196. Variable-Temperature and Variable-Pressure Kinetic and Equilibrium Studies of Formation and Dissociation of $[V(H_2O)_5NCS]^{2+}$

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The kinetics of formation and dissociation of $[V(H_2O)_5NCS]^{2+}$ have been studied, as a function of excess metal-ion concentration, temperature, and pressure, by the stopped-flow technique. The thermodynamic stability of the complex was also determined spectrophotometrically. The kinetic and equilibrium data were submitted to a combined analysis. The rate constants and activation parameters for the formation (f) and dissociation (r) of the complex are: $k_f^{298}/\mathrm{M}^{-1}\cdot s^{-1} = 126.4$, $k_r^{298}/s^{-1} = 0.82$; $\Delta H_f^{\neq}/kJ\cdot mol^{-1} = 49.1$, $\Delta H_r^{\neq}/kJ\cdot mol^{-1} = 60.6$; $\Delta S_f^{\neq}/J\cdot K^{-1}\cdot mol^{-1} = -39.8$, $\Delta S_r^{\neq}/J\cdot K^{-1}\cdot mol^{-1} = -43.4$; $\Delta V_f^{\neq}/cm^3\cdot mol^{-1} = -9.4$, and $\Delta V_r^{\neq}/cm^3\cdot mol^{-1} = -17.9$. The equilibrium constant for the formation of the monoisothiocynato complex is $K^{298}/\mathrm{M}^{-1} = 152.9$, and the enthalpy and entropy of reaction are $\Delta H^0/kJ\cdot mol^{-1} = -11.4$ and $\Delta S^0/J\cdot K^{-1}\ mol^{-1} = +3.6$. The reaction volume is $\Delta V^0/cm^3\cdot mol^{-1} = +8.5$. The activation parameters for the complex-formation step are similar to those for the water exchange on $[V(H_2O)_6]^{3+}$ obtained previously by NMR techniques. The activation volumes for the two processes are consistent with an associative interchange, I_a, mechanism.

Introduction. – During the last decade, the volume of activation [1–3] has become a recognized criterion to complement the traditional ways of assessing the mechanisms of solvent-exchange and complex-formation reactions. In particular, it has been shown that a gradual mechanistic changeover from an associative activation mode to a dissociative one is occurring for water exchange on di- and trivalent high-spin octahedral aqua-ions of the first-row transition-metal series [2]. This mechanistic changeover was also confirmed for monocomplex-formation reactions on the same divalent transition metal aqua-ions [1]. This was made possible by the development of the high-pressure NMR [4–7] and stopped-flow techniques [8–10].

Few variable-pressure studies have been performed on complex-formation reactions of trivalent first-row transition-metal aqua-ions. For the post transition-metal ion $[Ga(H_2O)_6]^{3+}$, the $\Delta V_f^{\neq}$ value of +4.0 $cm^3\cdot mol^{-1}$ for the formation of the mono(4-isopropyltropolone) complex [11], together with that of $\Delta V_{ex}^{\neq}/cm^3\cdot mol^{-1} = +5.0$ for water exchange [3], are indicative of an I_d mechanism of substitution. The $\Delta V_f^{\neq}$ values for complex formation on $[Fe(H_2O)_6]^{3+}$ range between −12 and +6.7 $cm^3\cdot mol^{-1}$ [12–16], and, therefore, do not allow a clear-cut mechanistic assignment for this ion. The only activation volume for $[Cr(H_2O)_6]^{3+}$, with the exception of the H_2O-exchange value of −9.6 $cm^3\cdot mol^{-1}$ [2], is a $\Delta V_f^{\neq}$ value of −2.2 $cm^3\cdot mol^{-1}$ for the formation of an oxalate complex [17]. No complex-formation studies have been reported at variable pressure with the earlier $[Ti(H_2O)_6]^{3+}$ and $[V(H_2O)_6]^{3+}$ transition-elements ions.

For $[V(H_2O)_6]^{3+}$, the measured volume of activation for H_2O exchange, $\Delta V_{ex}^{\neq}/cm^3\cdot mol^{-1} = -8.9$ [18], was used as evidence for an I_a mechanism, when compared to the value of −12.1 $cm^3\cdot mol^{-1}$, observed for $[Ti(H_2O)_6]^{3+}$ (*A* mechanism) [19]. Data on complex formation with $[V(H_2O)_6]^{3+}$ are scarce [20–22] and include ligands that are not directly comparable. The ligand dependence of the rate constants suggests that these substitution reactions proceed associatively. To strengthen this assignment and to compare pressure effects on complex formation and solvent exchange, we have studied the simple complex-formation reaction of $[V(H_2O)_6]^{3+}$ with SCN^- ion by variable-pressure stopped-flow. For this reaction, previously studied at ambient pressure [23][24], the whole volume diagram can be established, as required for a proper mechanistic assignment.

Experimental. – 1. *Chemicals and Solutions.* VCl_3 *(Jansen, purum)* was used as received. CF_3SO_3H (trivial name: triflic acid HT; *Alpha, purum*) was distilled at amb. pressure and degassed under reduced pressure. $V(CF_3SO_3)_3$ was prepared as described in [18]. NaSCN *(Merck, p.a.)* was recrystallized from H_2O and dried in vacuum. Sodium triflate (NaT), used as an inert electrolyte, was prepared by neutralizing a 1M HT soln. with NaOH *(Merck, p.a.)* to pH 6.2, evaporating H_2O and recrystallizing the white solid in H_2O/acetone mixture and drying the crystals in vacuum. Distilled H_2O was used to prepare all solns. Stock solns. of 1M HT were prepared by dilution of conc. acid and heating for 20 min at 45° to hydrolyse triflic anhydride impurities. The acid concentration, C_{HT}, was determined by titration with NaOH. Two stock solns., 0.1M in V^{3+} and $8 \cdot 10^{-3}$ M in NaSCN, were prepared by weight and used within one week. The vanadium concentration was controlled by its absorbance ($\varepsilon/M^{-1} \cdot cm^{-1} = 8.4$ at 398 nm). Sample solns. were prepared shortly before use under inert atmosphere by diluting the stock solns.

2. *Instrumentation.* A *Perkin-Elmer Lambda 5* spectrophotometer with thermostatted cells was used for the equilibrium studies. A high-pressure optical cell [25] was used for variable-pressure studies. The experimental setups for stopped-flow kinetic work at amb. pressure were as described previously [26]. For the variable pressure work, a new high-pressure stopped-flow apparatus was built. This version can support pressures up to 200 MPa on a temp. range of 223 to 373 K with an improved temp. stability, a better light throughput and a response time of 4 ms [10].

Results. – The kinetics of mono-complex formation and dissociation of $[V(H_2O)_5NCS]^{2+}$ *(Reaction 1)* were studied as a function of metal-ion concentration, temperature, and pressure. Under the pseudo-first-order conditions *(Eqn. 2)* of at least

$$[V(H_2O)_6]^{3+} + SCN^- \underset{k_r}{\overset{k_f}{\rightleftarrows}} [V(H_2O)_5NCS]^{2+} + H_2O \tag{1}$$

$$k_{obs} = k_f C_V + k_r \tag{2}$$

tenfold excess metal, the reaction was found to follow first-order kinetics over more than 4 half-lives and the observed rate constants, k_{obs}, were independent of the wavelength of observation (290 or 347 nm). Varying the concentration of acid from 0.25 to 1M produced no significant variation in the measured rate constants. A similar finding was previously observed by *Welch* and coworkers [23].

The k_{obs} values obtained at various temperatures between 273.2 and 328.2 K were analysed using *Eqn. 2* and the *Eyring* equation for the temperature dependence of k_f and k_r. A four-parameters simultaneous analysis of the data yielded the k_f^{298} (or $\Delta S_f^{\neq}$), k_r^{298} (or $\Delta S_r^{\neq}$), $\Delta H_f^{\neq}$, and $\Delta H_r^{\neq}$ values listed in *Table 1*. *Fig. 1* shows k_{obs} (average of 4 to 8 experiments) as a function of C_V at several temperatures. The variation of k_{obs} as a function of pressure *(Fig. 2)* was measured at 298 K with 5 solutions of increasing C_V. The data were analysed using *Eqn. 3*. with $k_{f,0}$ and $k_{r,0}$, the rate constants at zero pressure, and the pressure-independent $\Delta V_f^{\neq}$ and $\Delta V_r^{\neq}$, as parameters. The results are listed in *Table 1*.

$$\ln k_{obs} = \ln \{k_{f,0} C_V \exp - (\Delta V_f^{\neq} P/RT) + k_{r,0} \exp - (\Delta V_r^{\neq} P/RT)\} \tag{3}$$

Table 1. *Thermodynamic and Kinetic Parameters for Complex Formation and Dissociation of* $[V(H_2O)_5NCS]^{2+}$[a]

	Individual fits	Simultaneous fits
K^{298}/M^{-1}	158.5 ± 7.2[b]	152.9 ± 4.4[g]
$k_f^{298}/\mathrm{M}^{-1}\cdot\mathrm{s}^{-1}$	122.0 ± 3.2[c]	126.4 ± 1.8[g]
$k_r^{298}/\mathrm{s}^{-1}$	0.86 ± 0.02[c]	0.82 ± 0.01[g]
$\Delta H^0/\mathrm{kJ}\cdot\mathrm{mol}^{-1}$	−12.9 ± 0.3[d]	−11.4 ± 1.2[g]
$\Delta H_f^{\neq}/\mathrm{kJ}\cdot\mathrm{mol}^{-1}$	49.1 ± 1.0[c]	49.1 ± 0.6[g]
$\Delta H_r^{\neq}/\mathrm{kJ}\cdot\mathrm{mol}^{-1}$	60.2 ± 1.0[c]	60.6 ± 0.7[g]
$\Delta S^0/\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}$	−0.9 ± 0.8[d]	+3.6 ± 3.9[g]
$\Delta S_f^{\neq}/\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}$	−40.3 ± 3.4[c]	−39.8 ± 2.0[g]
$\Delta S_r^{\neq}/\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}$	−44.2 ± 3.4[c]	−43.4 ± 2.2[g]
ΔV^0 (298 K)/$\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$	+7.0 ± 0.1[e]	+8.5 ± 1.2[h]
$\Delta V_f^{\neq}$ (298 K)/$\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$	−9.1 ± 1.2[f]	−9.4 ± 0.6[h]
$\Delta V_r^{\neq}$ (298 K)/$\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$	−18.4 ± 1.2[f]	−17.9 ± 0.7[h]

[a] At 298 K, $I/\mathrm{M} = 0.5$ or 0.6, $\mathrm{HT}/\mathrm{M} = 0.4$; the errors quoted are one standard deviation.

[b] Equilibrium data at 298 K.

[c] Variable-temperature kinetic data.

[d] Variable-temperature equilibrium data: $\log(K^{298}/\mathrm{M}^{-1}) = 2.20$.

[e] Variable-pressure equilibrium data: $\log(K_0^{298}/\mathrm{M}^{-1}) = 2.20$.

[f] Variable-pressure kinetic data: $k_{f,0}^{298}/\mathrm{M}^{-1}\cdot\mathrm{s}^{-1} = 152.2$, $k_{r,0}^{298}/\mathrm{s}^{-1} = 0.81$.

[g] Ambient-pressure equilibrium and kinetic data.

[h] Variable-pressure equilibrium and kinetic data.

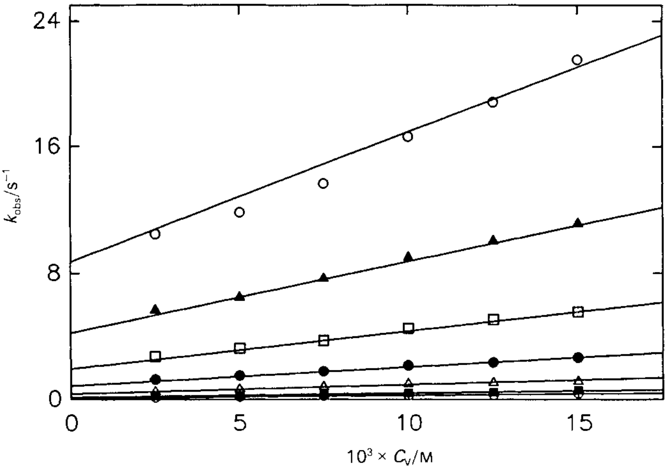

Fig. 1. *Temperature dependence* (from bottom to top: 273 K, then with ten degrees intervals between 278 and 328 K) *of the observed pseudo-first-order rate constant,* k_{obs}, *for the formation of* $[V(H_2O)_5NCS]^{2+}$ *as a function of* C_V. $\mathrm{HT}/\mathrm{M} = 0.4$, $I/\mathrm{M} = 0.5$.

A spectrophotometric determination of the stability constant, K^{298}, of the $[V(H_2O)_5NCS^{2+}]$ complex was also carried out. The equilibrium constant was determined from the least-squares analysis of the absorbance measurements ($C_{\mathrm{HT}}/\mathrm{M} = 0.4$, $I/\mathrm{M} = 0.6$) at various wavelengths between 282 and 322 nm and different concentrations ($0.9 \leqslant 10^3 \cdot C_V/\mathrm{M} \leqslant 10.0$, $0.8 \leqslant 10^3 \cdot C_{\mathrm{NCS}}/\mathrm{M} \leqslant 4.0$), with the equilibrium constant and extinc-

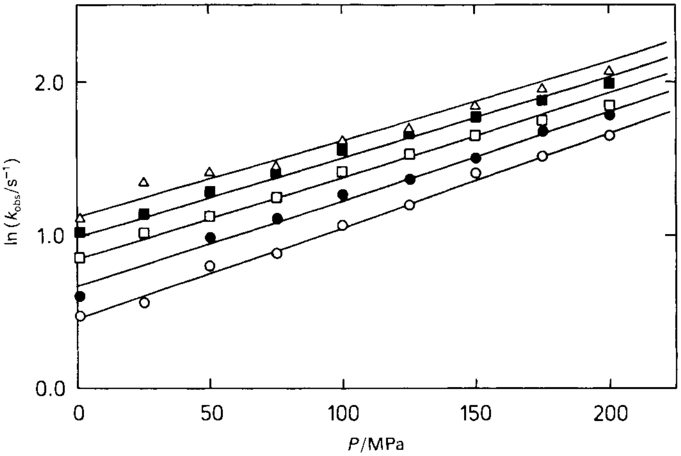

Fig. 2. *Pressure dependence of the observed first-order rate constants,* k_{obs}, *for the formation of* $[V(H_2O)_5NCS]^{2+}$ *at 298 K.* HT/M = 0.4, I/M = 0.6. C_{SCN}/M = $1 \cdot 10^{-4}$, $10^{-3} \cdot C_V$/M = 5.0 (○); 7.5 (●); (10 (□); 12.5 (■); 15 (△).

tion coefficients of metal ion and complex as parameters in the minimizing program SPECFIT [27]. When excess metal-ion concentration is used, the best fit is obtained for a 1:1 complex, with stability constant log (K^{298}/M^{-1}) = 2.20 ± 0.02 and molar absorptivity ε/M$^{-1}\cdot$cm^{-1} = 1706 at 290 nm. This is in reasonable agreement with the log K^{298} value calculated from the kinetics as log(k_f/k_r/M^{-1}) = 2.15. The variable-temperature (278.9 to 325.4 K) and variable-pressure (up to 200 MPa at 298 K) measurements were carried out at 290 nm with solutions of C_V/M = $4.0 \cdot 10^{-3}$ to $6.0 \cdot 10^{-3}$ and C_{NCS}/M = $1.0 \cdot 10^{-3}$ to $2.0 \cdot 10^{-3}$ (I/M = 0.5 or 0.6 NaT and C_{HT}/M = 0.4). *Fig. 3* shows the decrease in concentration of $[V(H_2O)_5NCS]^{2+}$ with increasing pressure. The analysis of the variable-temperature and variable-pressure equilibrium data taken separately yielded the ΔH^0 and ΔS^0, and ΔV^0 values reported in *Table 1*.

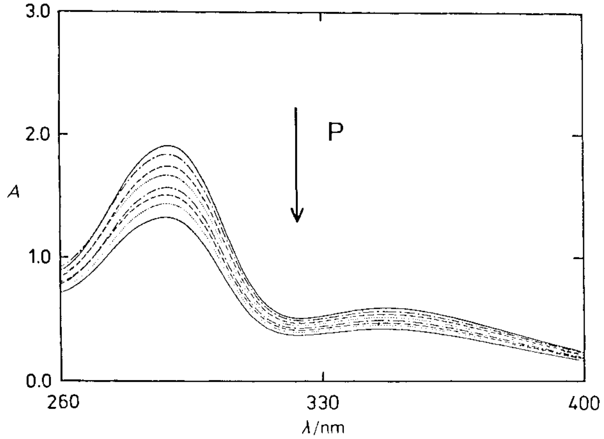

Fig. 3. *Absorption spectra of an aqueous solution* $3 \cdot 10^{-3}$ M *in* V^{3+} *and* $2 \cdot 10^{-3}$ M *in* NCS^- *at variable pressure* (3 < P/MPa < 200; HT/M = 0.4, I/M = 0.5; T/K = 298)

Finally, the variable-pressure kinetic and equilibrium data were fitted together using *Eqns. 3* and *4*, using $k_{f,0}$, $k_{r,0}$, $\Delta V_f^{\neq}$, and $\Delta V_r^{\neq}$ as adjustable parameters (K_0, ΔV^0 and their

$$\ln K_r = \ln (k_{f,0}/k_{r,0}) - (\Delta V_f^{\neq} - V_r^{\neq})P/RT \tag{4}$$

standard deviations, have been obtained by replacing $k_{f,0}$ by $K_o \cdot k_{r,0}$ and $\Delta V_f^{\neq}$ by $\Delta V^0 + \Delta V_r^{\neq}$ in these equations). Similarly, all variable-temperature data were fitted together and show, like the variable pressure data, excellent consistency between all kinetic and equilibrium data. The earlier data of *Welch* and coworkers [23], although obtained in perchlorate media and on a smaller temperature range (278 to 310 K), are in reasonable agreement but show less steep slopes in the *Eyring* plots: $k_f/\text{M}^{-1}\cdot\text{s}^{-1} = 114$, $k_r/\text{s}^{-1} = 1.03$, $\Delta H_f^{\neq}/\text{kJ}\cdot\text{mol}^{-1} = 31.8$, $\Delta S_f^{\neq}/\text{J}\cdot\text{mol}^{-1} = -99.5$; $\Delta H_r^{\neq}/\text{kJ}\cdot\text{mol}^{-1} = 44.7$, $\Delta S_r^{\neq}/\text{J}\cdot\text{mol}^{-1} = -94.5$.

Discussion. – The replacement of a H_2O molecule of an aquated transition-metal cation by a ligand is usually described by the *Eigen-Wilkins* mechanism [28]. Formation of an outer-sphere (or encounter) complex occurs first in a fast pre-equilibrium. This pre-association is followed by the interchange of one bound H_2O molecule for the ligand, as show in *Eqns. 5*. The second-order rate constant for complex formation, k_f, is related to

$$[M(H_2O)_6]^{3+} + L^{n-} \overset{K_{os}}{\rightleftarrows} [M(H_2O)_6L]^{(3-n)} \xrightarrow{k_I} [M(H_2O)_5L]^{(3-n)} + H_2O \tag{5}$$

the stability constant of the outer-sphere complex, K_{os}, and to the rate constant of the interchange, k_I, by *Eqn. 6*, which assumes $K_{os}\,[V(H_2O)_6]^{3+} \ll 1$. The derivative of *Eqn. 6* as a function of pressure gives *Eqn. 7*, relating the activation volume, $\Delta V_f^{\neq}$, to the volume

$$k_f = K_{os} \cdot k_I \tag{6}$$

$$\Delta V_f^{\neq} = \Delta V_{os}^0 + \Delta V_I^{\neq} \tag{7}$$

change during outer-sphere complex formation, ΔV_{os}^0, and to the activation volume for the interchange step, $\Delta V_I^{\neq}$. The next step is to evaluate ΔV_{os}^0 in order to obtain the mechanistically more directly interpretable $\Delta V_I^{\neq}$ value [26]. The pressure derivative of K_{os} leads, according to *van Eldik* and coworkers [16], to *Eqn. 8*, where k_B is the *Boltzmann*

$$\Delta V_{os}^0 = -RT\ \left\{\{[z_1 z_2 e^2(\zeta + 0.5a\kappa(\zeta + \beta))]/[(1 + a\kappa)^2 \varepsilon \cdot k_B \cdot T \cdot a]\} + \beta\right\} \tag{8}$$
$$\text{with } \kappa = (8 \cdot 10^{-3} \cdot \pi \cdot N \cdot e^2 \cdot I/\varepsilon \cdot k_B \cdot T)^{0.5}$$

constant, ε the dielectric constant and I the ionic strength. Using a distance of closest approach $a/\text{cm} = 5 \cdot 10^{-8}$, a pressure coefficient of the dielectric constant $\zeta/\text{MPa}^{-1} = 4.71 \cdot 10^{-4}$ [29], and a water isothermal compressibility $\beta/\text{MPa}^{-1} = 4.58 \cdot 10^{-4}$, we calculate the following $\Delta V_{os}^0/\text{cm}^3\cdot\text{mol}^{-1}$ values as function of ionic strength (I/M): +3.9 (0.0), +2.5 (0.05), +2.1 (0.1), and +1.1 (0.6). However, ΔV_{os}^0 cannot be estimated with such accuracy due to the deviation of the *Debye-Hückel* model at high ionic strength, the use of ζ and β values relative to pure H_2O and the limitations of the model. Thus, we use a ΔV_{os}^0 value of +2 ± 1 $\text{cm}^3\cdot\text{mol}^{-1}$ for the outer-sphere complex formation between $[V(H_2O)_6]^{3+}$

and SCN$^-$. This value, together with the experimentally determined $\Delta V_f^{\neq}$ and $\Delta V_r^{\neq}$ values, enables the volume diagram shown in *Fig. 4* to be build. The $\Delta V_I^{\neq}$ value of -11 cm$^3\cdot$mol^{-1} is indicative of an associative activation mode for the interchange step leading to the formation of $[V(H_2O)_5(NCS)]^{2+}$.

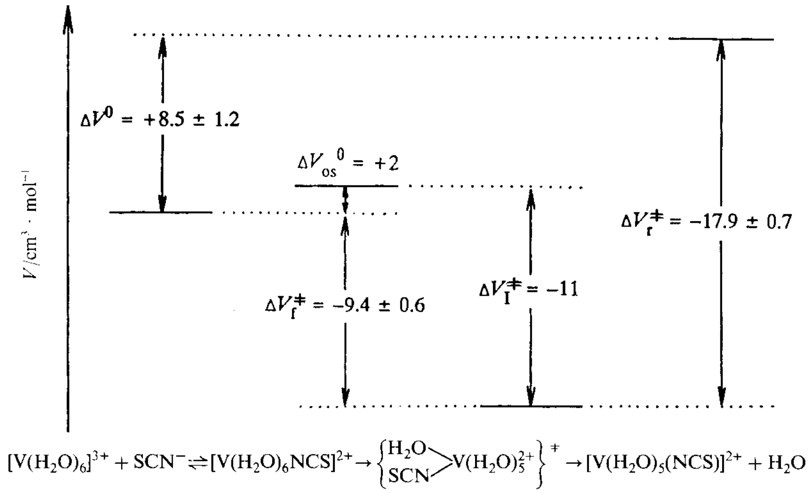

Fig. 4. *Volume diagram for the reaction between $[V(H_2O)_6]^{3+}$ and NCS^-*

During an associative process, the nature of the entering ligand plays a crucial role, and the k_I values are expected to be very much dependent on its characteristics, such as charge, nucleophilicity or size, as has been shown for $[V(H_2O)_6]^{3+}$ [18]. A ligand-dependent $\Delta V_I^{\neq}$ could be a further indication of an associative interchange mechanism, but the only other value to compare with is $\Delta V_{ex}^{\neq}$/cm$^3\cdot$mol^{-1} = -8.9 *(Table 2)* for the symmetrical H$_2$O-exchange reaction. The even more negative activation volume $\Delta V_r^{\neq}$/cm$^3\cdot$mol^{-1} = -17.9 for the reverse reaction can be discussed in terms of a positive volume of reaction ΔV^0/cm$^3\cdot$mol^{-1} = +8.5. This latter value is expected for a decreased electrostriction induced by a neutralisation of charges, and is of the same order of magnitude as earlier experimental observations: ΔV^0/cm$^3\cdot$mol^{-1} = +8.9 [12], +7.5 [13], +8.3 [14], +8.9 [30], and +7.6 [16] for $[Fe(H_2O)_6]^{3+} + SCN^-$, and +9.8 [31] for $[Cr(NH_3)_5(H_2O)]^{3+} + SCN^-$.

The comparison of rate constants and activation volumes for complex-formation reactions involving different cations and ligands makes it necessary to first separate the strongly charge-dependent outer-sphere contribution from the interchange contribution. However, it must be remembered that the k_I and especially $\Delta V_I^{\neq}$ values also contain a solvational contribution [32]. In this context, because of the difficulty of evaluating ΔV_{os}^0 and the possible variation of $\Delta V_I^{\neq}$ among associatively activated reactions, we have directly reported $\Delta V_f^{\neq}$ in *Table 2*. The activation volume values for H$_2$O exchange, complex formation, and dissociation on first-row octahedral trivalent transition-metal ions are all clearly indicative of a mechanistic changeover along the series from I_a for $[V(H_2O)_6]^{3+}$ to I_d for $[Ga(H_2O)_6]^{3+}$. They also confirm the stronger associative character of the reaction of the trivalent aqua-ion compared to the divalent aqua-ion of the early

Table 2. *Activation Volumes* [$cm^3 \cdot mol^{-1}$] *for H_2O Exchange on the Trivalent Octahedral First-Row Cations $[M(H_2O)_6]^{3+}$, $\Delta V_{ex}^{\neq}$, and for Complex Formation, $\Delta V_f^{\neq}$, and Dissociation, $\Delta V_r^{\neq}$, of their Monocomplexes with the Ligands L*

L		*M*				
		V^{3+}	Cr^{3+}	Fe^{3+}	Ga^{3+}	Ref.
H_2O	$\Delta V_{ex}^{\neq}$	−8.9	−9.6	−5.4	+5.0	[2]
Hahx[a])	$\Delta V_f^{\neq}$[b])			−10.0		[32][c])
Hipt[d])	$\Delta V_f^{\neq}$[b])			−8.7[e])	+4.0[f])	
Oxalate	$\Delta V_f^{\neq}$		−2.2			[17][g])
Br^-	$\Delta V_f^{\neq}$			−8		[33][h])
	$\Delta V_r^{\neq}$			−16		
Cl^-	$\Delta V_f^{\neq}$			−4.5		[34][i])
	$\Delta V_r^{\neq}$			−9.2		
SCN^-	$\Delta V_f^{\neq}$	−9.4[j])		−12 to +6.7[k])		
	$\Delta V_r^{\neq}$	−17.9[j])		−15.0 to −3.3[l])		
Mechanism		I_a	I_a	I_a	I_d	

[a]) Hahx = acetohydroxamic acid.
[b]) $\Delta V_f^{\neq} \approx \Delta V_I^{\neq}$ (ΔV_{os}^0 close to zero for uncharged ligands).
[c]) $I/\mathrm{M} = 1$.
[d]) Hipt = 4-isopropyltropolone.
[e]) [35], $I/\mathrm{M} = 1$.
[f]) [11], $I/\mathrm{M} = 0.5$.
[g]) $I/\mathrm{M} = 1$.
[h]) $I/\mathrm{M} = 2$.
[i]) $I/\mathrm{M} = 1.5$.
[j]) This work, $I/\mathrm{M} = 0.6$.
[k]) [12] $I/\mathrm{M} = 0.2$; [13] $I/\mathrm{M} = 0.4$; [14] $I/\mathrm{M} = 0.2$; [15] $I/\mathrm{M} = 1.5$; [16] $I/\mathrm{M} = 1$.
[l]) [12] $I/\mathrm{M} = 0.2$; [15] $I/\mathrm{M} = 1.5$, $\Delta V_r^{\neq} = \Delta V_f^{\neq} - \Delta V^0$; [16] $I/\mathrm{M} = 1$.

first-row transition series: $\Delta V_{ex}^{\neq}/cm^3 \cdot mol^{-1} = -8.9$ for $[V(H_2O)_6]^{3+}$ [18], −5.4 for $[V(H_2O)_6]^{2+}$ [2], and $\Delta V_f^{\neq}/cm^3 \cdot mol^{-1} = -9.4$ for $[V(H_2O)_5NCS]^{2+}$, −2.1 for $[V(H_2O)_5NCS]^{+}$ [26].

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REFERENCES

[1] 'Inorganic high pressure chemistry: Kinetics and Mechanisms', Ed. R. van Eldik, Elsevier, Amsterdam, 1986, Chapt. 2 and 3.
[2] A. E. Merbach, *Pure Appl. Chem.* **1987,** *59,* 161.
[3] R. van Eldik, T. Asano, W. J. Le Noble, *Chem. Rev.* **1989,** *89,* 549.
[4] H. Vanni, W. L. Earl, A. E. Merbach, *J. Magn. Reson.* **1978,** *29,* 11.
[5] W. L. Earl, H. Vanni, A. E. Merbach, *J. Magn. Reson.* **1978,** *30,* 571.
[6] D. L. Pisaniello, L. Helm, P. Meier, A. E. Merbach, *J. Am. Chem. Soc.* **1983,** *105,* 4528.
[7] U. Frey, L. Helm, A. E. Merbach, *High Pressure Res.*, in press.
[8] K. Heremans, *Rev. Sci. Instrum.* **1980,** *51,* 806.
[9] K. Ishihara, S. Funahashi, M. Tanaka, *Rev. Sci. Instrum.* **1982,** *53,* 34.
[10] P. Y. Sauvageat, G. Laurenczy, Y. Ducommun, A. E. Merbach, to be submitted.
[11] S. Yamada, A. Iwanaga, S. Funahashi, M. Tanaka, *Inorg. Chem.* **1984,** *23,* 3528.

[12] A. Jost, *Ber. Bunsenges. Phys. Chem.* **1976,** *80,* 316.
[13] K. Heremans, K. Snauwaert, J. Rijkenberg, *High-Pressure Sci. Technol.* AIRAPT Conf. 6 th, 1977, 646.
[14] R. Doss, R. van Eldik, H. Kelm, *Ber. Bunsenges. Phys. Chem.* **1982,** *86,* 925.
[15] K. Ishihara, S. Funahashi, M. Tanaka, *Inorg. Chem.* **1983,** *22,* 2020.
[16] P. Martinez, R. Mohr, R. van Eldik, *Ber. Bunsenges. Phys. Chem.* **1986,** *90,* 609.
[17] C. Schenk, H. Kelm, *J. Coord. Chem.* **1972,** *2,* 71.
[18] A. D. Hugi, L. Helm, A. E. Merbach, *Helv. Chim. Acta* **1985,** *68,* 508.
[19] A. D. Hugi, L. Helm, A. E. Merbach, *Inorg. Chem.* **1987,** *26,* 1763.
[20] P. N. Mathur, H. Fukutomi, *J. Inorg. Nucl. Chem.* **1981,** *43,* 2869, and ref. cit. therein.
[21] B. Perlmutter-Hayman, E. Tapuhi, *J. Coord. Chem.* **1980,** *10,* 219, and ref. cit. therein.
[22] J. Konstantatos, G. Kalatzis, E. Vrachnou-Astra, *J. Chem. Soc., Dalton Trans.* **1985,** 2461.
[23] B. R. Baker, T. J. Sutin, T. Welch, *Inorg. Chem.* **1967,** *6,* 1948.
[24] B. R. Kruse, W. Thusius, *Inorg. Chem.* **1968,** *7,* 464.
[25] D. T. Richens, Y. Ducommun, A. E. Merbach, *J. Am. Chem. Soc.* **1987,** *109,* 603.
[26] P. J. Nichols, Y. Ducommun, A. E. Merbach, *Inorg. Chem.* **1983,** *22,* 3993.
[27] H. Gampp, M. Maeder, C. J. Meyer, A. D. Zuberbühler, *Talanta* **1985,** *32,* 252.
[28] A. E. Martell, 'Coordination Chemistry', Ed. A. E. Martell, ACS Monograph, Washington, 1978, Chapt. 1.
[29] K. R. Srinivasan, R. L. Kay, *J. Phys. Chem.* **1974,** *60,* 3646.
[30] S. Funahashi, K. Sengoku, T. Amari, M. Tanaka, *J. Sol. Chem.* **1988,** *17,* 109.
[31] D. A. Palmer, H. Kelm, *Inorg. Chem.* **1977,** *16,* 3139.
[32] S. Funahashi, K. Ishihara, M. Tanaka, *Inorg. Chem.* **1983,** *22,* 2070.
[33] B. B. Hasinoff, *Can. J. Chem.* **1979,** *57,* 77.
[34] B. B. Hasinoff, *Can. J. Chem.* **1976,** *54,* 1820.
[35] K. Ishihara, S. Funahashi, M. Tanaka, *Inorg. Chem.* **1983,** *22,* 194.