2(acac))$^+$ peak (VII) increases, as would be expected from this approach.

In discussing these results we have not considered the geometry of the species, *e.g.*, whether the L_2Cr^+ ions are tetrahedral or square planar. We have assumed that any geometrical rerrangement does not have a great effect on the mass spectra. The results suggest that this is a valid assumption, since, apart from the electronic effects of one ring at the central metal atom, the rings fragment independently of each other, and in most cases one ring fragments completely before fragmentation of the next begins.[3]

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CALIFORNIA STATE COLLEGE AT LOS ANGELES, LOS ANGELES, CALIFORNIA 90032

A Proton Magnetic Resonance Ligand Preference Study of Complexes of Acetone, Diethyl Ether, N,N-Dimethylformamide, Dimethyl Sulfoxide, Tetrahydrofuran, Tetramethylene Sulfone, Tetramethylene Sulfoxide, and Tetramethylurea with Boron Trifluoride

BY ANTHONY FRATIELLO AND RONALD E. SCHUSTER

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A proton magnetic resonance ligand preference study of complexes of acetone (A), diethyl ether (EE), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), tetramethylene sulfone ($TMSO_2$), tetramethylene sulfoxide (TMSO), and tetramethylurea (TMU) with boron trifluoride has been completed. By adding boron trifluoride to pure, excess ligand and cooling to temperatures suitable to slow solvent exchange, proton magnetic resonance signals were observed for bulk and complexed ligand molecules. By studying samples containing two organic bases and integrating all signal areas, a direct, quantitative measure was made of the amount of boron trifluoride complexed by each component. In this way complexing ability was estimated to decrease in the order TMSO > DMF, DMSO > TMU ≫ THF ≫ EE > A > $TMSO_2$. This order reflects the relative basic strengths of these molecules toward BF_3.

Introduction

Many calorimetric[1-5] and spectroscopic[6-12] studies of metal ion or boron trihalide complexes have been carried out with the purpose of assessing the relative acceptor strengths of these Lewis acids or the donor strengths of the variety of organic bases investigated. Some of these representative calorimetric studies include complexes of the boron trihalides with pyridine and nitrobenzene,[1] alkyl ethers, sulfides, and amines,[2] and dimethyl sulfoxide and ethyl acetate.[3] By similar methods, the relative acceptor strengths of the gallium halides toward pyridine and triethylamine[4] and ethyl ether and methyl and ethyl sulfides[5] have been estimated. Nuclear magnetic resonance (nmr) chemical shift investigations of boron trihalide complexes include ligands such as trimethylamine,[6] ethers,[7,8] benzophenone, pyridine, and triethylamine (^{11}B resonance),[9] N,N-dimethylformamide,[10] ureas and thioureas,[11] and water (^{19}F and proton resonance).[12] The proton magnetic resonance (pmr) studies are based on the observation of chemical shift differences between pure ligand and the presumed 1:1 complex, each investigated in an inert solvent. It has been demonstrated recently[13-15] that a more quantitative approach involves the study of the complex in the presence of excess ligand, at temperatures low enough to slow solvent exchange and permit the direct observation of pmr signals of bulk and complexed molecules of the base. This method allows a more accurate measure of the chemical shift separation between pure and complexed ligand proton signals and a quantitative measure of the composition of the complex. Systems already reported include ethers,[13,14] pyridines,[15] and several biochemicals.[15]

Another problem which has been approached by a variety of experimental methods is the evaluation of

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relative basicities of organic molecules. In a comprehensive review of a wealth of protonation basicity data, Arnett[16] has pointed out many of the difficulties encountered with these conductivity, cryoscopic, spectroscopic (nmr, Raman, uv), and titration techniques, among others. The pmr method to be discussed here may provide a more suitable way of estimating relative basicities toward a variety of Lewis acids in a less ambiguous manner. The compounds chosen, namely, acetone (A), diethyl ether (EE), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), tetramethylene sulfone ($TMSO_2$), tetramethylene sulfoxide (TMSO), and tetramethylurea (TMU), are commonly used, oxygen-containing bases, for most of which proton basicity data are available. Thus it was anticipated that the utility of this method would be clearly demonstrated.

Experimental Methods

All solvents were of the highest commercial quality available, and with the exception of acetone and DMF, which decompose with such treatment, they were dried over molecular sieves before use. Samples were prepared *in vacuo* by adding fractionated BF_3 to mixtures of the pure solvents. They were then sealed and stored in liquid nitrogen until the spectrum could be recorded. Duplicate samples were prepared for each system.

The spectra and peak area integrations were recorded in triplicate on a Varian A-60 nmr spectrometer, equipped with a variable-temperature device permitting measurements from −150 to +200°. The experiments were carried out by preparing a sample containing two organic bases and BF_3, cooling the sample to slow solvent exchange, and recording the spectrum, which revealed in all cases signals arising from bulk and complexed molecules of one or both solvent components. Peak area integrations then gave a quantitative measure of the amount of BF_3 complexed by each solvent component. A more complete description of the pmr experiments has been provided previously.[13-15]

Results

The amounts of BF_3 complexed by each solvent component of several mixtures are summarized in Table I. Listed in the first column of Table I are the mole ratios of the systems studied, each containing two bases in approximately equal amounts, and BF_3.

TABLE I

FRACTIONS OF BF_3 COMPLEXED IN PAIRWISE MIXTURES OF ACETONE (A), DIETHYL ETHER (EE), N,N-DIMETHYLFORMAMIDE (DMF), DIMETHYL SULFOXIDE (DMSO), TETRAHYDROFURAN (THF), TETRAMETHYLENE SULFONE ($TMSO_2$), TETRAMETHYLENE SULFOXIDE (TMSO), AND TETRAMETHYLUREA (TMU)

A	B	A:B:BF_3	Temp, °C	Fractions of BF_3 complexed A	B
DMSO	TMSO	5.0:5.0:1	+32	0.33	0.67
DMSO	TMSO	6.3:3.1:1	+32	0.47	0.55
DMF	DMSO	5.0:5.0:1	0	0.46	0.44
DMF	TMU	5.0:5.0:1	0	0.83	0.13
DMSO	$TMSO_2$	4.7:4.7:1	−10	0.94	...
DMSO	THF	5.0:5.0:1	0	0.96	...
THF	TMU	4.8:4.8:1	−30	...	0.96
A	THF	4.9:4.9:1	−70	...	1.09
A	EE	4.9:4.9:1	−90	0.46	0.52

(16) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

The temperatures at which the integrations were made are given in column 2. In the next two columns, the fractions of the BF_3 complexed by the solvent components in each system are given. A lack of an entry in the A–THF, DMSO–THF, DMSO–$TMSO_2$, and THF–TMU systems indicates signals for complexed molecules of the particular component were not observed. The quantities listed in columns 3 and 4 are precise to approximately 5–10%, as a result of small errors in sample preparation and signal integration. The low total of about 0.9 for the fraction of BF_3 complexed in the DMF–DMSO system was reproducible and it may reflect some sample decomposition, probably of the DMF. Results obtained with methanol and ethanol are not included in Table I for reasons to be mentioned later. Several of the spectra from which the data of Table I were derived are shown in Figures 1-5.

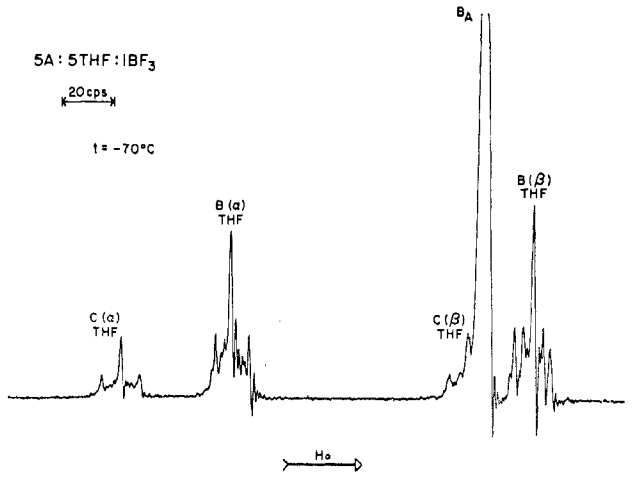

Figure 1.—The proton magnetic resonance spectrum of a 5:5:1 mole ratio mixture of A–THF–BF_3, recorded at −70°, on a Varian A-60 spectrometer. Signals arising from bulk [$B_{THF}(\alpha)$ and $B_{THF}(\beta)$] and complexed [$C_{THF}(\alpha)$ and $C_{THF}(\beta)$] THF and bulk acetone (B_A) are labeled in the figure.

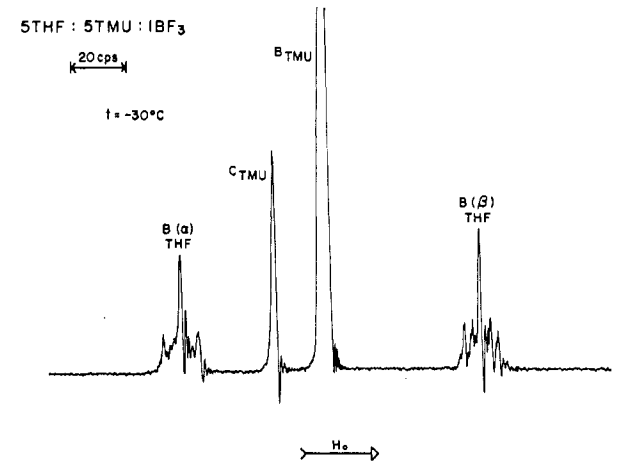

Figure 2.—The proton magnetic resonance spectrum of a 5:5:1 mole ratio mixture of THF–TMU–BF_3, recorded at −30°, on a Varian A-60 spectrometer. Signals arising from bulk THF [$B(\alpha)$ and $B(\beta)$] and bulk (B_{TMU}) and complexed (C_{TMU}) TMU are labeled in the figure.

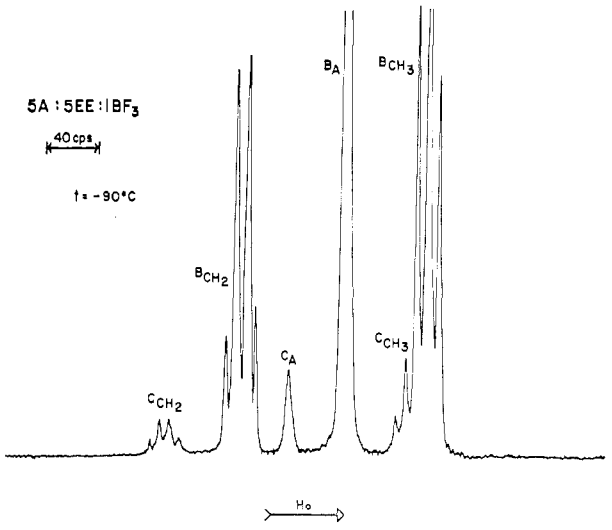

Figure 3.—The proton magnetic resonance spectrum of a 5:5:1 mole ratio mixture of A–EE–BF_3, recorded at −90°, on a Varian A-60 spectrometer. Signals arising from bulk (B_A) and complexed (C_A) acetone and bulk (B_{CH_2} and B_{CH_3}) and complexed (C_{CH_2} and C_{CH_3}) diethyl ether are labeled in the figure.

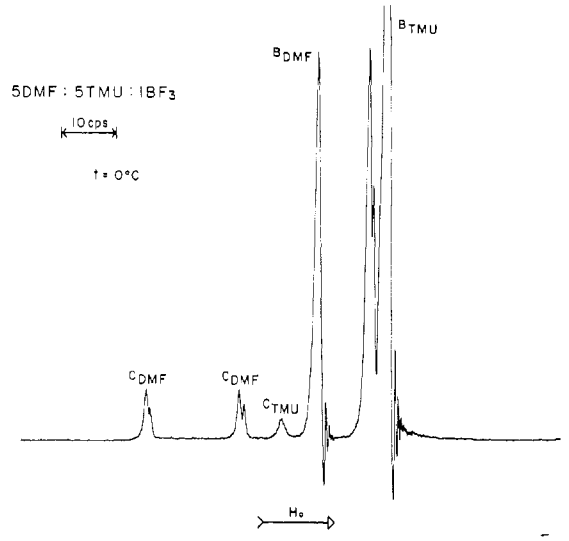

Figure 5.—The proton magnetic resonance spectrum of a 5:5:1 mole ratio mixture of DMF–TMU–BF_3, recorded at 0°, on a Varian A-60 spectrometer. Signals arising from bulk (B_{DMF}) and complexed (C_{DMF}) DMF and bulk (B_{TMU}) and complexed (C_{TMU}) TMU are labeled in the figure.

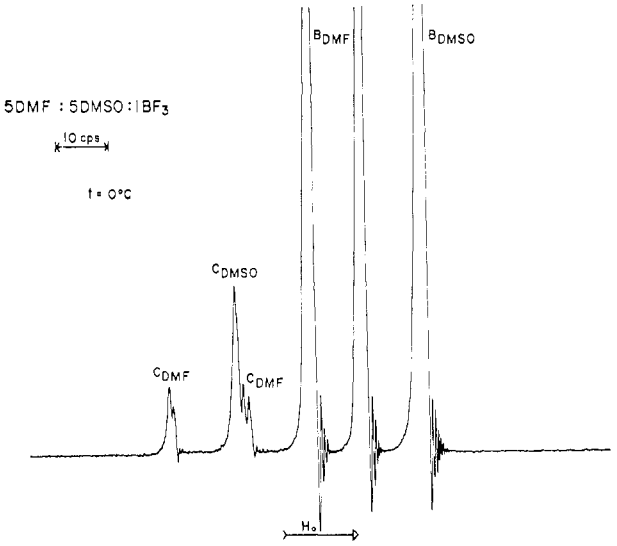

Figure 4.—The proton magnetic resonance spectrum of a 5:5:1 mole ratio mixture of DMF–DMSO–BF_3, recorded at 0°, on a Varian A-60 spectrometer. Signals arising from bulk (B_{DMF}) and complexed (C_{DMF}) DMF and bulk (B_{DMSO}) and complexed (C_{DMSO}) DMSO are labeled in the figure.

Discussion

As illustrated in Figures 1–5 which show the pmr spectra of several solutions of two organic bases and BF_3, signals arising from protons of complexed ligand molecules are clearly evident, and although broader, they are similar in all respects to the corresponding bulk solvent signals. The large signal separations allow accurate integrations of all peak areas, and, consequently, as shown in Table I, they permit a quantitative measure of the ability of solvents to compete directly with each other for BF_3. This is a much more reliable way of estimating ligand preferences than studying the solvents individually with BF_3 and drawing conclusions in an indirect manner.

In the DMSO–THF, DMSO–$TMSO_2$, and as illustrated in Figures 1 and 2, respectively, the A–THF and THF–TMU solutions, the BF_3 is complexed solely by one component within experimental error. For example, while THF complexes BF_3 completely within the limit of the measurements in an acetone solution (Figure 1), it is unable to compete with TMU (Figure 2). In the remaining systems listed in Table I, represented in part by Figures 3–5 for the BF_3 solutions of A–EE, DMF–DMSO, and DMF–TMU, respectively, an active competition for the Lewis acid was reflected by the appearance of resonance signals for bulk and complexed molecules of each solvent component. From such spectral observations and from the integration results listed in Table I, the complexing ability of the eight solvents toward BF_3 decreases in the order TMSO > DMF, DMSO > TMU ≫ THF ≫ EE > A > $TMSO_2$. Because of the high freezing point of $TMSO_2$, this solvent could not be studied directly with acetone or ether, which requires low temperatures for measurement. Thus, the position of $TMSO_2$ in this series is assumed, principally on the basis of the work of Arnett and Douty,[17] who demonstrated that the basicity of this compound in aqueous acid solution is comparable to that of nitromethane, which has a $pK_{BH^+} = -12$.

In Table II, the dipole moments of most of these solvents[18,19] and their relative basicities in aqueous solution, as indicated by their pK_{BH^+} values,[16,20,21]

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TABLE II
SOLVENT DIPOLE MOMENTS AND RELATIVE BASICITIES

Solvent	TMSO	DMF	DMSO	TMU	THF	EE	A	$TMSO_2$
μ, D	(4)	3.9	3.9	3.9	1.6	1.1	2.8	4.7
pK_{BH^+}	(0–1)	0	+1 to −3	(−1)	−2	−3.5	−7	(<−7)

are listed. Although the dipole moment of TMSO is not available, it is most likely as polar in nature as DMSO and $TMSO_2$. Numerical values for the relative basicities of TMSO, $TMSO_2$, and TMU also could not be found, although as previously mentioned the low basic strength of $TMSO_2$ has been demonstrated.[17] A value of pK_{BH^+} equal to −1 is included in Table II for TMU, this value corresponding to the basicity of urea and N-methylurea.[16] One must recognize the inherent differences between aqueous solution media and the solvent systems under study here, mixtures of two organic bases. Thus pK_{BH^+} values may reflect solvation effects, similar to that recently proposed for the 2,6-di-*t*-butylpyridine system.[22] In addition, the more bulky nature of a Lewis acid such as BF_3 introduces the possibility of steric hindrance to complex formation. Thus, while the relative basicities of the compounds in Table I toward BF_3 are established by this nmr method, any correlation of these basicity results with those observed in aqueous solution must be made with caution, and it can only be qualitative.

From Tables I and II, it is obvious that a correlation of complexing ability with dipole moment does not exist. For example, acetone and $TMSO_2$ have dipole moments similar in magnitude to those of DMF and DMSO, yet the latter are much more effective in complexing BF_3. Also, EE and THF complex BF_3 more readily than acetone, which has a higher dipole moment. However, a similarity of this trend in complexing ability with the relative basicities of the eight solvents in aqueous solution is evident. The most basic compounds in aqueous solution, DMF and the sulfoxides, readily complex BF_3, while weakly basic A, EE, THF, and $TMSO_2$ are much less effective in this regard. These results exactly parallel those obtained by several nmr solvation studies of Al(III) in aqueous mixtures of all of the solvents listed in Table I, with the exception of EE.[23–25] Coordination numbers obtained by direct observation and integration of proton resonance signals arising from bulk and complexed water molecules and molecules of the nonaqueous component revealed a trend in complexing ability toward Al(III), similar to that observed here using BF_3. For example, while DMF, DMSO, and TMSO were able to solvate Al(III) in aqueous solution, acetone, THF, TMU, and $TMSO_2$ were completely inactive and behaved merely as diluents.

A comparison of the results shown in Table I and the relative aqueous solution basicities of Table II seems to indicate that if the pK_{BH^+} values of two ligands differ by more than 1 unit, complexing of BF_3 will occur primarily by the more basic component, in the absence of the solvation and steric effects mentioned above. For example, TMU ($pK_{BH^+} = -1$) complexes only a small fraction of BF_3 in the presence of the more basic DMF ($pK_{BH^+} = 0$), but TMU complexes all of the BF_3, within experimental error, in a mixture with THF ($pK_{BH^+} = -2$). This empirical observation may imply that the pK_{BH^+} value of DMSO lies closer to 0 or 1,[21] rather than −3.[20] In aqueous solvent mixtures, as previously mentioned, DMSO also exhibits a greater basic strength toward hydrated Al(III) than THF or TMU.[23,25] However, in view of the problems involved with drawing an analogy to aqueous solution results, this feature should serve only as a stimulus for further experimentation and comparison.

The different basicities exhibited by A and EE in aqueous solution and toward BF_3 reflect the steric and, perhaps, the solvation effects noted previously. Since these compounds complex almost equal fractions of BF_3, their relative basic strengths in these systems must be about equal. Molecular models indicate the A–BF_3 complex encounters much less steric hindrance than the BF_3 complex with the more bulky EE.

A brief comparison may be made of the two DMSO–TMSO mixtures studied. In a 5:5:1 mole ratio mixture of DMSO–TMSO–BF_3, respectively, TMSO complexes two-thirds of the BF_3 present. This fact implies a greater basicity for this molecule as compared to DMSO. However, one can compensate for the effect of basicity by adjusting concentrations, as shown by the second entry for this pair in Table I. When the concentration of DMSO is twice that of TMSO, the two components complex roughly equal amounts of BF_3.

Several measurements also were made of methanol and ethanol mixtures with DMF and DMSO but some confusing observations prevent any definite conclusions from being drawn. In these systems, separate resonance signals were observed for bulk and complexed molecules of DMF and DMSO, but only one set of signals for either alcohol. This in itself is not too surprising since a previous study of CH_3OH–BF_3 complexes[14] revealed a separation of only ~5 cps between the methyl proton signals of the bulk and complexed molecules. Also, the hydroxyl signals could not be separated even at −100°, presumably because of a very rapid proton exchange.[14] However, an integration of the DMF and DMSO signals resulting from their respective alcohol mixtures indicated only about 30% of the BF_3 was complexed by these compounds. This fraction decreased to about 0.20–0.25 when the samples were allowed to stand at room temperature for any period of time. Since this fact may reflect a decomposition of these alcohol samples or some process such as proton exchange, which occurs in these systems, the results which imply a greater basicity of the alcohols

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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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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BRANDEIS UNIVERSITY, WALTHAM, MASSACHUSETTS 02154

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

BY G. DAVIES AND K. KUSTIN

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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.

(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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