$$\text{rate} = k_{obsd}[Mn(CO)_5X] = k[Mn(CO)_5X] \quad (6)$$

summarized in Table S11, and complete lists of experimental values of k_{obsd} are given in Tables S8, S9, and S10 in the supplementary material; the activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$ are compiled in Table IV. The present kinetic data are in agreement with the mechanism shown in Scheme II. They agree well with previous data for the reactions of $Mn(CO)_5X$[10] and $Mn(CO)_4(py)_2$[19] species with monodentate and bidentate ligands. A limiting dissociative (D) mechanism is proposed with dissociative loss of one carbonyl ligand in $Mn(CO)_5X$ (oriented cis to the ligand X) as the rate-determining step. Subsequent rapid losses of a second carbonyl and a halide lead to product formation. Under our experimental conditions with $[L] \gg [Mn(CO)_5X] > [CO]$ the reverse reactions k_{-1}, k_{-2}, and k_{-3} can be neglected.

The fact that the first-order rate constants obtained by monitoring absorbance changes spectrophotometrically and by monitoring changes of the conductivity of the solution are identical proves conclusively that release of the halide ligand in $Mn(CO)_5X$ is not the rate-determining step. The volume of activation for the system $Mn(CO)_5Cl$/L/acetone is markedly positive (+20.6 $cm^3\ mol^{-1}$), in agreement with the dissociative nature of the rate-determining step.

Considering the well-established cis-labilizing effect of X in $Mn(CO)_5X$[20] and the resulting facial arrangement of the coordinated thioether sulfur atoms in the product $[LMn(CO)_3]^+$, it is plausible to assume that both leaving CO groups were oriented cis relative to X in the starting complex $Mn(CO)_5X$. Interestingly, it is observed that $k(Cl) > k(Br) > k(I)$; the ratio is 167:21:1 at 35 °C. We propose that this reflects the increasing Mn-C bond strength of the cis-carbonyl groups in $Mn(CO)_5X$ with decreasing electronegativity of X^-. A linear relationship between the Pauling electronegativity of X^- and the relative activation enthalpy $\Delta(\Delta H^{\ddagger})$ of the reactions between $Mn(CO)_5X$ (X = Cl, Br, I) and L may be constructed. This effect is readily interpreted in terms of the Dewar-Chatt-Duncanson bonding model: X^- with a strong electron-withdrawing capacity reduces the electron density at the manganese center, and consequently, the extent of π-back-bonding to CO is reduced.

Acknowledgment. Sponsorship of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Professor R. van Eldik (Universität Witten) for access to his high-pressure facilities and for his help with the measurements.

Supplementary Material Available: Tables of complete crystallographic data, hydrogen atom positional parameters, bond distances and angles, thermal parameters, and pseudo-first-order rate constants for the ligand substitution reactions (9 pages); a table of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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Variable-Pressure Kinetic and Equilibrium Study of Monocomplex Formation of Copper(II) and Zinc(II) with 2-Chloro-1,10-phenanthroline in Aqueous Solution

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The kinetics of formation and dissociation of $Cu(Cl\text{-}phen)^{2+}$ and of dissociation of $Zn(Cl\text{-}phen)^{2+}$ (Cl-phen = 2-chloro-1,10-phenanthroline) have been studied in aqueous solution as a function of excess metal ion, temperature, and pressure. Dissociation of $Zn(Cl\text{-}phen)^{2+}$ has been followed by displacing the equilibrium with an excess of Cu^{2+}. The stability constants of the monocomplexes were determined spectrophotometrically. The rate constants, activation enthalpies, entropies, and volumes, and the corresponding thermodynamic parameters obtained for $Cu(Cl\text{-}phen)^{2+}$ (and for $Zn(Cl\text{-}phen)^{2+}$) are as follows: $k_f^{298}/M^{-1}\ s^{-1} = 1.1 \times 10^7$ (1.1×10^6); $k_r^{298}/s^{-1} = 102$ (887); $\Delta H_f^{\ddagger}/kJ\ mol^{-1} = 33.6$ (37.9); $\Delta H_r^{\ddagger}/kJ\ mol^{-1} = 60.6$ (57.3); $\Delta S_f^{\ddagger}/J\ K^{-1}\ mol^{-1} = +3$ (-2); $\Delta S_r^{\ddagger}/J\ K^{-1}\ mol^{-1} = -3$ (+4); $\Delta V_f^{\ddagger}/cm^3\ mol^{-1} = +7.1$ (+5.0); $\Delta V_r^{\ddagger}/cm^3\ mol^{-1} = 5.2$ (+4.1); $\log(K^{298}/M^{-1}) = 5.03$ (3.10); $\Delta H^{\circ}/kJ\ mol^{-1} = -27.0$ (-19.4); $\Delta S^{\circ}/J\ K^{-1}\ mol^{-1} = +6$ (-6); $\Delta V^{\circ}/cm^3\ mol^{-1} = +1.9$ (+0.9). On the basis of the data on complex formation reactions, the water-exchange rate constants can be estimated to be $0.7 \times 10^9\ s^{-1} < k_{ex}^{298} < 5 \times 10^9\ s^{-1}$ for Cu^{2+} and $0.3 \times 10^8\ s^{-1} < k_{ex}^{298} < 6 \times 10^8\ s^{-1}$ for Zn^{2+}. It is concluded that the complex-formation and water-exchange reactions on both metal ions take place via dissociative interchange I_d mechanisms.

Introduction

The rates of inorganic reactions range from extremely fast to very slow when referring to the experimental techniques available to access them. The scheme of reactions can also vary from simple to very complicated. To understand their mechanisms, one has to start from the simplest, solvent-exchange reaction, and progress toward the understanding of multistep processes via the simplest complex-formation reactions.

Water-exchange rate constants have been determined for a majority of transition-metal cations. For kinetically inert cations, the isotopic dilution techniques have been applied,[1] whereas for the more labile metal ions, nuclear magnetic resonance (NMR) studies on different nuclei have proven very informative.[2] There are however few cations for which water-exchange rate constants are inaccessible by direct measurements, among which are copper(II) (the Jahn-Teller distortion accelerates the exchange, and the rate of water exchange is not measurable in the present stage of instrumentation) and zinc(II) (it is diamagnetic, and NMR cannot be applied with success to study its very fast water-exchange rate).

The interpretation of the effect of pressure on the rate of chemical reactions is now a well-accepted way of elucidating reaction mechanisms. During recent years, a large number of variable-pressure kinetic studies of solvent exchange and complex formation reactions have been reported.[3] The activation volumes for solvent-exchange reactions give the most direct information on their mechanisms. It also becomes clear from available data on a given metal ion that simple complex-formation reactions take place via the same mechanism in aqueous solution as does water exchange. Reciprocally, the study of simple complex-formation

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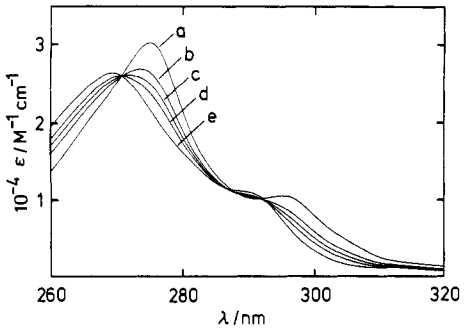


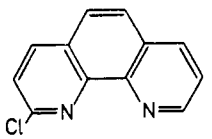
Figure 1. Normalized absorption spectra of Cl-phen–Zn^{2+} solutions at 298.2 K. $C_{Cl\text{-}phen} = 1 \times 10^{-5}$ M; C_{Zn} = (a) 5×10^{-2}, (b) 1×10^{-3}, (c) 5×10^{-4}, (d) 2.5×10^{-4}, and (e) 0 M.

reactions of copper(II) and zinc(II) provide a possibility to access the water-exchange rate constants and mechanisms.

The extreme lability of Cu^{2+} and Zn^{2+} is probably the reason for the paucity of variable-pressure data for their substitution reactions in aqueous solution.[4,5] In the present paper, we report a comparative variable-pressure study of monocomplex formation of Cu^{2+} and Zn^{2+} with a neutral ligand, 2-chloro-1,10-phenanthroline.

Experimental Section

2-Chloro-1,10-phenanthroline (Cl-phen, **1**), was synthesized from 1,10-phenanthroline (Fluka) via *o*-phenanthroline methiodide and 1-methyl-2-*o*-phenanthrolone.[6] It was recrystallized twice from hot doubly



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distilled water. Purity was controlled by proton NMR and elemental analysis (calcd/found: C, 67.15/66.96; H, 3.29/3.32; N, 13.05/13.12; Cl, 16.52/16.63). The $Cu(ClO_4)_2$ stock solution was prepared by dissolving $Cu(ClO_4)_2 \cdot 6H_2O$ (Fluka) in doubly distilled water. The $Zn(ClO_4)_2$ stock solution was prepared from ZnO (Fluka) and concentrated $HClO_4$ (Merck) by using a slight excess of metal oxide followed by filtration. The metal ion concentrations were checked by complexometric titration with EDTA. The ionic strength was fixed to $I = 0.05$ M by $NaClO_4$ (Merck, recrystallized from doubly distilled water). The pH of the samples was chosen between 5.7 and 5.9, to avoid ligand protonation ($pK_a = 4.17$ for Cl-phen[7]) and metal ion hydrolysis. The experimental setups for variable-pressure stopped-flow kinetic[8] and equilibrium[9] UV–visible experiments were as described previously. Series of five to nine kinetic data were averaged at each of the experimental conditions. The errors quoted are 1 standard deviation.

Results

Equilibrium Study. The stability constant of the monocomplex $M(Cl\text{-}phen)^{2+}$ (eq 1), where M = Cu and Zn, were determined from UV spectrophotometric measurements. The absorption

$$M(H_2O)_6^{2+} + Cl\text{-}phen \underset{k_r}{\overset{k_f}{\rightleftharpoons}} M(Cl\text{-}phen)(H_2O)_4^{2+} + 2H_2O \quad (1)$$

spectra (between 260 and 320 nm) of a series of solutions of fixed ligand concentration ($C_{Cl\text{-}phen} = 1 \times 10^{-5}$ M) and variable metal ion concentrations ($C_{Cu} = 0$, 1×10^{-5}, 2×10^{-5}, and 5×10^{-3} M; see caption of Figure 1 for C_{Zn}) were taken at 298.2 K (Figure 1). The equilibrium constants were calculated from the least-squares analysis[10] of the spectra, with the equilibrium constant and the molar absorptivities of the complex and of the ligand as adjustable parameters in the program. With excess metal conditions, the best fit was obtained in both cases for a 1:1 complex, with $\log K^{298} = 5.03 \pm 0.05$ for $Cu(Cl\text{-}phen)^{2+}$ and 3.10 ± 0.02 for $Zn(Cl\text{-}phen)^{2+}$. The resulting molar absorptivities used for the further variable-temperature and -pressure studies were $\epsilon_{Cl\text{-}phen} = (2.40 \pm 0.06) \times 10^4\ M^{-1}\ cm^{-1}$ and $\epsilon_{Cu(Cl\text{-}phen)} = (3.10 \pm 0.04) \times 10^4\ M^{-1}\ cm^{-1}$ for Cu^{2+} at 274 nm, and $\epsilon_{Cl\text{-}phen} = (2.13 \pm 0.02) \times 10^4\ M^{-1}\ cm^{-1}$ and $\epsilon_{Zn(Cl\text{-}phen)} = (2.80 \pm 0.06) \times 10^4\ M^{-1}\ cm^{-1}$ for Zn^{2+} at 276 nm. The stability constants resulting from variable-temperature (from 274 to 330 K), and variable-pressure (up to 200 MPa) absorbance studies are reported in Table I (see also Figure 2a). The data were analyzed by using eq 2 and 3 to yield the reaction enthalpy, $\Delta H°$, entropy, $\Delta S°$, and volume, $\Delta V°$ (Table II).

$$\ln K = -\Delta H°/RT + \Delta S°/R \quad (2)$$

$$\ln K = \ln K° - \Delta V°P/RT \quad (3)$$

Table I. Stability Constant, K, as a Function of Temperature and Pressure for $Cu(Cl\text{-}phen)^{2+}$ and $Zn(Cl\text{-}phen)^{2+}$ Complex Formation

$Cu(Cl\text{-}phen)^{2+}$				$Zn(Cl\text{-}phen)^{2+}$			
T/K	$10^{-4}K$/M^{-1}	P/MPa	$10^{-4}K$/M^{-1} [a]	T/K	$10^{-2}K$/M^{-1}	P/MPa	$10^{-2}K$/M^{-1} [a]
275.1	25.4	2	22.1	274.1	25.8	2	12.5
284.3	18.3	65	21.1	288.2	16.3	62	12.2
298.2	11.8	139	20.3	298.2	12.5	130	11.9
312.8	6.69	202	18.7	303.2	11.0	201	11.6
327.1	3.85			318.2	8.33		
				333.2	5.40		

[a] At 298.2 K.

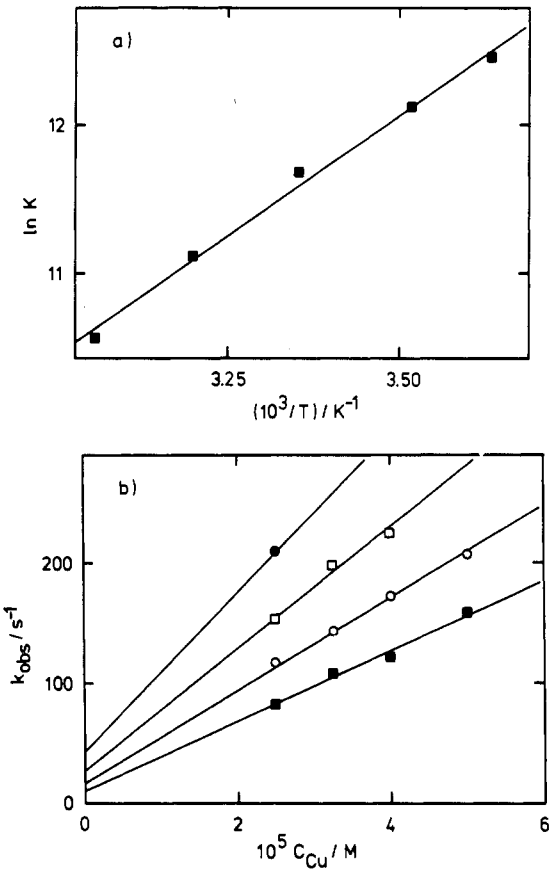

Figure 2. Temperature dependence of (a) the logarithm of the stability constant, K, of $Cu(Cl\text{-}phen)^{2+}$, (b) the observed pseudo-first-order rate constant, k_{obs}, for the formation of $Cu(Cl\text{-}phen)^{2+}$ as a function of C_{Cu}: T = 273.2 (■), 278.2 (○), 283.2 (□), and 288.2 K (●).

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Table II. Thermodynamic and Kinetic Parameters for Cu(Cl-phen)$^{2+}$ and Zn(Cl-phen)$^{2+}$

	Cu(Cl-phen)$^{2+}$	Zn(Cl-phen)$^{2+}$
log (K^{298}/M^{-1})	5.03 ± 0.05[a,b]	3.10 ± 0.02[c]
k_f^{298}/M^{-1} s^{-1}	(1.1 ± 0.1) × 10^7	1.1 × 10^6[d]
k_r^{298}/s^{-1}	102 ± 11	887 ± 93
$\Delta H°$/kJ mol^{-1}	−27.0 ± 1.6	−19.4 ± 0.8
$\Delta H_f^{\ddagger}$/kJ mol^{-1}	33.6 ± 1.7	37.9[d]
$\Delta H_r^{\ddagger}$/kJ mol^{-1}	60.6 ± 1.8	57.3 ± 3.4
$\Delta S°$/J K^{-1} mol^{-1}	+6 ± 5	−6 ± 3
$\Delta S_f^{\ddagger}$/J K^{-1} mol^{-1}	+3 ± 6	−2[d]
$\Delta S_r^{\ddagger}$/J K^{-1} mol^{-1}	−3 ± 6	+4 ± 12
$\Delta V°$/cm^3 mol^{-1}	+1.9 ± 0.4	+0.9 ± 0.4
$\Delta V_f^{\ddagger}$/cm^3 mol^{-1}	+7.1 ± 0.5	+5.0[d]
$\Delta V_r^{\ddagger}$/cm^3 mol^{-1}	+5.2[d]	+4.1 ± 0.4

[a] Obtained from a simultaneous fit of K and k_{obs} values (see text). A least-squares fit of the K values alone as a function of T leads to the same results within 0.1 standard deviation. [b] Literature value:[25] 5.07. [c] Literature value:[25] 3.3. [d] Obtained by difference.

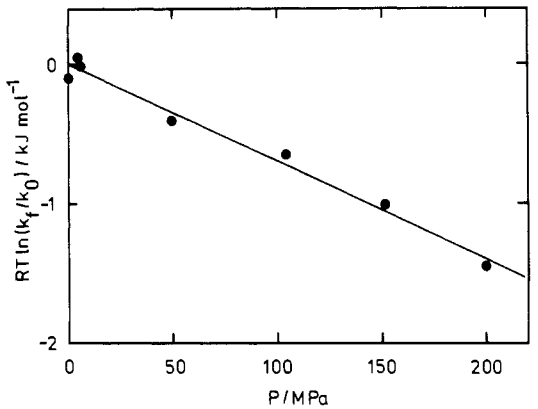

Figure 3. Pressure effect on the normalized logarithm of the rate constant of formation, k_f, of Cu(Cl-phen)$^{2+}$ at 273.2 K.

Kinetic Study. The kinetics of Cu(Cl-phen)$^{2+}$ monocomplex formation (eq 1) was investigated at 274 nm as a function of Cu^{2+} concentration. Under the pseudo-first-order conditions of at least 5 times excess Cu^{2+}, the monocomplex is the only species formed. The rate constants for the formation, k_f, and dissociation, k_r, of the complex are usually calculated from the slopes and intercepts of the k_{obs} dependence on C_{Cu} (eq 4). However, as can be seen

$$k_{obs} = k_r + k_f C_{Cu} \quad (4)$$

from Figure 2b, the extrapolated k_r values are not well-defined, and it was decided to use the previously determined stability constant, K, to calculate the k_r values according to eq 5. The

$$K = k_f/k_r \quad (5)$$

$$k = (k_B T/h) \exp(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT) \quad (6)$$

measured k_{obs} (Figure 2b) and the stability constant (Figure 2a) were thus simultaneously fitted to eq 2, 4, 5, and 6, with $\Delta H°$, $\Delta S°$ (or K^{298}), $\Delta H_f^{\ddagger}$, and $\Delta S_f^{\ddagger}$ (or k_f^{298}) as adjustable parameters. The errors given for the kinetic parameters for the reverse reaction in Table II were obtained by repeating the fit with these and the thermodynamic parameters as adjustables, yielding the values in Table II. The pressure dependence of k_f was determined at 273.2 K, at concentrations ($C_{Cl\text{-}phen}$ = 5 × 10^{-6} M, C_{Cu} = 4 × 10^{-5} M), where the contribution of k_r to k_{obs} can be neglected (see Figure 2b). The data were fitted to eq 7, where k_0, the rate constant at zero pressure, is also an adjustable parameter, and are shown in Figure 3.

$$\ln k = \ln k_0 - \Delta V^{\ddagger} P/RT \quad (7)$$

The kinetics of the corresponding Zn^{2+} reaction could not be studied in the same way, the k_{obs} values being too large to be measured by stopped flow. However, the rate of dissociation of

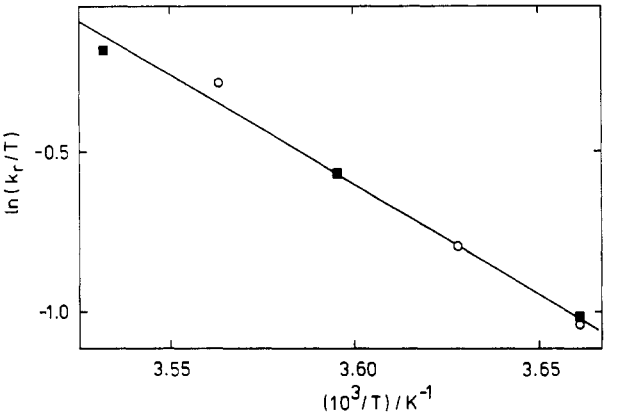

Figure 4. Eyring plot of the dissociation rate constant, k_r, of Zn(Cl-phen)$^{2+}$. $C_{Zn(Cl\text{-}phen)}$ = 2.5 × 10^{-4} M; C_{Cu} = 2.5 × 10^{-4} M (■) and 5 × 10^{-4} M (○).

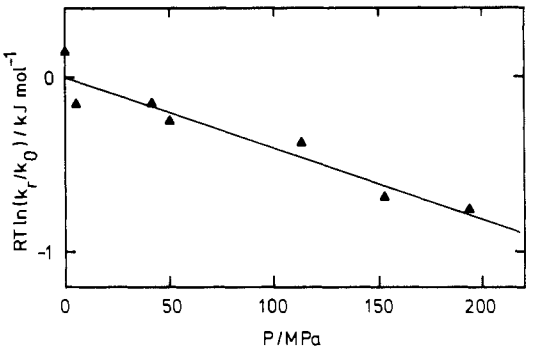

Figure 5. Pressure effect on the normalized logarithm of the rate constant of dissociation, k_r, of Zn(Cl-phen)$^{2+}$ at 273.2 K. $C_{Zn(Cl\text{-}phen)}$ = 2.5 × 10^{-4} M; C_{Cu} = 2.5 × 10^{-4} M.

Zn(Cl-phen)$^{2+}$ could be accessed by adding Cu^{2+} to a solution of Zn(Cl-phen)$^{2+}$. The formation of Cu(Cl-phen)$^{2+}$ is much faster than the dissociation of Zn(Cl-phen)$^{2+}$ and more favorable (K_{Cu}/K_{Zn} = 85). Moreover, Cu^{2+} has no influence on the dissociation rate of the Zn(Cl-phen)$^{2+}$ complex (see Figure 4). The equilibrium is completely displaced toward formation of Cu(Cl-phen)$^{2+}$, with dissociation of Zn(Cl-phen)$^{2+}$ as the rate-controlling step. The dissociation of Zn(Cl-phen)$^{2+}$ was followed at 281 nm, where the difference in molar absorbances between the complexes is a maximum ($\epsilon_{Cu(Cl\text{-}phen)} - \epsilon_{Zn(Cl\text{-}phen)}$ = 4.25 × 10^3 M^{-1} cm^{-1}), with two different concentrations in added Cu^{2+}. The k_r values obtained at variable temperature (273.2–283.2 K) were fitted to eq 6, giving the Eyring plot shown in Figure 4. The pressure dependence of the Zn(Cl-phen)$^{2+}$ dissociation was measured in the same way at 273.2 K (up to 200 MPa). The obtained k_r values were fitted to eq 7 and are shown in Figure 5. The kinetic parameters are summarized in Table II.

Discussion

Complex formation reactions of divalent metal ions are believed to take place according to the Eigen–Wilkins mechanism.[11] Formation of an outer-sphere (or encounter) complex occurs first, in a fast preequilibrium. This preassociation is followed by the inner-sphere, rate-limiting interchange of water for the entering ligand molecule. In the case of a bidentate ligand, ring closure represents an extra step in the reaction (eq 8, where K_{os} is the

$$[M(H_2O)_6]^{2+} + L\text{-}L \overset{K_{os}}{\rightleftharpoons} [M(H_2O)_6{}^{2+},L\text{-}L] \xrightarrow{k_I} [M(H_2O)_5L\text{-}L]^{2+} + H_2O \xrightarrow{fast} [(H_2O)_4M\text{-}L\text{-}L]^{2+} + 2H_2O \quad (8)$$

stability constant of the outer-sphere complex and k_I is the rate constant of the interchange). It is generally accepted that the

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Table III. Formation Rate Constants, k_f^{298}, Activation and Reaction Volumes, ΔV_f^* and ΔV°, for Reactions of Selected Octahedral First-Row $M(H_2O)_6^{2+}$ with Entering Ligands L[a]

L	param	Mn (d^5)	Co (d^7)	Ni (d^8)	Cu (d^9)	Zn (d^{10})
H_2O[b]	k_{ex}/s^{-1}	2.1×10^7	3.2×10^6	3.2×10^4	$(0.7–5) \times 10^9$[c]	$(0.3–6) \times 10^8$[c]
	$\Delta V_{ex}^*/cm^3\ mol^{-1}$	−5.4	+6.1	+7.2	≤+6[d]	+6[d]
NH_3	$k_f/M^{-1}\ s^{-1}$		1.5×10^5[e]	4.5×10^3[e]	2×10^8[f]	8×10^6[g]
	$\Delta V_f^*/cm^3\ mol^{-1}$		+4.8[h]	+6.0[h]		
	$\Delta V^\circ/cm^3\ mol^{-1}$		−8.6[h]	−2.3[h]		
gly^-[i]	$k_f/M^{-1}\ s^{-1}$		3×10^6	2.1×10^4	3.4×10^9	1.5×10^8[j]
	$\Delta V_f^*/cm^3\ mol^{-1}$[k]		+5	+7	+9	+4
	$\Delta V^\circ/cm^3\ mol^{-1}$		+7.3	+2.1	+13.4	+5.2
bpy	$k_f/M^{-1}\ s^{-1}$	2.8×10^5[l]	6.3×10^4[m]	1.6×10^3[m]	5×10^7[n]	2.3×10^6[o]
	$\Delta V_f^*/cm^3\ mol^{-1}$	−1.2[p]	+5.9[r]	+5.3[r]		+7.1[o]
	$\Delta V^\circ/cm^3\ mol^{-1}$	+3.0[p]				+3.5[o]
phen	$k_f/M^{-1}\ s^{-1}$	2×10^5[s]	3×10^5[m]	3.9×10^3[m]	6.4×10^7[n]	2×10^6[m]
Cl-phen[t]	$k_f/M^{-1}\ s^{-1}$			1×10^3[u]	1.1×10^7	1.1×10^6
	$\Delta V_f^*/cm^3\ mol^{-1}$				+7.1	+5.0
	$\Delta V^\circ/cm^3\ mol^{-1}$				+1.9	+0.9

[a] Abbreviations: gly^- = glycinate, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, Cl-phen = 2-chloro-1,10-phenanthroline. [b] Water-exchange data from ref 26 (k_{ex} refers to the exchange of one particular water molecule). [c] Estimated value from this work; see text. [d] Predicted values from ref 17. [e] Reference 27. [f] Reference 28. [g] Value from ref 27 (measured at 284 K) corrected to 298 K by using an estimated value of $\Delta H_f^* = 30$ kJ mol^{-1}. [h] Reference 29. [i] Reference 4. [j] Reference 30. [k] $\Delta V_I^* = \Delta V_f^* - \Delta V_{os}^\circ$; see text. [l] Reference 31. [m] Reference 32. [n] Reference 33. [o] Reference 5. [p] Reference 34. [r] Reference 35. [s] Value from ref 32 (measured at 284 K) corrected to 298 K by using an estimated value of $\Delta H_f^* = 30$ kJ mol^{-1}. [t] This work. [u] References 36, 32.

rate-determining step is the first coordination, because the second coordination is statistically more probable than the first; as a further support, the water-exchange rates for mono- or disubstituted cations are faster than those for the hexaaqua species.[12] The second-order rate constant for complex formation, k_f, is related to K_{os} and k_I by eq 9. Its derivative as a function of pressure

$$k_f = K_{os}k_I \tag{9}$$

$$\Delta V_f^* = \Delta V_{os}^\circ + \Delta V_I^* \tag{10}$$

gives eq 10, relating the activation volume, ΔV_f^*, to the volume change during outer-sphere complex formation, ΔV_{os}°, and to the activation volume for the interchange step, ΔV_I^*.

Table III shows the present results and the literature values of the water-exchange rate constants, k_{ex}, and formation rate constants, k_f, for some divalent first-row transition-metal ions with a few selected ligands (for a complete survey see ref 11). Glycinate anion (gly^-) and 2,2′-bipyridine (bpy) data are listed because there are the only ligands for which activation volumes have been measured for Cu^{2+} and/or for Zn^{2+}; NH_3 is the simplest ligand binding via nitrogen, and 1,10-phenanthroline (phen) is similar to the investigated 2-chloro-1,10-phenanthroline.

The symmetrical solvent-exchange reactions and the formation of NH_3, bpy, phen, and Cl-phen complexes do not involve charge separation or cancellation. The outer-sphere contribution, ΔV_{os}°, can thus be neglected in a polar solvent, and ΔV_I^* equated to ΔV_f^*. The sign of the experimentally determined activation volume therefore gives direct information on the activation mode.[13] Complex formation between gly^- and divalent transition-metal ions involves neutralization of charges. To obtain the activation volume for the interchange step, ΔV_I^*, in this reaction, the measured ΔV_f^* value has to be corrected to take into account the volume change in forming the outer-sphere complex. The estimated value of this ΔV_{os}° is +3.2 $cm^3\ mol^{-1}$ for a divalent cation with a uninegatively charged anion with a distance of closest approach of 0.5 nm[4], and the ΔV_I^* values can be derived as the difference $\Delta V_f^* - \Delta V_{os}^\circ$ (Table III).

The Langford–Gray formalism,[14] widely used to classify the mechanisms of ligand-substitution reactions on metal centers, divides reaction mechanism into associative mechanism (intermediate of increased coordination number, A), dissociative mechanism (intermediate of decreased coordination number, D), and interchance (concerted bond breaking/making at transition state, I). Two subgroups of interchange mechanism are also defined: associative interchange, I_a, when the rate of the reaction mainly depends on the nature of the entering ligand; and dissociative interchange, I_d, when there are not more influences from the entering ligand than from the leaving ligand. The positive activation volumes and the small reaction volumes obtained for formation of $Cu(Cl\text{-}phen)^{2+}$ and $Zn(Cl\text{-}phen)^{2+}$ give confidence that both reactions proceed according to dissociative activation modes.[15] Swaddle[16] has proposed a semiempirical model to estimate the limiting ΔV_{ex}^* value for a D mechanism. It corresponds to the difference between the absolute partial molar volumes of the hexa- and pentaaqua ions, and yields an average value for divalent transition metals of $\Delta V_{ex}^* = +13.1$ $cm^3\ mol^{-1}$. The values of +7.1 and +5.0 $cm^3\ mol^{-1}$ for $Cu(Cl\text{-}phen)^{2+}$ and $Zn(Cl\text{-}phen)^{2+}$ formation indicate that these two reactions take place via dissociative interchange, I_d, mechanisms. If the ΔV_I^* and ΔV_{ex}^* values in Table III are compared, it can be seen that the predicted activation volumes for water exchange on Cu^{2+} and Zn^{2+} are not unrealistic.[17] Although this is in agreement with our knowledge of the reaction mechanisms of the first-row divalent transition-metal ions in aqueous solution, the changeover from an associative interchange (V^{2+} and Mn^{2+}) to a dissociative one (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) along the series does not seems to be complete, that is, a limiting D mechanism is not reached at Zn^{2+}.

The second-order rate constants k_f in Table III cannot be directly compared to first-order rate constants k_{ex}. If eq 9 is used, first-order rate constants k_I must first be derived and compared with k_{ex} through eq 11, where F is a statistical factor.[18] The

$$k_I = Fk_{ex} \tag{11}$$

outer-sphere stability constant, K_{os}, may sometimes be experimentally determined and has been so determined in a few cases.[11] Fuoss[21] has proposed a model equation to calculate the outer-sphere association constant on the basis of statistical arguments

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and the theory of diffusion. For a divalent cation with a uninegatively charged ligand, the calculated K_{os} value is around 1 M^{-1}, although it depends on the estimated value of the metal to ligand distance in forming the outer-sphere complex. For uncharged ligands, values calculated with a distance of closest approach of 500 pm[11,22] are between 0.05 and 0.15 M^{-1}. For the large Cl-phen ligand, with a chlorine atom next to the binding nitrogen,[7] the distance of closest approach is probably larger. With an estimated value of a = 600 pm, the resulting K_{os} amounts to 0.02–0.07 M^{-1}. The yielded K_{os} values are in good agreement with the data derived from water-exchange and complex-formation rate constants (0.02 $M^{-1} < K_{os} < 0.14\ M^{-1}$) for Co^{2+} and Ni^{2+}. It is consistent with the starting assumption of an Eigen–Wilkins mechanism and supports the assignment of I_d for Co^{2+} and Ni^{2+}. As a parallel, we can attempt to predict or estimate k_{ex}, the water-exchange rate constants on Cu^{2+} and Zn^{2+} using eq 9: $7 \times 10^8\ s^{-1} < k_{ex} < 5 \times 10^9\ s^{-1}$ and $3 \times 10^7\ s^{-1} < k_{ex} < 6 \times 10^8\ s^{-1}$, respectively. Using incoherent quasi-electric neutron scattering, Salmon[23,24] has studied the proton-exchange rates on some aquametal ions. For these very fast exchanges on divalent cations, the proton-exchange rate can be assumed to be equal to the water-exchange rate. This method allows one to give limits for the rate of water exchange on Cu^{2+} ($k_{ex} \geq 1 \times 10^{10}\ s^{-1}$) and Zn^{2+} ($2 \times 10^8\ s^{-1} < k_{ex} < 1 \times 10^{10}\ s^{-1}$), which are close to our estimation.

In conclusion, our study together with other kinetic and neutron scattering data gives a coherent image of the substitution mechanisms on Cu^{2+} and Zn^{2+} aqua ions, both ions reacting according to a dissociative interchange, I_d, mechanism. The water-exchange rate, k_{ex}, is 1–2 orders of magnitude larger for Cu^{2+} than for Zn^{2+}.

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Registry No. $Cu(H_2O)_6^{2+}$, 14946-74-8; $Zn(H_2O)_6^{2+}$, 15906-01-1; Cl-phen, 7089-68-1.

Supplementary Material Available: Observed pseudo-first-order rate constants, k_{obs}, as a function of temperature and pressure (Tables SI and SII) and normalized absorption spectra of Cl-phen–Cu^{2+} solutions at 298.2 K (Figure S1) (3 pages). Ordering information is given on any current masthead page.

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Thermal Decomposition of the Halide and Pseudohalide Derivatives of Bis(cyclopentadienyl)titanium(IV)

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The thermal decomposition reactions of $Ti(Cp)_2(X)_2$, where Cp is η^5-C_5H_5 and X is Cl^-, Br^-, NCS^-, NCO^-, and N_3^-, were studied at atmospheric pressure by temperature-programmed pyrolysis with analysis of the evolved gas by mass spectroscopy. The gas evolution versus temperature profile showed that the compounds decomposed in a single, sharp, symmetrical step with the loss of cyclopentadiene observed from all compounds. The pseudohalide-containing compounds evolved products of the breakdown of this moiety simultaneously with C_5H_6. The gas evolution versus temperature profiles were used to measure $\Delta H^{\ddagger}$ for the decomposition of the azide and cyanate compounds. The compound $Ti(Cp)_2(N_3)_2$ was used for the chemical vapor deposition of titanium-containing films on quartz or CaF_2 substrates at 400 °C. Additional pyrolysis converts the film to an adherent, chemically resistant, refractory material. The infrared spectrum of the initial deposition product on a CaF_2 substrate was obtained. Chemical analysis and IR spectroscopy suggest the film contains a large excess of carbon over that required for stoichiometric TiC. Hydrocarbon evolution probably occurs by a hydrogen abstraction mechanism, which leads to dehydrogenation of coordinated cyclopentadienyl. This dehydrogenated ring system appears to be the source of the excess carbon in the solid film.

Introduction

The design of generalized, low-temperature synthetic routes to the carbides, nitrides, and borides of titanium is an area of active research. These materials have many desirable properties; however, the synthesis of these materials in useful forms such as fibers, whiskers, or films is a difficult task. The traditional powder metallurgical preparative methods require high temperatures and yield a product that must be further processed by grinding, sintering, and pressing.[1] Metalloorganic compounds may be attractive as precursor compounds to these refractory materials since the presence of the organic group will allow the properties of the precursor to be changed so that it can be readily processed. This strategy has been discussed within the context of polymeric precursors to ceramic materials.[2,3]

The metalloorganic chemical vapor deposition (MOCVD) technique is used in the electronics industry to prepare materials such as GaAs. It is highly desirable to find single-source precursor compounds for the chemical vapor deposition (CVD) of binary refractory materials. Girolami and co-workers[4] have demonstrated that tetraneopentyltitanium is a useful reagent for the CVD of

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