ could both occur. In the absence of further evidence (*e.g.*, experiments in D_2O) we cannot eliminate the possibility that both Mn(III) species react *via* electron transfer with all four substrates, each of which contain a suitable coordinating site and three of which are strongly hydrogen bonded in solution. Coordination is not as easy and H bonding is greatly reduced in O-methylhydroxylamine.

Complex formation between reactants has been implicated in previous studies of oxidation reactions of this type. Although it cannot be ruled out, no direct evidence was obtained for the presence of complexes. The lack of clear evidence for complex formation such as was found, for example, in the reaction with HN_3,[11,16] would indicate the presence of very weak complexes.

The radical $NH_2O\cdot$ is apparently more easily oxidized than is $\cdot NHOCH_3$. Waters and Wilson[2b] have postulated from stoichiometric measurements that dimerization of $NH_2O\cdot$ produces N_2 in the oxidation of hydroxylamine by Ce(IV) in H_2SO_4, as in

$$2NH_2O\cdot \longrightarrow N_2 + 2H_2O \qquad (8)$$

The stoichiometry of this reaction is acid dependent,[2a] however, and the rates of reaction are much lower than for Mn(III), where N_2 appears as a minor product only in the presence of large excesses of NH_3OH^+ (Table V).

The simplest explanation for the stoichiometry of the O-methylhydroxylamine reaction can be given in terms of a radical dimerization reaction analogous to (8) to give $CH_3ONHNHOCH_3$ as a product at low *R*. We have found[9] that 1,2-dimethylhydrazine is oxidized with a stoichiometry of $\Delta[Mn(III)]/\Delta[CH_3NH_2NHCH_3^+] = 4$ under the present conditions, which would be consistent with a stoichiometry of $\Delta[Mn(III)]/\Delta[CH_3ONH_3^+] = 3$ at high *R*, if the reactivities of these two molecules are similar. Characterization of this product at low *R* has not been attempted, however, since it would be extremely difficult in the presence of such a large excess of substrate. The apparent deviation from linearity at $[HClO_4] > 3.0$ *M* may be due to the presence of more highly protonated species at higher acidities.

The high rate of oxidation of nitrous acid by Mn(III) compared to that of hydroxylamine makes it a likely intermediate in the oxidation of NH_3OH^+. A radical mechanism (eq 5–7) might be expected by comparison of the rate constants with those for reaction with H_2O_2 (Table IX).

None of the present reactions exhibits the retarding effect on the rate of increasing [Mn(II)] which is a feature of the oxidation of HN_3 (at high excess of substrate)[11] and H_2O_2.[7] The radicals formed are therefore much weaker oxidizing agents than those formed in the previously studied systems. The observation that reaction rates are also independent of a large excess of nitrate and qualitative examination of the spectrum of Mn(III) in nitric acid[17] strongly suggest that, at most, only very weak complexes are formed between Mn(III) and nitrate. Thus, extinction coefficients of the species in the two media are very similar in the visible region.

The most rapid reaction in the series, that with nitrous acid, may proceed in the inner sphere of the oxidant, with water exchange on Mn^{3+} or $MnOH^{2+}$ as the rate-determining process. If the reaction with NH_3OH^+ is also inner sphere, then the rate might be expected to be lower than that of nitrous acid because of the positive charge on the reductant.

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(16) C. F. Wells and D. Mays, *J. Chem. Soc., A*, 1622 (1968).

(17) G. Davies and K. Kustin, unpublished results.