Table II. Physical Properties of Silicon and Silicon–Boron Fluorides

Compound	Mp, °C	Bp, °C	Trouton's constant, eu
Si_3F_8	−1	+42	27.8
Si_4F_{10}	+66	+85	30.2
$F_3SiSiF_2BF_2$	0	+42	29.2
$F_3Si(SiF_2)_2BF_2$	+11	+85	32.6
$F_2Si(BF_2)_2$	−47	+39	28.1
$FSi(BF_2)_3$	+11	+68	28.7

effects. First, there must be a high activation energy for the direct insertion reaction $SiF_4 + BF \rightarrow SiF_3BF_2$, although the analogous reaction $BF_3 + BF \rightarrow B_2F_4$ goes readily at −196°.[3] Second, most other reactions of the high-temperature species probably form a radical intermediate containing at least a two-atom skeleton as the first step which then reacts with a boron fluoride to form a final molecule with at least a three-atom skeleton. The molecule Si_2F_6, which was often a reaction product, may have been formed during the polymerization of radical intermediates[1,10] rather than by a direct process.

Table II shows collected physical data for the silicon–boron and silicon fluorides. The similar volatility of the three perfluorinated compounds containing Si_3, Si_2B, and SiB_2 skeletons indicates little difference in polar character for $-SiF_3$ and $-BF_2$ groups. The properties of $FSi(BF_2)_3$ should only be compared with those of iso-Si_4F_{10} which have not been reported.

Acknowledgments. This work was sponsored in part by the Army Research Office, Durham. One of us (P. L. T.) is grateful to the Trustees of the Ramsay Memorial Fellowships for present support.

Ammonia Exchange in Manganese(II)–Liquid Ammonia Solutions

Michael Grant, Harold W. Dodgen, and John P. Hunt[1]

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99163. Received April 19, 1969

Abstract: Kinetic information on the $Mn(NH_3)_6^{2+}$–$NH_3(l)$ exchange reaction was obtained. The value for k_1 (25°) from the rate law $R = 6k_1[Mn(II)]$ is $3.6 \pm 0.3 \times 10^7$ sec^{-1}; $\Delta H^* = 8 \pm 0.5$ kcal/mole and $\Delta S^* = 5 \pm 3$ cal mole^{-1} deg^{-1}. The results are very similar to those for the aquo system. Comparisons with related studies are made.

The study reported here is a part of a general nmr program in exchange kinetics of labile species in aqueous and nonaqueous solutions. Comparisons of kinetic parameters among systems of differing metals and solvents may aid in an understanding of the mechanisms of reaction. An understanding of the behavior of solvated species is needed in order to approach more complex processes.

Experimental Section

We have employed ^{14}N nmr techniques as in previous studies.[2] The equipment used has been described.[3] An important modification was that a 24.6-kG Varian magnet was employed. The ^{14}N resonance in ammonia was observed at 7.56 MHz. Sample temperatures were controlled to within ±0.2° using a thermostated ethanol circulation system. Signal enhancement was obtained by using a Fabri-tek 1052 LSH signal averager.

Liquid ammonia and air-free solutions were prepared and handled using standard vacuum-line techniques. Other reagents used were $Mn(ClO_4)_2 \cdot 6H_2O$, prepared from $MnCO_3$ and $HClO_4$, recrystallized from water, and analyzed; NH_4ClO_4 was prepared from analytical reagent grade NH_4OH and $HClO_4$. Drying the manganese salt by repeated condensation and evaporation of ammonia produced no changes in observed results. All solutions contained 1.63×10^{-2} M NH_4ClO_4 although no effects were noted due to $NHClO_4$, $NaClO_4$, or $NaNO_3$ at that concentration or tenfold higher.

Results

No chemical shifts in the $^{14}NH_3$ nmr line could be observed (>20 ppm). The line-broadening data are given in Table I. The quantity Δ' is the line broadening, in gauss, produced by addition of Mn(II). It is the difference in full line widths, measured at half-maximum intensity in the absorption curve, for the Mn(II) and the reference solutions. The reference was identical in composition with the manganese solution except that $Zn(ClO_4)_2$ was substituted for manganese. The measured line width of the reference (which varied from 0.20 to 0.11 G over the temperature range) was within 0.02 G of that for pure ammonia. The quantity P_MT_{2p} is equal to $2P_M/\gamma\Delta'$, where P_M is the fraction of ^{14}N nuclei bound to manganese (assuming 6 NH_3/Mn) and γ is the magnetogyric ratio for ^{14}N (1934 G^{-1} sec^{-1}).

---

[1] To whom inquiries should be addressed. This work supported by U.S.A.E.C. Contract No. AT(45-1)-2040 and is Report No. RLO-2040-13.

[2] H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 4, 1061 (1965).

[3] R. Murray, H. W. Dodgen, and J. P. Hunt, *ibid.*, 3, 1576 (1964).

Table I. Line-Broadening Data for Mn(II) Solutions in $^{14}NH_3$[a]

Temp, °C	Δ', G	$10^7P_MT_{2p}$, sec^{-1}	Temp, °C	Δ', G	$10^7P_MT_{2p}$, sec^{-1}
Solution A:			Solution B:		
Mn(II) = 2.44×10^{-3} *m*			Mn(II) = 4.90×10^{-3} *m*		
$P_M = 2.49 \times 10^{-4}$			$P_M = 5.00 \times 10^{-4}$		
−30.4	0.31	8.29	−19.1	1.06	4.87
−25.8	0.395	6.51	−16.8	1.34	3.85
−20.8	0.533	4.82	−13.9	1.53	3.37
−15.4	0.675	3.81	−10.8	1.71	3.01
−10.2	0.85	3.02	−6.8	2.16	2.39
0.7	1.39	1.85	−3.0	2.49	2.07
4.0	1.48	1.74	0.7	2.75	1.87
7.7	1.66	1.55	4.0	3.03	1.70
11.0	1.68	1.53	7.7	3.41	1.51
15.1	1.71	1.50	11.0	3.41	1.51
18.8	1.80	1.43	15.1	3.57	1.45
22.3	1.71	1.50	18.75	3.61	1.43
26.2	1.66	1.55	22.3	3.41	1.51
29.5	1.59	1.62	26.2	3.29	1.57
34.5	1.45	1.77	29.5	3.23	1.60
39.8	1.30	1.98	34.4	3.05	1.69
44.8	1.20	2.12	39.7	2.64	1.95
49.8	1.08	2.47	44.8	2.32	2.22
62.4	0.76	3.38	49.8	2.10	2.46
			55.5	1.85	2.79
Solution C:			Solution D:		
$Mn^{2+} = 7.33 \times 10^{-3}$ *m*			$Mn^{2+} = 1.22 \times 10^{-2}$ *m*		
$P_M = 7.48 \times 10^{-4}$			$P_M = 1.25 \times 10^{-3}$		
−34.6	0.72	10.7	−47.0	0.424	30.2
−30.4	0.88	8.77	−42.0	0.618	20.7
−25.8	1.26	6.13	−34.4	1.10	11.6
−20.8	1.53	5.04	−25.8	1.93	6.63
−19.1	1.81	4.27			
−16.8	2.05	3.77	Solution E:		
−13.8	2.30	3.35	$Mn^{2+} = 2.72 \times 10^{-2}$ *m*		
−10.8	2.57	3.00	$P_M = 2.77 \times 10^{-3}$		
−6.8	3.40	2.27	−46.5	1.07	10.0
49.8	3.15	2.45	−42.0	1.47	19.5
55.4	2.72	2.84	−34.0	2.86	26.8
62.3	2.28	3.39			

[a] All solutions 1.63×10^{-2} *m* in NH_4ClO_4, molality units throughout.

Table II. Nmr Exchange Data

System	k_1 (25°), sec^{-1}	ΔH^*, kcal/mol	T_{1e}, sec	A/h, cps
Mn(II)–NH_3(l)	$3.6 \pm 0.3 \times 10^7$	8 ± 0.5	2.4×10^{-8}	2.4×10^6
Mn(II)–H_2O[a]	3×10^7	8	3.8×10^{-9}	9.2×10^6
Co(II)–NH_3(l)[b]	7.2×10^6	11	...	7.5×10^6
Co(II)–H_2O[c]	2×10^6	10.4	4.6×10^{-13}	1.7×10^7
Ni(II)–NH_3(l)[d]	1.0×10^5	11	...	...
Ni(II)–H_2O[e]	3.0×10^4	11	...	1.9×10^7

[a] Reference 4. [b] Reference 2. [c] A. M. Chmelnick and D. Fiat, *J. Chem. Phys.*, **47**, 3986 (1967). [d] H H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 206 (1965). [e] R. E. Connick and D. Fiat, *J. Chem. Phys.*, **44**, 4103 (1966).

The plot of P_MT_{2p} *vs.* $10^3/T$ is given in Figure 1. The results appear to be explainable in a manner completely analogous to those of Swift and Connick[4] for the aqueous Mn(II) system. Measurements of line width at a field of *ca.* 12,000 G showed no effect compared to 24,600 G consistent with the failure to observe a chemical shift and the treatment of Swift and Connick. As given by these authors, $P_MT_{2p} = \tau_M + (1/\tau_M + 1/T_{1e})/C$ where τ_M is the mean lifetime for exchange of an ammonia molecule in the complex, T_{1e} is the longitudinal relaxation time for the electron spin relaxation in $Mn(NH_3)_6^{2+}$ and $C = S(S + 1)(A/\hbar)^2/3$, where $S = 5/2$, A/h is the scalar coupling constant, and $\hbar$ is Planck's constant divided by 2π. At low temperature P_MT_{2p} approaches τ_M. It would be desirable to have a precise independent value for T_{1e}. Such a value is, however, not directly available. Measurements of the esr spectrum of Mn(II) in liquid ammonia were made. The lines are similar to those found in water but are narrower. Using the sharpest line to estimate T_{2e}, we obtain $T_{2e} \simeq 1 \times 10^{-8}$ sec at 25°. The apparent "activation energy" for T_{2e} was calculated to be −0.36 kcal/mole. It is expected that $T_{2e} \leqslant T_{1e}$. Since the low-temperature data should give a good value for τ_M, we proceeded to fit our

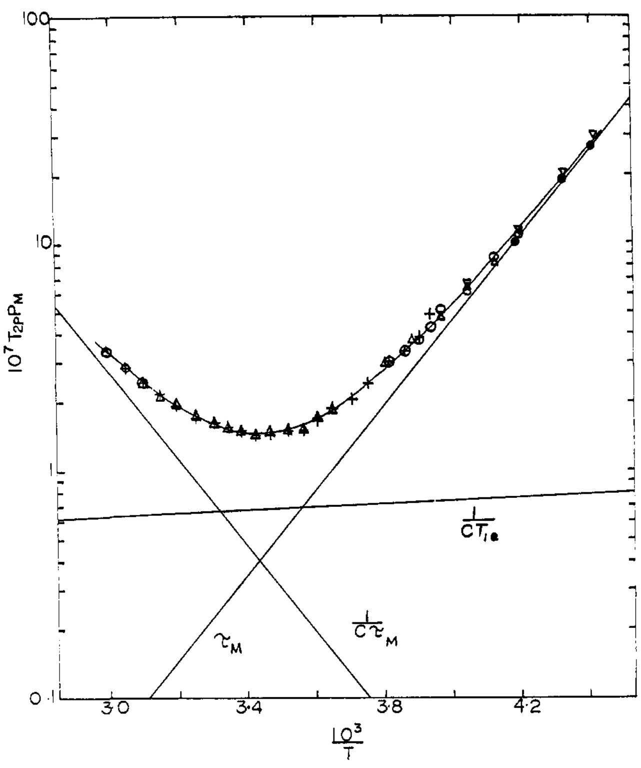

Figure 1. Semilogarithmic plot of P_MT_{2p} *vs.* $10^3/T$ for Mn(II)-NH_3 solutions: △, solution A; +, solution B; ○, solution C; ▽, solution D; ●, solution E.

---

(4) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37, 307 (1962).

data as done by Swift and Connick. The fitting process does not give a precise estimate of T_{1e} but we obtained a value of 2.4 × 10^{-8} sec at 25° using an activation energy of −0.36 kcal/mole. In view of the various uncertainties involved, the relative values for T_{2e} and T_{1e} are at least reasonable. The curves used in the fitting are shown in Figure 1. Our results and some related ones are given in Table II.

Discussion

The most striking comparison is the close similarity of the data in water and ammonia. The manganese(II)–H_2O data are somewhat ambiguous as a well-defined low-temperature rate controlled region was not observed. The more recent work on Co(II)–H_2O (footnote *c*, in Table II) removes the apparent discrepancy with the NH_3 system.[2] If crystal field effects are important in the differences between cobalt and nickel, they do not appear in the observed ΔH^* values. It is true that the d^5 Mn(II) system has a low activation enthalpy as predicted. The scalar coupling constants are also lower for Mn(II), suggesting perhaps a more "ionic" bonding for it.

It may also be noted that our ammonia exchange studies on aqueous $Ni(NH_3)_6^{2+}$ (footnote *d*, Table II) and $Co(NH_3)_6^{2+}$ solutions[5] show a fairly close similarity to the results in Table II.

Acknowledgment. We wish to thank Dr. Bernhard Scharf for preliminary work which showed the feasibility of this study.

---

(5) R. Murray, S. F. Lincoln, H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **8**, 554 (1969).