$\Delta H_0^{\ddagger}$ would have on the value of $\Delta S_0^{\ddagger}$ for X = Br, but it is likely that the value of $\Delta S_0^{\ddagger}$ would be more positive than that given in Table VII. A reasonably linear correlation between $\Delta S_0^{\ddagger}$ and ΔS is obtained for X = Cl, Br, and I even if $\Delta S_0^{\ddagger}$ for X = Br is as much as 5 eu more positive than the value in Table VII, while $\Delta S_0^{\ddagger}$ for X = H_2O deviates significantly from this correlation. It should be noted that the uncertainty on the values of $\Delta S_0^{\ddagger}$ are sufficiently large to preclude any rigorous quantitative treatment of the correlation, but the value of $\Delta S_0^{\ddagger}$ for X = H_2O is definitely too positive compared to the values for the other X, implying an abnormally disordered transition state for X = H_2O. This is opposite to the deviation that would be expected were it caused by charge effects and increased electrostriction of solvent due to a more highly charged transition state with X = H_2O. A possible explanation for the positive deviation lies in the structure of the transition state. Solution X-ray studies have established that $HgCl_2$ exists in aqueous solution as *trans*-$Hg(H_2O)_4Cl_2$ in a distorted octahedral configuration.[29] Assuming that the transition states for the *trans*-$CrCl_2^+$–$Hg^{II}X$ reactions have a similar linear configuration about Hg(II), $\{Cl–Cr^{III}–Cl{-}{-}{-}Hg^{II}–X\}^{\ddagger}$, the steric requirements for formation of the transition state with X = Cl, Br, and I would be much more stringent than with X = H_2O, since in the former reactions only one H_2O coordinated to Hg(II) would be in a suitable position to be displaced by $CrCl_2^+$, while with X = H_2O, any of the six coordinated H_2O's could be displaced. The transition states for X = Cl, Br, and I would then have a higher degree of order than that with X = H_2O, leading to an excessively positive $\Delta S_0^{\ddagger}$ in the latter case.

Acknowledgment.—Partial support of this work by the Advanced Research Projects Agency and by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

[29] C. L. Van Panthaleon Van Eck, Thesis, Leiden, 1958; quoted by G. B. Deacon, *Rev. Pure Appl. Chem.*, **13**, 189 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
WASHINGTON STATE UNIVERSITY, PULLMAN, WASHINGTON 99163

Water Exchange between Solvent and Aquomanganese(II) and Aquophenanthrolinemanganese(II) Complexes[1]

BY MICHAEL GRANT, HAROLD W. DODGEN, AND JOHN P. HUNT*

Received June 11, 1970

Water-exchange rates with $Mn(H_2O)_6^{2+}$, $Mn(phen)(H_2O)_4^{2+}$, and $Mn(phen)_2(H_2O)_2^{2+}$ are reported. k_1 (per water molecule) values at 0° are 5.9×10^6, $(1.3 \pm 0.2) \times 10^7$, and $(3.1 \pm 0.3) \times 10^7$ sec^{-1}, respectively. $\Delta H^{\ddagger}$ values for all three species are in the range (9 ± 2) kcal mol^{-1}. Estimates of A/h are made, and electronic relaxation times from ^{17}O nmr and epr measurements are compared.

Introduction

In this laboratory, we have examined the effect of coordinated ligands on the lability of coordinated water molecules using ^{17}O nmr measurements. Attention was initially concentrated on various nickel(II) complexes and revealed an interesting difference between nonaromatic and aromatic nitrogen donors.[2,3] We are extending this work to manganese(II) and cobalt(II)[4] to see if a general pattern emerges.

There is very little information on substitution effects in manganese(II) complexes. Levanon and Luz[5] examined the effect of chloride ion on the proton line widths in methanol solutions of Mn^{2+} and estimated a rate of exchange for the monochloro complex. A small rate enhancement was observed. The manganese(II)–phenanthroline system was chosen for this study because of the relatively stable complexes formed and the existence of good equilibrium data.

Experimental Section

$MnCl_2 \cdot 4H_2O$ was used as the source of manganese(II) because the perchlorate salts of the phenanthroline complexes were found to be insoluble; purity was checked by EDTA titration. Hydrated 1,10-phenanthroline was dried by vacuum sublimation followed by double recrystallization from dry benzene, mp 117°, lit.[6] mp 117°. 1,10-Phenanthroline hydrochloride was prepared as the monohydrate by treating 1,10-phenanthroline with concentrated aqueous hydrochloric acid, evaporating to dryness, and purifying by repeated precipitation from aqueous solution with acetone. Equivalent weight found (by titration with base) was 236; that calculated for phen·HCl·H_2O was 234.5. *Anal.* Calcd for phen·HCl·H_2O: Cl, 15.1. Found: Cl, 15.1.

In order to avoid working with solutions of pH around 7 (which could cause uncertainties in the blank line width and hydrolysis

---

* To whom correspondence should be addressed.

[1] This research supported by USAEC Contract AT(45-1)-2221-T4 and this report is RLO-2221-T4-1.

[2] A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **91**, 5001 (1969); **92**, 798 (1970).

[3] M. Grant, H. W. Dodgen, and J. P. Hunt, *ibid.*, **92**, 2321 (1970); D. Rablen and G. Gordon, *Inorg. Chem.*, **8**, 395 (1969).

[4] P. Hoggard, H. W. Dodgen, and J. P. Hunt, to be submitted for publication.

[5] H. Levanon and Z. Luz, *J. Chem. Phys.*, **49**, 2031 (1968).

[6] G. Anderegg, *Helv. Chim. Acta*, **46**, 2397, 2813 (1963).

TABLE I

SOLUTION COMPOSITION AT 20°[a]

Soln	Total concn × 10^3, *M*: Mn(II)	phen·HCl	phen	pH (25°)	Calcd pH (25°)	% $Mn(H_2O)_6^{2+}$	% Mn(phen)-$(H_2O)_4^{2+}$	% $Mn(phen)_2$-$(H_2O)_2^{2+}$	% $Mn(phen)_3^{2+}$
A	1	1	1	4.15	4.10	28.2	50.4	20.1	1.3
B	2	2	4	4.34	4.37	4.2	30.9	51.2	13.7
C	2	2	6	4.76	4.79	0.6	11.1	50.7	37.5

[a] Equilibrium data from ref 6: log β = 4.13, 7.61, 10.3; ΔH = 3.5, 7.0, 9.0 kcal/mol.

TABLE II

KINETIC AND NMR PARAMETERS

	$10^{-6}k_1(0°)$, sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	$10^{-7}A/h$, Hz	T_{1e}(20 kG), sec	T_{2e}(3.5 kG), sec
$Mn(H_2O)_6^{2+}$	5.9 ± 0.6	8.8 ± 1	5 ± 3	0.7	10^{-8}	3×10^{-9}
$Mn(phen)(H_2O)_4^{2+}$	13 ± 2	9 ± 2	6 ± 7	1 ± 0.5	$>10^{-9}$	$<10^{-10}$
$Mn(phen)_2(H_2O)_2^{2+}$	31 ± 3	9 ± 2	8 ± 9	2 ± 0.6	$(1 \pm 0.6) \times 10^{-9}$	$\sim 8 \times 10^{-10}$

problems) solutions for nmr measurements (A, B, and C) of the composition shown in Table I were used. The pH of the solutions was in the range 4–5. The equilibrium data of Anderegg[6] and a computer program were used to calculate solution compositions as a function of temperature. The compositions were strongly temperature dependent; only values at 20° are shown in Table I. The hexaaquomanganese(II) solution was prepared from $MnCl_2 \cdot 4H_2O$ and acidified with HCl to give a pH of 4.3. No evidence for complexation by chloride ion at these concentrations ($\sim 10^{-3}$ *M*) could be seen in the epr spectra. The blank used was also acidified to pH 4 with HCl.

The nmr equipment has been previously described.[2] The ^{17}O resonance was observed at 11.5 MHz. The water used was enriched to *ca.* 7% in ^{17}O and was doubly distilled before use. Epr measurements were made on the Varian E-3 spectrometer at 9.52 GHz using a quartz aqueous solution sample tube.

Nmr Measurements. Hexaaquomanganese(II).—The only previous ^{17}O nmr line broadening measurements on aqueous Mn(II) are those of Swift and Connick,[7] who used $Mn(ClO_4)_2$ at a pH of 1. Because of the different conditions (chloride salt, pH ~4) required for this study, we have repeated their work. We find that the line broadenings of perchlorate and chloride salts are closely similar and proportional to the concentration of Mn(II). However, there is some disagreement with the earlier measurements over the whole temperature range; this could be due to a pH effect or to the small line broadenings and low ^{17}O and Mn(II) concentrations employed in the earlier work.

The quantity T_{2p}' (defined previously in ref 2) is related to τ_m, the mean lifetime for exchange of a water molecule in the complex, and T_{1e}, the longitudinal relaxation time, by[7] $T_{2p}' = [(H_2O)/6](\tau_m + (1/\tau_m + 1/T_{1e})/C]$ where $C = S(S+1) \cdot (A/\hbar)^2/3$; $S = {}^5/_2$ and A/h is the scalar coupling constant in hertz (the equation given in ref 7 has been corrected). In order to fit the T_{2p}' data, we must either have an independent estimate of T_{1e} or else find τ_m or $1/C\tau_m$ by measurements in the low- or high-temperature limit. Unfortunately, in the temperature range available (−5 to 100°) limiting conditions were not found, and so an estimate of T_{1e} was made. Bloembergen and Morgan[8] have derived an expression for T_{1e} using a model where impact by solvent molecules modulates the crystal field parameters. They find that $1/T_{1e}$ is proportional to $[\tau_v/(1 + \omega_s^2\tau_v^2) + 4\tau_v/(1 + 4\omega_s^2\tau_v^2)]$, where τ_v is the correlation time for the modulation (*ca.* 3×10^{-12} sec) and ω_s is the electron resonance frequency. Taking T_{1e} at 3500 G and 25° to be 3×10^{-9} sec (equal to T_{2e}), we calculate T_{1e} at 20 kG to be 10^{-8} sec and to have a very small temperature coefficient. Using this value and assuming it to be constant with temperature, the kinetic parameters and coupling constant obtained are given in Table II; the T_{2p} data and the calculated curve are shown in Figure 1. It is to be noted, however, that a good fit to the data may be obtained with a fairly large variation in the parameters $\Delta H^{\ddagger}$, *C*, and T_{1e}. We hope to extend the measurements to much higher temperature to remove this ambiguity. The rate at 0° is fairly well determined and rate comparisons have therefore been made at this temperature.

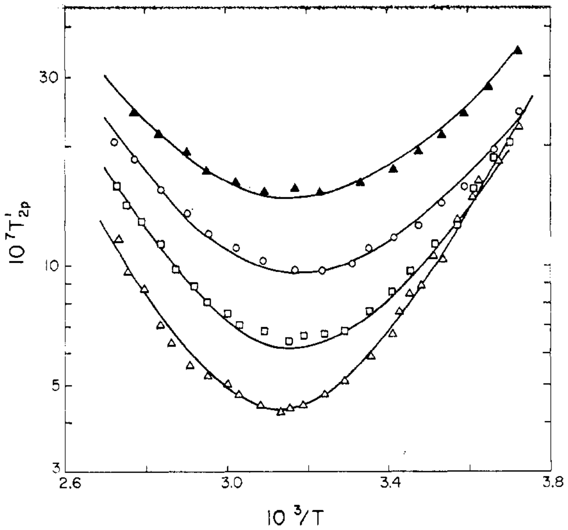

Figure 1.—Experimental points and calculated resultant T_{2p}' curves. From the bottom to the top: $Mn(H_2O)_6^{2+}$, solution A, solution B, solution C. The $Mn(H_2O)_6^{2+}$ data are from solutions of two different concentrations (1 and 4×10^{-3} *M*).

Manganese(II)–Phenanthroline Solutions.—For solution A, a few measurements were made using $Mn(ClO_4)_2$; the line broadening was identical with that of a solution made up with $MnCl_2$. Addition of a large excess of phenanthroline showed that the $(phen)_3$ complex caused no line broadening. No chemical shifts were observed for the solutions and temperatures used. The T_{2p}' data for solutions A, B, and C are plotted in Figure 1. Using the known T_{2p}' values for $Mn(H_2O)_6^{2+}$ and the solution compositions, the individual T_{2p}' curves for the mono- and bisphenanthroline species were obtained by the method previously described.[2] Examination of the resolved curves showed that T_{2p}' could be described for both the mono and bis species by an equation similar to that used for $Mn(H_2O)_6^{2+}$. However the curve-fitting problems already mentioned apply here in an exaggerated form. The three terms in the equation for T_{2p}' are of comparable magnitude over the temperature range available and epr measurements did not give a meaningful independent estimate T_{1e} (see the next section). Accordingly, only rough estimates of the various parameters can be made. T_{1e} was assumed to be temperature independent. The rates at 0° are relatively well defined, however. Kinetic and nmr parameters are listed in Table II, and the solid lines in Figure 1 are calculated T_{2p}'

---

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

(8) N. Bloembergen and L. O. Morgan, *ibid.*, **34**, 842 (1961).

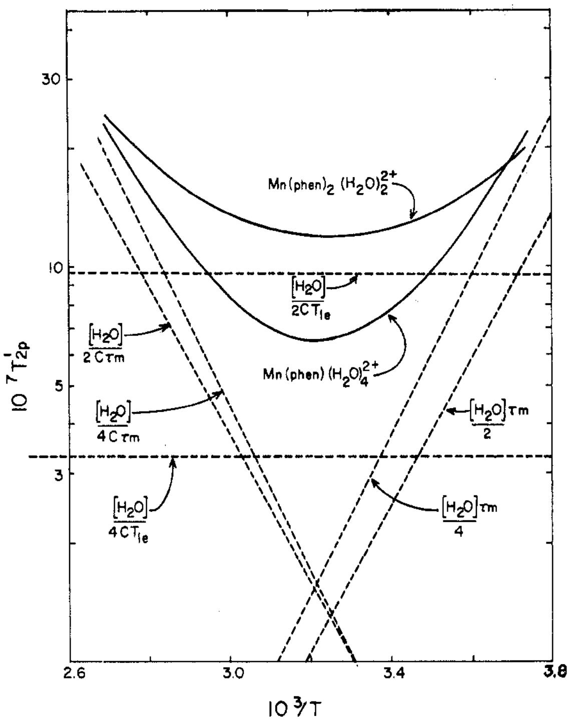

Figure 2.—T_{2p}' curves for the individual species Mn(phen)-$(H_2O)_4^{2+}$ and $Mn(phen)_2(H_2O)_2^{2+}$ resolved into their constituent components.

curves for the three solutions. Figure 2 shows calculated individual T_{2p}' curves for $Mn(phen)(H_2O)_4^{2+}$ and $Mn(phen)_2(H_2O)_2^{2+}$; the uncertainty of the resolution of these curves into their constituent components should be borne in mind. No evidence for kinetically nonequivalent water molecules could be found, and they were treated as equivalent. Small differences would be difficult to detect in these systems.

Epr Measurements.—The epr spectra of the manganese(II)–phenanthroline system were examined at room temperature. Previous studies[5,9] on other systems have given information on solution composition and electronic relaxation times. Solutions contained equimolar quantities of $MnCl_2$ and phen·HCl [1 or 4 × 10^{-3} *M*] and the phenanthroline concentration was increased from an equimolar amount to a sixfold excess. Up to a phen/Mn ratio of 1.5 the spectrum was identical in line width and spacing with that of $Mn(H_2O)_6^{2+}$ but there was a marked reduction in intensity. It was concluded that the signal was due to uncomplexed $Mn(H_2O)_6^{2+}$, and, in fact, the concentration of this species deduced from peak height measurements agreed quantitatively with that calculated from the known equilibrium constants. When the phen/Mn ratio was 2, the spectrum was a superposition of the $Mn(H_2O)_6^{2+}$ spectrum and a broad-line spectrum. For phen/Mn ratios of 4–6 the spectrum was practically unchanged and consisted of six broad overlapping lines. We deduce that the mono-phenanthroline complex has a very short T_{2e} and does not contribute to the epr spectrum. The bis and tris species have considerably larger and similar T_{2e} values and produce the broad-line spectrum. A first-order computer fit to the broad-line spectra gave a line width of about 80 G and a hyperfine splitting constant of 85 G. The T_{2e} values estimated for the three species are shown in Table II.

Comparison of the T_{1e} and the T_{2e} values for the phenanthroline complexes in Table II reveals a large difference for the mono complex. The origin of this is not known; it is unlikely to be simply an effect of the different magnetic fields in the two measurements. The T_{1e} and T_{2e} values for the bis complex are quite similar as expected.

Substitution of phenanthroline on manganese(II) labilizes the coordinated water molecules. This labilizing effect has been found for a wide range of ligands[2,10,11] substituted on nickel(II). As found also for the nickel(II)–bipyridyl complexes,[3] the labilizing effect here is relatively small. Activation parameters for the three species are the same within experimental error. The coupling constant for the mono species is similar to that for $Mn(H_2O)_6^{2+}$ but that of the bis species is appreciably larger. (It is interesting that a similar trend was observed for the nickel(II)–bipyridyl system; coupling constants in general seem remarkably insensitive to ligand substitution.)

Discussion

The long electron spin relaxation time for Mn^{2+} ions and the relatively rapid exchange rates make precise kinetic studies very difficult. We calculate k_1 at 25° for $Mn(H_2O)_6^{2+}$ as 2.3 × 10^7 sec^{-1} which can be compared to 3.1 × 10^7 sec^{-1} obtained by Swift and Connick.[7] Our value for k_1 in liquid ammonia for $Mn(NH_3)_6^{2+}$ is 3.6 × 10^7 sec^{-1} with $\Delta H^{\ddagger} = 8 \pm 0.5$ kcal/mol.

The substitution rate constant for phen on $Mn(H_2O)_6^{2+}$ is estimated[12] as *ca.* 4 × 10^5 M^{-1} sec^{-1}. For the so-called "Eigen mechanism" this corresponds to an outer-sphere association constant (K_{os}) of *ca.* 0.02. A similarly small apparent K_{os} was found in the nickel(II)–dipyridyl system.[3]

Acknowledgment.—This investigation was supported in part by funds provided by the Graduate School Research Funds from the National Science Foundation Institutional Grant.

---

[9] S. I. Chan, B. M. Fung, and H. Lütje, *J. Chem. Phys.*, **47**, 2121 (1967).

[10] S. F. Lincoln, F. Aprile, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **7**, 929 (1968).

[11] R. B. Jordan, H. W. Dodgen, and J. P. Hunt, *ibid.*, **5**, 1906 (1966).

[12] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *ibid.*, **4**, 929 (1965).