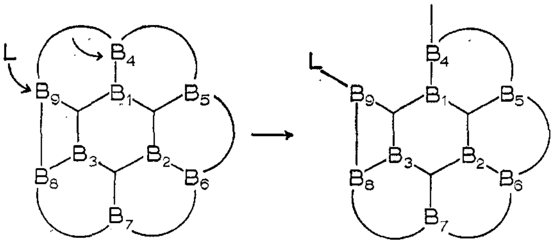
form a BH_2 group results in greater crowding with the bridge hydrogens than protonation of a 4,6,8 position.

Bridge–Terminal Exchange in $B_9H_{14}^-$.—The course of the scambling between bridge and 4,6,8 terminal hydrogens is probably similar to the intramolecular bridge migration in decaborane(14),[3,4] although an intermolecular process cannot be excluded on the basis of this study. The intramolecular exchange might begin with attack by a donor water molecule on a 5,7,9 boron followed by a shift of the associated bridge deuterium to an adjacent 4,6,8 boron to form a BHD group. Such an intermediate is related to the hypothetical 4342 $B_9H_{15}^{2-}$ (eq 2). The slow appearance of deuterium in bridge positions in acidic deuterium oxide probably also occurs by this process.



(2)

Base-Catalyzed Exchange.—A probable mechanism for bridge exchange in weakly basic deuterium oxide involves removal of a slightly acidic bridge proton by a deuterioxide ion to form a doubly charged $B_9H_{13}^{2-}$ intermediate (eq 3).

$$B_9H_{14}^- + OD^- \longrightarrow [B_9H_{13}^{2-}] + HDO \qquad (3)$$

$$[B_9H_{13}^{2-}] + D_2O \longrightarrow \mu\text{-}B_9H_{13}D^- + OD^-$$

The exchange of both bridge and 4,6,8 terminal hydrogens in strongly basic deuterium oxide has no parallel in the known reactions of decaborane(14). One possible course is direct removal of protons from both sites by deuterioxide ion under highly alkaline conditions, but a more satisfying explanation might simply be an enhanced rate of intramolecular exchange brought about by the high concentration of the more nucleophilic deuterioxide ion.

Bridge–Terminal Exchange in Isononaborane(15).—Exchange of bridge and terminal hydrogens is established for a few of the more labile boron hydrides such as tetraborane(10),[12] although little is known about the details of these processes. It is somewhat curious that only the 4,6,8 terminal hydrogens appear to participate in exchange with the hydrogen bridges in isononaborane(15). Unfortunately the experiments described in this paper shed little light upon how this process occurs, or even whether the reaction is inter- or intramolecular. At the present time there is little basis for speculation on this interesting phenomenon.

[12] A. D. Norman and R. Schaeffer, *Inorg. Chem.*, **4**, 1225 (1965).

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Proton Magnetic Resonance Study of Aluminum(III) Chloride in Water–Dimethyl Sulfoxide Solvent Mixtures

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In water–dimethyl sulfoxide solvent mixtures the aluminum(III) ion is preferentially solvated by water at water mole fractions approximately equal to 0.80 or greater and by dimethyl sulfoxide at water mole fractions approximately equal to 0.75 or less. Evidence is presented that bonding water molecules donate more charge to the central aluminum(III) ion in the solvated $Al(DMSO)_n(H_2O)_{6-n}{}^{3+}$ ion than do bonding dimethyl sulfoxide molecules. Measurements of the rate of exchange of dimethyl sulfoxide molecules between coordinated and bulk solvent sites suggest that dimethyl sulfoxide molecules can exchange by two mechanisms: direct exchange of dimethyl sulfoxide molecules between bulk and coordinated sites at mole fractions of water less than 0.75 and indirect exchange of dimethyl sulfoxide molecules by replacement of dimethyl sulfoxide by water followed by replacement of water by dimethyl sulfoxide at mole fractions of water approximately equal to 0.8 and greater. Measurement of the water–proton exchange rates gave an apparent first-order rate constant with a hydrogen ion concentration dependence given by $k_{app} = k_1[H^+] + k_2/[H^+]$. The existence of the acid-catalyzed path is consistent with the results of Swift and coworkers for hydrated cations in aqueous media. The path dependent on $[H^+]^{-1}$ is consistent with the mechanism postulated by Fong and Grunwald for aqueous solutions of $AlCl_3$.

The solvation of aluminum(III) in various solvents has received considerable attention. The use of nuclear magnetic resonance techniques has given the value of 6 for the primary solvation number, *i.e.*, the number of solvent molecules in the first coordination shell, of aluminum(III) in water,[1-3] in dimethyl sulfoxide[4] (DMSO), in dimethylformamide[5,6] (DMF), and in ammonia.[7] In water–acetone, water–dioxane, wa-

[1] R. E. Connick and D. N. Fiat, *J. Chem. Phys.*, **39**, 1349 (1963).

[2] M. Alei and J. A. Jackson, *ibid.*, **41**, 3402 (1964).

[3] R. E. Schuster and A. Fratiello, *ibid.*, **47**, 1554 (1967).

[4] S. Thomas and W. L. Reynolds, *ibid.*, **44**, 3148 (1966).

[5] A. Fratiello and R. Schuster, *J. Phys. Chem.*, **71**, 1948 (1967).

[6] W. G. Movius and N. A. Matwiyoff, *Inorg. Chem.*, **6**, 847 (1967).

[7] H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *J. Am. Chem. Soc.*, **89**, 3065 (1967).

ter–tetrahydrofuran, and water–tetramethylurea mixtures the aluminum(III) ion preferentially bonded to water and the ion present was[8] $Al(H_2O)_6{}^{3+}$; in water–DMSO mixtures in the range 0.67–0.91 mole fraction water, the aluminum(III) ion did not discriminate between water and DMSO[8,9] although both solvents were present in the coordination shell giving $Al(H_2O)_{6-n}(DMSO)_n{}^{3+}$ ions in solution. In water–dimethylformamide mixtures some DMF was coordinated to the aluminum(III) ion but the water solvation number was not determined experimentally. Pseudo-first-order rate constants and enthalpies of activation for solvent molecule exchange between coordinated and bulk solvent sites have also been determined for water,[10] DMSO,[4] DMF,[5,6] and acetonitrile.[11] Rates of exchange of protons between $Al(OH_2)_6{}^{3+}$ coordination sites and bulk water sites have been determined as functions of pH and temperature and mechanisms of exchange have been postulated.[12] In the present work, we have extended the study of solvation of aluminum(III) over a wider range of experimental conditions for water–DMSO mixtures and found a change in the composition of the aluminum(III) solvation shell due to a change in the bulk solvent–solvent interaction. We have also determined DMSO and water–proton exchange rates at various water:DMSO ratios, acid concentrations, and temperatures.

Experimental Section

The DMSO was purified as previously described.[4] Sublimed anhydrous $AlCl_3$ was used to make the aluminum(III) solutions. The spectra were recorded with a Varian A-60 spectrometer equipped with a V-6020 heat exchanger and a V-6040 variable-temperature controller. Temperatures were measured with a copper–constantan thermocouple. Areas of absorption peaks were determined with the integrator of the spectrometer, a minimum of five times for each area determination. Shifts and line widths were measured by bracketing the resonance of interest with side bands.

Results and Discussion

Solvation Numbers of Aluminum(III).—In the absence of the aluminum salt, the pmr spectrum of a water–DMSO mixture showed two main peaks, one due to the methyl protons of DMSO at −152.5 cps downfield from DDS, sodium salt of trimethylsilylpropanesulfonic acid, and one due to the water protons which was downfield from the DMSO resonance. The spectrum also showed two small peaks due to the ^{13}C in DMSO. The position of the DMSO peak was independent of temperature and solvent composition within ±0.5 cps. This result strongly indicates that the methyl protons of DMSO are not involved in hydrogen bonding with water. The water–proton resonance was dependent on both solvent composition and temperature. The water–proton resonance shifted downfield with increasing water content as a result of the deshielding of the water protons caused by increased water–water hydrogen bonding at a given temperature.[18] The water–proton resonance shifted upfield with increasing temperature at constant solvent composition as a result of the breaking of water–water hydrogen bonds with increasing temperature. The shift was linearly dependent on the temperature with a slope of 0.52 ± 0.01 cps deg^{-1} over the range 240–280°K for mole fractions of water equal to 0.596, 0.652, 0.750, 0.808, and 0.895.

TABLE I

SOLVATION NUMBERS OF Al(III) FOR DMSO AND WATER AS A FUNCTION OF SOLVENT COMPOSITION[a]

H_2O:DMSO[b]			n_{DMSO}[c]	n_{H_2O}[c]
Total	Free	Bound		
1.56	1.67	1.1	2.8	3.1
1.79	2.09	1.1	2.8	3.1
2.44	2.87	1.3	2.6	3.4
2.98	3.62	1.7	2.2	3.7
3.47	3.49	3.4	1.4	4.7
4.15	4.10	4.9	1.0	4.9
5.87	5.84	6.4	0.8	5.1
8.38	8.33	8.6	0.6	5.2

[a] The integrations were carried out where the signals were sharpest. [b] Mole ratios of total, free, and coordinated solvent calculated only on the basis of the solvents present. [c] The error in these numbers is approximately ±0.1.

The results of the measurements of solvation numbers of aluminum(III) are given in Table I.

It is observed from Table I that the total solvation number of aluminum(III) was approximately 6 in agreement with Fratiello and Schuster.[9,14] Furthermore, it is also observed that, for total water:DMSO mole ratios equal to 3 or less, aluminum(III) preferentially bonded to DMSO because the ratio of coordinated water:DMSO is significantly less than the water:DMSO ratio for the total amounts of solvent present. At the three largest total water:DMSO ratios the aluminum(III) preferentially bonded to water because the mole ratio of the coordinated solvents is significantly greater than the mole ratio for the total solvents. This shift of preferential bonding from water to DMSO with decreasing water concentration has not been reported before and it can be explained on the basis of solvent structure. Many physical properties of water–DMSO mixtures show an extremum at a 2:1 water:DMSO mole ratio[15–18] and the activity coefficient of water[19,20] decreases rapidly at mole fractions of water less than 0.8, *i.e.*, at mole ratios of water:DMSO less than 4.0. Hence, at lower water mole fractions, the DMSO is preferentially bound to aluminum(III) because the water–DMSO interactions lower the water activity sufficiently to permit the change of preference from water to DMSO.

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(8) A. Fratiello, R. E. Lee, V. M. Nishida, and R. E. Schuster, *J. Chem. Phys.*, **47**, 4951 (1967); **48**, 3705 (1968).

(9) A. Fratiello and R. E. Schuster, *Tetrahedron Letters*, 4641 (1967).

(10) D. N. Fiat and R. E. Connick, *J. Am. Chem. Soc.*, **90**, 608 (1968).

(11) J. F. O'Brien, Ph.D. Thesis, University of Minnesota, 1968.

(12) D.-W. Fong and E. Grunwald, *J. Am. Chem. Soc.*, **91**, 2413 (1969).

(13) W. Drinkard and D. Kivelson, *J. Phys. Chem.*, **62**, 1494 (1958).

(14) A. Fratiello, R. E. Lee, V. M. Nishida, and R. E. Schuster, *Inorg. Chem.*, **8**, 69 (1969).

(15) J. M. G. Cowie and P. M. Toporowski, *Can. J. Chem.*, **39**, 2240 (1961).

(16) R. G. LeBel and D. A. I. Goring, *J. Chem. Eng. Data*, **7**, 100 (1962).

(17) R. N. Havenmeyer, *J. Pharm. Sci.*, **55**, 851 (1966).

(18) J. Kenttämaa and J. J. Lindberg, *Suomen Kemistilehti*, **B33**, 32 (1960).

(19) B. G. Cox and P. T. McTigue, *Australian J. Chem.*, **20**, 1815 (1967).

(20) J. Kenttämaa and J. J. Lindberg, *Suomen Kemistilehti*, **B33**, 98 (1960).

TABLE II
DEPENDENCE OF THE CHEMICAL SHIFT OF COORDINATED DMSO ON n_{DMSO}

n_{DMSO}	$-\Delta\nu_{\mathrm{DMSO}}$, cps	n_{DMSO}	$-\Delta\nu_{\mathrm{DMSO}}$, cps
2.8	18.0	1.0	14.6
2.6	16.5	0.8	14.0
2.2	16.0	0.6	13.5
1.4	15.2		

It has been observed previously[8] and we have corroborated the result that the number of DMSO molecules in the first coordination sphere of aluminum(III) increased with increasing $AlCl_3$ concentration for a given water:DMSO mole ratio in the solvent mixture. No explanation of this result could be given at that time.[8] A probable explanation of this behavior is that it results from increased chloride ion–water hydrogen bonding as the chloride ion concentration is increased. It is evident from the results given in Table I that the $AlCl_3$ is essentially completely ionized since no significant amount of chloride ion was present in the first solvation shell of aluminum(III). The increased quantity of chloride ion resulting from the increased $AlCl_3$ concentration is preferentially solvated by water because the solvent activity coefficient of chloride ion in DMSO with respect to a hydroxylic solvent is large.[21] The result is a decrease of the water activity by chloride ion and a preferential solvation of aluminum(III) by DMSO.

The solvation numbers n_{DMSO} and $n_{\mathrm{H_2O}}$ for a given $AlCl_3$ concentration and a given over-all solvent ratio were independent of perchloric acid concentration within experimental error over the range from 0.54 to 2.3 *M*. This result indicates that hydrogen ion does not show such a marked discrimination for either one of the solvents as does chloride ion. There is evidence to support this statement. Reynolds and Lampe[22] found, using the Hammett H_0 method, that the thermodynamic equilibrium constant for the dissociation of protonated DMSO in dilute aqueous solution was 100 mol/l. If this constant is divided by the concentration of water to give a unitless quanity and the resulting expression is given in terms of mole fraction, the result is

$$\frac{x_{\mathrm{DMSO}}x_{\mathrm{H_3O^+}}}{x_{\mathrm{DMSO\cdot H^+}}x_{\mathrm{H_2O}}} \simeq 2$$

In solvent mixtures containing equal mole fractions of water and DMSO, the ratio of hydrated to solvated protons is approximately 2; that is, the proton shows much less discrimination between the hydroxylic and aprotic solvents used than does chloride ion.[21]

The shift of the coordinated DMSO resonance relative to the uncoordinated DMSO resonance was dependent on the value of n_{DMSO} as shown in Table II. With decreasing n_{DMSO}, *i.e.*, increasing $n_{\mathrm{H_2O}}$, the coordinated DMSO peak moved upfield because the methyl protons became more shielded. This result indicates that there is more charge transfer from H_2O to the aluminum ion than there is from DMSO to the aluminum ion. Increased charge transfer to aluminum ion would decrease the importance to the Al(III)–DMSO bonding of the canonical structure

$$\mathrm{Al^{III}}-\underset{\cdot\cdot}{\ddot{\mathrm{O}}}-{}^{+}\mathrm{S(CH_3)_2}$$

which places a positive formal charge on the sulfur atom of the DMSO ligand and which decreases the shielding of the methyl protons.

TABLE III
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR EXCHANGE OF DMSO MOLECULES AT 25°

H_2O: DMSO[a]	$x_{\mathrm{H_2O}}$[a]	k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg mol
1.56	0.609	0.6	20.1 ± 2.0	8 ± 6
1.79	0.642	0.6	19.5 ± 1.5	6 ± 6
2.44	0.709	1.3	18.8 ± 0.6	5 ± 2
2.98	0.749	0.8	18.3 ± 1.5	2 ± 5
3.47	0.776	3.2	16.6 ± 1.2	−1 ± 4
4.15	0.806	3.6	11.0 ± 0.4	−20 ± 2
5.87	0.854	3.3	10.9 ± 1.1	−20 ± 4
8.38	0.893	3.8	10.6 ± 0.6	−21 ± 2

[a] Mole ratio and mole fraction based on total solvents only.

The breadth of the bound water peak obscured the shift, if any, of the coordinated water–proton peak with change in the composition of the first solvation shell.

DMSO Exchange.—The rate constant for exchange of DMSO between bulk and coordinated sites was calculated from the measured broadening of the coordinated DMSO line using the expression $k = 1/\tau = 2\pi\Delta\nu$, where τ is the average lifetime of a DMSO molecule in the aluminum(III) coordination shell and $\Delta\nu$ is the increase in half-width at half-height in cycles per second in the region where the line width is increasing due to chemical exchange. The activation enthalpy was determined from a least-squares plot of log $\Delta\nu$ *vs.* T^{-1} and the activation entropy was calculated from a knowledge of k and $\Delta H^{\ddagger}$ using the absolute rate theory expression for k. The results are listed in Table III.

The results in Table III suggest that there are two mechanisms for DMSO exchange, namely, direct exchange of coordinated and bulk DMSO molecules at high $\Delta H^{\ddagger}$ as in anhydrous DMSO solutions[4] and indirect exchange of coordinated DMSO by water followed by exchange of coordinated water by DMSO at low $\Delta H^{\ddagger}$. The former mechanism is favored at mole fractions of water less than 0.75 where the water activity is low and the latter at mole fractions of water greater than 0.8 where the activity of DMSO is low.

Water–Proton Exchange.—The rate constant for the exchange of protons between first-coordination-sphere sites and bulk solvent sites was calculated from the equation

$$k_{\mathrm{app}} = \frac{1}{\tau_{\mathrm{b}}} = \frac{P_{\mathrm{f}}}{P_{\mathrm{b}}}(2\pi\Delta\nu)$$

where τ_{b} is the average lifetime of a proton in the first-coordination-shell site, P_{f} and P_{b} are the fractions of water protons in the free and bound water molecules, and $\Delta\nu$ is the increase in half-width at half-height of the bulk water line.

Variation of perchloric acid concentration over the

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(21) R. Alexander and A. J. Parker, *J. Am. Chem. Soc.*, **89**, 5549 (1967).

(22) W. L. Reynolds and K. A. Lampe, *J. Inorg. Nucl. Chem.*, **8**, 2862 (1968).

TABLE IV

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR WATER–PROTON EXCHANGE AT 25° IN THE ABSENCE OF ACID

H_2O: DMSO	$10^{-3}k$, sec^{-1}	$\Delta H_2 ^{\ddagger}$, kcal/mol	$\Delta S ^{\ddagger}$, eu
1.56	0.5	9.2 ± 0.5	−15 ± 2
1.79	0.5	8.3 ± 0.6	−10 ± 2
2.44	1.0	7.4 ± 0.6	−20 ± 2
2.98	1.1	8.4 ± 0.6	−17 ± 2
3.47	1.7	8.4 ± 0.5	−16 ± 2
4.15	3.5	8.8 ± 0.5	−13 ± 2
5.89	5.4	10.8 ± 0.5	−5 ± 2
8.38	6.9	9.6 ± 0.5	−9 ± 2

range $0.20 \leqslant \mathrm{pH} \leqslant 1.23$ at constant temperature and solvent composition showed that the apparent first-order rate constant was given by $k_{app} = k_1[H^+] + (k_2/[H^+])$. The least-squares values of k_1 and k_2 at 7° for 0.67 mol fraction water were 420 ± 50 M^{-1} sec^{-1} and 35 ± 6 M sec^{-1}. Since the composition of the aluminum(III) coordination shell was independent of acid concentration, the observed hydrogen ion concentration dependence of k_{app} was not due to changes in the composition of the first solvation shell of aluminum. Instead, mechanisms such as those postulated by Swift and coworkers[23–25] may be used to explain the hydrogen ion catalyzed path.

The existence of a water–proton exchange path involving $[H^+]^{-1}$ is consistent with the results of Fong and Grunwald[12] for water–proton exchange in aqueous aluminum(III) chloride solutions in the pH range 2–3.3. Fong and Grunwald[12] obtained evidence that this path arose from reactions 1 and 2 where H is the exchanging proton. The concentration of (HO)Al$(H_2O)_5{}^{2+}$ was dependent on H^+ ion concentration. In water–DMSO mixtures, the chain reaction represented by reactions 1 and 2 may be expected to be much shorter than in water solutions because DMSO has replaced much of the water and recombination of $(HO)Al(H_2O)_5{}^{2+}$ with a proton from the bulk solvent phase will terminate the chain reaction. In this case the rate of supply of $(HO)Al(H_2O)_5{}^{2+}$ for reaction 1 by acid dissociation of $Al(H_2O)_6{}^{3+}$ may become the rate-limiting step in the absence of added acid. In Table IV are listed values of rate constants, k, and activation parameters obtained for various water:DMSO ratios in the absence of added acid. When log k was plotted *vs.* the inverse of the bulk dielectric constant, D^{-1}, as in Figure 1 and linearly extrapolated to the value of $D^{-1} = 1.27 \times 10^{-2}$ for pure water, it was found that for purely aqueous media $k \approx 2 \times 10^4$ sec^{-1}. In view of the possibility that the extrapolation may not be linear, this value in in reasonable agreement with the value of 7.9×10^4 sec^{-1} obtained by Fong and Grunwald[12] and of 1.1×10^5 sec^{-1} obtained by Holmes, Cole, and Eyring[26] by a field relaxation method. Also, a value of 3.7×10^4 sec^{-1} may be calculated from values of 1.1×10^{-5} M for the acid dissociation constant[27] and 3.4×10^9 M^{-1} sec^{-1} for the rate constant of the acid recombination reaction.[26]

$$(H_2O)_5Al(HO\mathit{H})^{3+}\cdot aq + (HO)Al(H_2O)_5\cdot aq \longrightarrow [(H_2O)_5Al(OH)^{2+}\cdot \mathit{H}OH\cdot(HOH)Al(H_2O)_5{}^{3+}] \longrightarrow (H_2O)_5Al(OH)^{2+}\cdot \mathit{H}OH\cdot aq + Al(H_2O)_6{}^{3+} \quad (1)$$

$$(H_2O)_5Al(OH)^{2+}\cdot \mathit{H}OH\cdot aq + HOH\cdot aq \longrightarrow (H_2O)_5Al(OH)\cdot aq + \mathit{H}OH\cdot aq \quad (2)$$

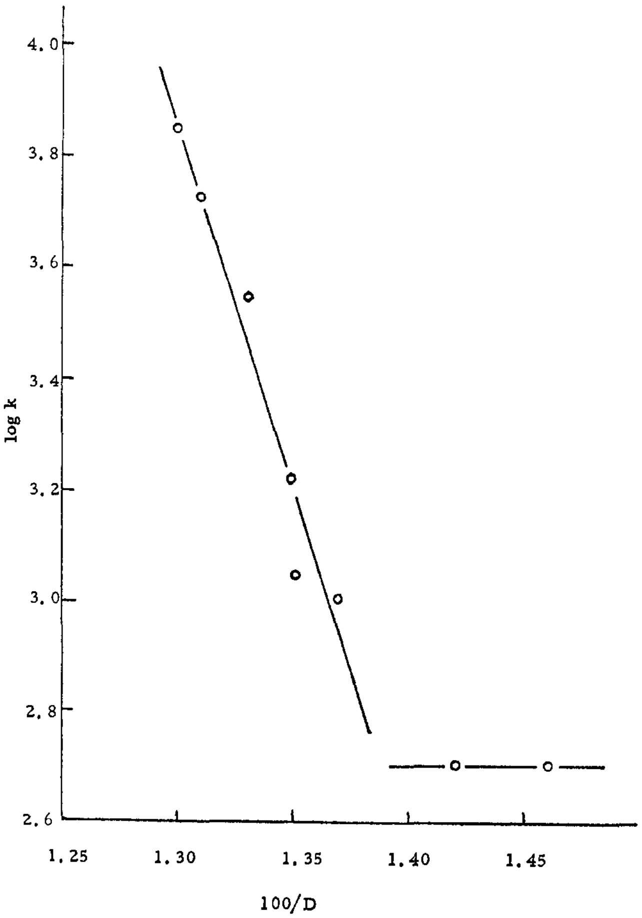

Figure 1.—Dependence of the logarithm of the rate constant for water–proton exchange on the inverse of the dielectic constant of the solvent.

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(23) T J. Swift and T. A. Stephenson *Inorg. Chem.*, **5**, 1100 (1966).

(24) T. J. Swift, T. A. Stephenson, and G. R. Stein, *J. Am. Chem. Soc.*, **89**, 1611 (1967).

(25) T. A. Stephenson, T. A. Swift, and J. B. Spencer, *ibid.*, **90**, 4291 (1968).

(26) L. P. Holmes, D. C. Cole, and E. M. Eyring, *J. Phys. Chem.*, **72**, 301 (1968).

(27) C. R. Frink and M. Peech, *Inorg. Chem.*, **2**, 473 (1963).