

Water Exchange on Hexaaquagallium(III): High-Pressure Evidence for a Dissociative Interchange Exchange Mechanism¹⁻³

Deirdre Hugi-Cleary, Lothar Helm, and Andre E. Merbach*

Contribution from the Institut de Chimie Minérale et Analytique, University of Lausanne, 1005 Lausanne, Switzerland. Received December 23, 1986

Abstract: Rate constants and activation parameters for water exchange on hexaaqua- and monohydroxypentaaquagallium(III) have been determined by measurement of the transverse relaxation rate of bound H₂O as a function of temperature (254–347 K) and pressure (up to 220 MPa) at several different acidities (0.25–3.0 M) using the ¹⁷O NMR line-broadening technique. Mn²⁺ was used as relaxation agent for the bulk water, and noncoordinating perchlorate was used as counterion. The observed rate constant was of the form $k_{ex} = k_1 + k_2/[H^+]$ where the subscripts 1 and 2 refer to the exchange pathways on Ga(H₂O)₆³⁺ and Ga(H₂O)₅OH²⁺, respectively. The kinetic parameters are as follows: $k_1^{298} = 403 \pm 39 \text{ s}^{-1}$, $\Delta H_1^\ddagger = 67.1 \pm 2.5 \text{ kJ mol}^{-1}$, $\Delta S_1^\ddagger = +30.1 \pm 7.7 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta V_1^\ddagger = +5.0 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$; $k_2^{298} = 14 \pm 5 \text{ m s}^{-1}$, $\Delta H_2^\ddagger = 111 \pm 10 \text{ kJ mol}^{-1}$, $\Delta S_2^\ddagger = +149.2 \pm 29.6 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta V_2^\ddagger = +7.7 \pm 1.4 \text{ cm}^3 \text{ mol}^{-1}$. Estimations of the first-order rate constant (using the relation $k_2 = k_{OH}K_{a1}$) and the corresponding activation volume for Ga(H₂O)₅OH²⁺ are $k_{OH}^{298} \approx (0.6\text{--}2.0) \times 10^5 \text{ s}^{-1}$ and $\Delta V_{OH}^\ddagger \approx +6 \text{ cm}^3 \text{ mol}^{-1}$. These kinetic results imply dissociative activation for both solvated species, and dissociative interchange, I_d, exchange mechanisms have been assigned. The gradual changeover in substitution mechanism, already observed in the case of divalent first-row transition-metal hexaaqua ions, is thus also established for trivalent hexaaqua ions.

An important aid in mechanistic elucidation in recent years has been the study of the effect of pressure on the rate of a substitution reaction, which can be interpreted as a volume change in the activation step.⁴ In the absence of the creation or dissipation of charges or dipoles at the transition state, the interpretation of the activation volume, ΔV^\ddagger , is facilitated and can be directly linked to the reaction mechanism. A positive ΔV^\ddagger indicates dissociative activation, and a negative ΔV^\ddagger indicates associative activation.⁴ This is the case for solvent-exchange reactions, and high-pressure NMR is particularly suited to their study. Furthermore, experimental determination of ΔV^\ddagger is subject to less error than ΔS^\ddagger determination,⁵ so mechanistic assignment on the basis of ΔV^\ddagger is unambiguous for solvent exchange.

High-pressure NMR studies of solvent exchange on hexasolvated gallium(III) in nonaqueous solvents have shown that exchange proceeds via a limiting dissociative, D, mechanism.⁶ However, current interpretation of complexation on this cation in aqueous solution is controversial, and both associative⁷⁻¹² and dissociative¹³⁻¹⁵ activation have been proposed. The facility of Ga(H₂O)₆³⁺ for hydrolysis¹⁶ complicates its study and thus, in complex formation reactions involving weakly acidic ligands such as salicylates, several pathways must be considered, comprising hydrolyzed and unhydrolyzed Ga³⁺ and protonated and un-

protonated ligand. This leads to the problem of "proton ambiguity" and adds to the difficulties in interpreting the observed reaction rates. The contributions from hydrolytic species have not been taken into account in the analyses of the two variable-temperature NMR studies of water exchange on Ga(H₂O)₆³⁺ available to date.^{17,18}

Furthermore, the mechanism of solvent exchange on the divalent high-spin first-row transition-metal ions has been shown to change gradually from I_a to I_d across the series, the changeover occurring after the d⁵ configuration.⁶ Evidence so far in nonaqueous solvents has indicated that a similar mechanistic changeover exists also for the trivalent high-spin solvated ions.⁶ In aqueous solution, negative activation volumes for water exchange on trivalent titanium,³ vanadium,¹⁹ chromium,²⁰ and iron²¹ corroborate the assignment of associative activation modes for these ions in nonaqueous solution. Therefore unambiguous activation parameters and mechanistic assignment for Ga(H₂O)₆³⁺ (d¹⁰) are of supreme interest.

In the light of the above arguments we decided to undertake a complete variable-temperature and variable-pressure NMR study of water exchange on hexaaquagallium(III).

Experimental Section

A. Chemicals and Solutions. Hydrated gallium perchlorate (Ventron) and manganese perchlorate hexahydrate (Merck, p.a.) were analyzed complexometrically with Na₂H₂EDTA (Siegfried) for their metal ion content.²² Perchloric acid (70%, Merck, p.a.) and oxygen-17-enriched water (Yeda, 20 or 40 atom %, normalized in ¹H) were used as received. The samples used for the variable-temperature and variable-pressure studies were 0.5 M in Ga³⁺, 0.5 M in Mn²⁺, and with three concentrations of HClO₄ (3.0, 0.4, and 0.25 M; m = molal).

B. Instrumentation. Oxygen-17 NMR spectra were recorded on a Bruker CXP-200 spectrometer equipped with a wide-bore cryomagnet (4.67 T), and some variable-temperature spectra were also recorded on a Bruker WH-360 spectrometer (8.4 T). For the variable-temperature measurements the sample temperature was held constant within $\pm 0.3 \text{ K}$ by using a Bruker BVT-1000 thermostating unit and was measured before and after spectral accumulation by substituting the sample with a calibrated platinum resistance (accuracy $\pm 0.5 \text{ K}$ at extreme temperatures).²³ Variable-pressure measurements were made by using the

(1) This paper is to be considered part 30 of the series *High Pressure NMR Kinetics*. For part 29, see ref 3.

(2) This work is part of the Ph.D. thesis of D.H.-C., University of Lausanne, 1984, and was presented at the XXIIIrd International Conference on Coordination Chemistry, Boulder, CO, July, 1984.

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high-pressure probe described previously.²⁴ A built-in platinum resistor allows temperature measurement, with an accuracy of ± 1 K after all corrections.²⁵

C. NMR Measurements. In all cases 2048 data points were recorded, resulting from 2000 to 900 000 scans using sweepwidths of 30–100 kHz. Before Fourier transform the data were treated with an exponential filter function, resulting in line broadening of approximately 5% of $\Delta\nu_{1/2}$, the signal width at half-height. The NMR signal was fitted to a Lorentzian line shape, and the transverse relaxation rate of the bound water, $1/T_2^b$, was determined from $\Delta\nu_{1/2}$, after correction for the line broadening.

Results and Data Treatment

A. Spectra. In the slow exchange limit two resonances are observed in the spectrum of a hexaaquated metal ion, due to the free and coordinated water. In the case of some diamagnetic ions, e.g., Ga^{3+} , the chemical shift between these two signals is small compared with their linewidth. Therefore, in order to study the kinetically interesting bound water signal the two resonances must be separated, usually by the addition of a paramagnetic shift or relaxation reagent. One shift reagent is Co^{2+} , which causes an average shift of the bulk water resonance due to the strong interaction of the rapidly exchanging bulk water with the paramagnetic ions.²⁶ However this shift is not sufficient for the accurate measurement of the bound water line width of the diamagnetic ion. Mn^{2+} is a very efficient relaxation agent, and due to a strong interaction with the electron spin of Mn^{2+} , the bulk water relaxes so rapidly that its resonance becomes extremely large and of negligible amplitude. It has previously been shown that the presence of 0.2–0.5 *m* Mn^{2+} has no effect on the bound water relaxation rate;²⁷ thus we used this method. The noncoordinating perchlorate ion was used as counterion in this study. Despite the relatively high perchlorate concentrations present, it can be assumed that none is coordinated,²⁸ all the more so because no evidence for perchlorate coordination was found in a similar study of water exchange on the smaller Al^{3+} ion.²⁹

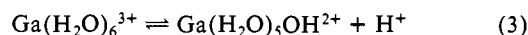
B. Equations. In the slow exchange limit, the transverse relaxation rate of water bound to a diamagnetic metal ion is given by eq 1, where τ is the mean lifetime of water in the first coor-

$$1/T_2^b = 1/\tau + 1/T_{2Q}^b \quad (1)$$

dination sphere of the metal ion and T_{2Q}^b is the quadrupolar relaxation time. If the hexaaqua metal ion is prone to hydrolysis, then the species $\text{M}(\text{H}_2\text{O})_5\text{OH}^{2+}$ may also participate in the water-exchange reaction. In the case of Ga^{3+} , the species $\text{Ga}(\text{H}_2\text{O})_5\text{OH}^{2+}$ is present in very low concentration, thus the observed rate constant is given by eq 2, where k_1 is the rate constant

$$1/\tau = k_{\text{ex}} = k_1 + k_2/[\text{H}^+] \quad (2)$$

for water exchange on the hexaaqua species and $k_2 = k_{\text{OH}}K_{a1}$, the product of k_{OH} , the rate constant for water exchange on the monohydroxy species, and K_{a1} , the first hydrolysis constant for $\text{Ga}(\text{H}_2\text{O})_6^{3+}$, for the reaction shown in eq 3. All six oxygens in



$\text{Ga}(\text{H}_2\text{O})_5\text{OH}^{2+}$ were assumed to contribute equally to the observed k_2 value.²¹ From transition-state theory, k_1 and k_2 can be expressed by eq 4, where ΔS_i^\ddagger and ΔH_i^\ddagger are, respectively, the

$$k_i = k_B T/h \exp[\Delta S_i^\ddagger/R - \Delta H_i^\ddagger/RT] \quad (i = 1, 2) \quad (4)$$

entropy and enthalpy of activation. An Arrhenius temperature

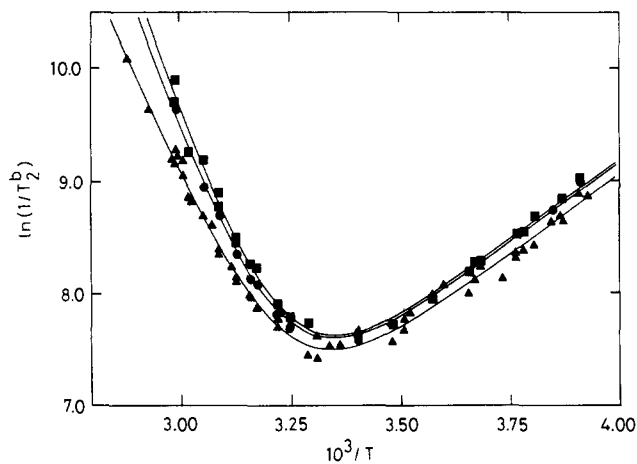


Figure 1. Temperature dependence of the transverse relaxation rate, $1/T_2^b$, from the bound water ^{17}O NMR signal of 0.5 *m* $\text{Ga}(\text{ClO}_4)_3$ and 0.5 *m* $\text{Mn}(\text{ClO}_4)_2$ solutions at various acidities: (\blacktriangle) 3.01, (\bullet) 0.38, and (\blacksquare) 0.25 *m* H^+ .

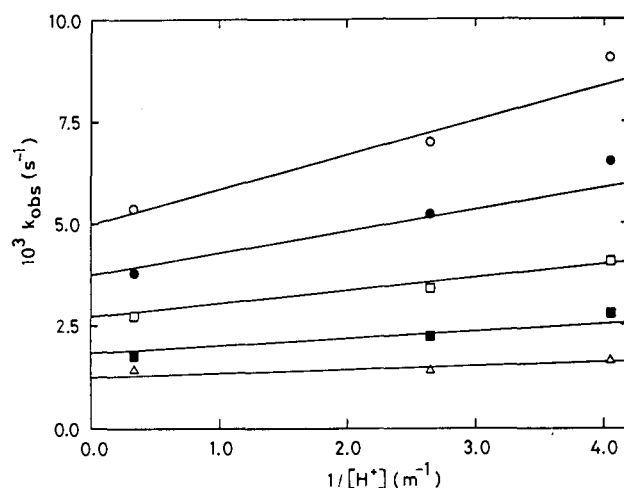


Figure 2. Acid dependence of the water-exchange rate constant of 0.5 *m* $\text{Ga}(\text{ClO}_4)_3$ and 0.5 *m* $\text{Mn}(\text{ClO}_4)_2$ solutions at various temperatures: (\triangle) 327.4, (\blacksquare) 323.8, (\square) 319.9, (\bullet) 315.3, and (\circ) 310.7 K.

Table I. Derived NMR and Kinetic Parameters for the Variable-Temperature Study of Water Exchange on Gallium(III)

k_1^{298} , s^{-1}	403 ± 39
ΔH_1^\ddagger , kJ mol^{-1}	67.1 ± 2.5
ΔS_1^\ddagger , $\text{J K}^{-1} \text{mol}^{-1}$	$+30.1 \pm 7.7$
k_2^{298} , m s^{-1}	14 ± 5
ΔH_2^\ddagger , kJ mol^{-1}	110.9 ± 9.7
ΔS_2^\ddagger , $\text{J K}^{-1} \text{mol}^{-1}$	$+149.2 \pm 29.6$
E_Q^b , kJ mol^{-1}	23.5 ± 0.7
$(1/T_{2Q}^b)^{298}$, s^{-1}	1384 ± 48 (3.0 <i>m</i> H^+)
$(1/T_{2Q}^b)^{298}$, s^{-1}	1539 ± 48 (0.4 <i>m</i> H^+)
$(1/T_{2Q}^b)^{298}$, s^{-1}	1567 ± 59 (0.25 <i>m</i> H^+)

dependence was assumed for the quadrupolar relaxation rate, eq 5, where $(1/T_{2Q}^b)^{298}$ is the contribution at 298.15 K and E_Q^b is $1/T_{2Q}^b = (1/T_{2Q}^b)^{298} \exp[E_Q^b/R(1/T - 1/298.15)]$ (5)

the corresponding activation energy. The variable pressure dependence of $\ln k_1$ and $\ln k_2$ can be described by the linear equation, eq 6, since we can assume that the corresponding volumes of

$$\ln(k_i)p = \ln k_{i,0} - P\Delta V_i^\ddagger/RT \quad (i = 1, 2) \quad (6)$$

activation are pressure independent, as is usual for simple solvent-exchange reactions.³⁰ $k_{i,0}$ values are the exchange rates at

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zero pressure. A similar equation, eq 7, describes the pressure

$$\ln(1/T_{2Q}^b)_P = \ln(1/T_{2Q}^b)_0 - P\Delta V_Q^*/RT \quad (7)$$

dependence of the quadrupolar exchange rate as a function of the quadrupolar activation volume ΔV_Q^* and the contribution at zero pressure $(1/T_{2Q}^b)_0$.

C. Variable Temperature. Figure 1 shows the inverse temperature dependence of the logarithm of the transverse relaxation rate for samples of three different acidities at temperatures between 254 and 347 K. It is clear that $1/T_2^b$ is inversely proportional to the acid concentration. Assuming that the acid dependence was due to water exchange on the monohydroxy pentaqua ion, all of the data were fitted simultaneously to eq 1, 2, 4, and 5 by using a nonlinear least-squares iteration program (reported errors are 1 standard deviation). The 10 simultaneously fitted parameters are listed in Table I. Figure 2 shows that eq 2 represents the data accurately. The quadrupolar contribution, calculated at representative temperatures by using eq 5 and the parameters listed in Table I, was subtracted from the measured $1/T_2^b$ values. The resulting k was plotted against $1/[H^+]$. The lines drawn through the data were calculated by using the kinetic parameters obtained from the least-squares analysis of the variable-temperature data.

D. Variable Pressure. The transverse relaxation rate was determined at pressures up to 220 MPa for the same three acid concentrations as used for the variable-temperature study. We measured each concentration at several temperatures between 295 and 342 K to define the kinetic (high-temperature) and quadrupolar (low-temperature) pressure dependences. The experimental data are illustrated in Figure 3. All of the data were fitted simultaneously to eq 1, 2, 6, and 7. In theory, $k_{1,0}$, $k_{2,0}$, and $(1/T_{2Q}^b)_0$ at each temperature could be fixed at the values obtained from the variable-temperature analysis at atmospheric pressure. In practice however, small variations in concentration, field homogeneity corrections, and differences in temperature calibration between the variable-temperature and -pressure experiments could cause nonrandom errors in the $1/T_2^b$ measurements. Thus we would like to leave all the zero pressure contributions as adjustable parameters, but this is not possible in the cases where the individual contributions donate only a small part to $1/T_2^b$. A good fit could be obtained by fixing at their atmospheric pressure values those parameters which contributed less than 37% to $1/T_2^b$. This leaves 12 zero pressure contributions plus the three activation volumes, ΔV_1^* , ΔV_2^* , and ΔV_Q^* in the iteration routine. The results of the computer fit are listed in Table II, and the calculated lines are illustrated in Figure 3.

Discussion

A. $\text{Ga}(\text{H}_2\text{O})_6^{3+}$. The negative entropy ($\Delta S^\ddagger = -92 \text{ J K}^{-1} \text{ mol}^{-1}$) and small enthalpy ($\Delta H^\ddagger = 26 \text{ kJ mol}^{-1}$) of activation obtained from early variable-temperature water-exchange studies^{17,18} have been used as evidence for the associative activation of water exchange on $\text{Ga}(\text{H}_2\text{O})_6^{3+}$. However, they can be dismissed because contributions from hydrolyzed species have not been taken into account. The clearly positive activation volume found in this study unambiguously indicates dissociative activation, and the positive entropy of activation is compatible with this (Table III).

Solvent exchange on some group III metal ions has been studied by NMR spectroscopy. The results obtained are conclusive of dissociative activation for Al^{3+} and Ga^{3+} and are as convincing of associative activation for Sc^{3+} and In^{3+} . Solvent-exchange studies on Al^{3+} and Ga^{3+} using nonaqueous solvents in nitromethane diluent yielded first-order rate laws and large positive volumes and entropies of activation. These results point toward dissociative activation and limiting dissociative, D, substitution mechanisms. Our previous water-exchange results on Al^{3+} and this study on Ga^{3+} show definite dissociative activation in both cases, but the distinction between a dissociative interchange, I_d , mechanism and a limiting D case is not obvious as the limiting

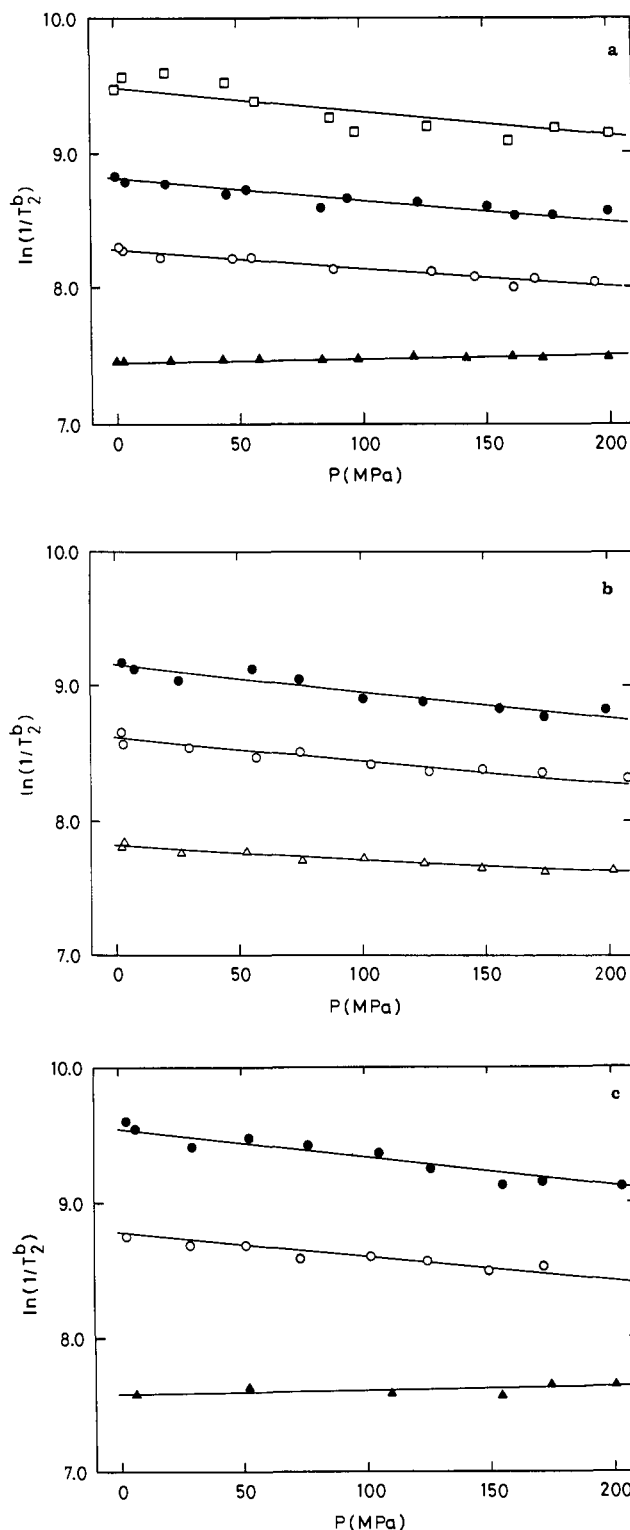


Figure 3. Pressure dependence of the transverse relaxation rate, $1/T_2^b$, from the bound water ^{17}O NMR signal of 0.50 m $\text{Ga}(\text{ClO}_4)_3$ and 0.50 m $\text{Mn}(\text{ClO}_4)_2$ solutions at various acidities and temperatures: (a) $[\text{H}^+] = 3.02 \text{ m}$; (\square) 342.6, (\bullet) 331.8, (\circ) 322.6, and (\blacktriangle) 294.2 K. (b) $[\text{H}^+] = 0.40 \text{ m}$; (\bullet) 331.5, (\circ) 324.2, and (\triangle) 311.9 K. (c) $[\text{H}^+] = 0.25 \text{ m}$; (\bullet) 332.5, (\circ) 324.5, and (\blacktriangle) 294.6 K.

activation volume for dissociative water exchange is not known. It has been semiempirically estimated³³ at $+13.5 \text{ cm}^3 \text{ mol}^{-1}$, and since our values of $+5.7 \pm 0.2$ (Al^{3+}) and $+5.0 \pm 0.5$ (Ga^{3+}) $\text{cm}^3 \text{ mol}^{-1}$ are well below this (and below the highest positive value obtained so far on a hexaaqua metal ion, $+7.2 \text{ cm}^3 \text{ mol}^{-1}$ for

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Table II. Derived NMR and Kinetic Parameters for the Variable-Pressure Study of Water Exchange on Gallium(III)^a

[H ⁺], <i>m</i>	T, K	(1/T _Q ^b) ₀ , s ⁻¹	% 1/T ₂ ^b	k _{1,0} , s ⁻¹	% 1/T ₂ ^b	k _{2,0} , m s ⁻¹	% 1/T ₂ ^b
3.0	342.6	(404)	3	10993 ± 226	83	(5399)	14
	331.8	(529)	8	5708 ± 121	85	(1470)	7
	322.6	(674)	17	3124 ± 73	79	(455)	4
0.4	294.2	1438 ± 34	84	(275)	16	(8)	0.2
	331.5	(593)	6	5342 ± 175	57	(1406)	37
	324.2	(718)	13	3403 ± 94	62	(560)	25
0.25	311.9	871 ± 204	35	1363 ± 252	55	(106)	10
	332.5	(588)	4	6998 ± 290	50	1609 ± 77	46
	324.5	(725)	11	3497 ± 128	53	(582)	36
	294.6	1627 ± 52	83	(295)	15	(9)	2

^a ΔV₁[‡] = +5.0 ± 0.5 cm³ mol⁻¹, ΔV₂[‡] = +7.7 ± 1.4 cm³ mol⁻¹, and ΔV_Q[‡] = -1.6 ± 0.5 cm³ mol⁻¹. The values within parentheses were fixed during the fitting procedure. Each contribution is also expressed as a percentage of the value of 1/T₂^b.

Table III. Kinetic Parameters for Solvent Exchange on Trivalent Group III Cations in CD₃NO₂ as Diluent

	r _i ^a , pm	k ₁ ²⁹⁸ , s ⁻¹	k ₂ ²⁹⁸ , s ⁻¹ mol ⁻¹	ΔH [‡] , kJ mol ⁻¹	ΔS [‡] , J K ⁻¹ mol ⁻¹	ΔV [‡] , cm ³ mol ⁻¹	mechanism	ref
Al(H ₂ O) ₆ ^{3+b}	54	1.29		84.7	+41.6	+5.7	I _d	29
Al(Me ₂ SO) ₆ ^{3+c}		0.30		82.6	+22.3	+15.6	D	31
Al(DMF) ₆ ^{3+c}		5 × 10 ⁻²		88.3	+28.4	+13.7	D	31
Al(TMP) ₆ ^{3+d}		0.78		85.1	+38.2	+22.5	D	6
Ga(H ₂ O) ₆ ^{3+b}	62	4.0 × 10 ²		67.1	+30.1	+5.0	I _d	this work
Ga(Me ₂ SO) ₆ ^{3+d}		1.87		72.5	+3.5	+13.1	D	31
Ga(DMF) ₆ ^{3+d}		1.72		85.1	+45.1	+7.9	D	31
Ga(TMP) ₆ ^{3+d}		6.4		76.5	+27.0	+20.7	D	6
Sc(TMP) ₆ ^{3+b}	75	736	85	34.1	-75.6	-23.8	A, I _a	6
Sc(TMP) ₆ ^{3+d}			39	21.2	-143.5	-18.7	D	6
In(TMP) ₆ ^{3+d}	80		7.6	32.8	-118	-21.4	A, I _a	6

^a Reference 32. ^b In neat solvent. ^c DMF, dimethylformamide; TMP, trimethylphosphate.

Table IV. Water-Exchange Rate Constants and Rate Constants for Complex Formation on Ga(III) in Aqueous Solutions, According to Scheme I[‡]

ligand ^a	k ₁ ^b , M ⁻¹ s ⁻¹	K _{os} ^c , M ⁻¹	k _i , s ⁻¹	k ₋₁ , M ⁻¹ s ⁻¹	k ₂ , M ⁻¹ s ⁻¹	k ₃ , M ⁻¹ s ⁻¹	k ₆ , M ⁻¹ s ⁻¹	method ^d	ref
H ₂ O			403		(6–20) × 10 ⁴ (s ⁻¹)				this work
SO ₄ ²⁻	2.1 × 10 ⁴	~1000	~20	21	1.0 × 10 ⁵			T, P-J	8
SO ₄ ²⁻	6.5 × 10 ³	1300	5					P-J	13
SCN ⁻	57	7.5	7.6	3.1	1.1 × 10 ⁵			S-F	14
Sal ⁻	≤670	5.3	≤130		≤3.4 × 10 ⁴	≤1.1 × 10 ³	≤3.3 × 10 ⁵	T-J	9
Sal ⁻	392			794	7.0 × 10 ³	≤2.7 × 10 ^{3f}	≤1.1 × 10 ^{6f}	S-F	10
ClSal ⁻	185			416	4.3 × 10 ³	≤2.6 × 10 ^{3f}	≤1.4 × 10 ^{6f}	S-F	10
NO ₂ Sal ⁻	62.7			36.7	2.1 × 10 ³	≤3.0 × 10 ^{3f}	≤2.4 × 10 ^{6f}	S-F	10
NO ₂ Sal ⁻	≤410	5.0	≤81.2	≤0.81	≤6.4 × 10 ³	≤1.9 × 10 ³	≤1.7 × 10 ⁵	T-J	11
(NO ₂) ₂ Sal ⁻	8.0			3.5	1.9 × 10 ²	≤1.5 × 10 ^{4f}	≤8.5 × 10 ^{6f}	S-F	10
TROP	38	0.3	126		7.8 × 10 ³			S-F	15
PCV ⁻	65	~4	~16	1.01	8.7 × 10 ³			S-F	12
TIR ²⁻	14	0.3	50		2.5 × 10 ³			S-F	15
SXQ ²⁻	≤690							S-F	38
MTB ²⁻ (6 °C)	24.4 ^e							Spec	39
MTB ²⁻ (15 °C)	77.1 ^e							Spec	39

^a XSal⁻, substituted salicylates; TROP, tropolone; PCV, pyrocatechol violet; TIR, Tiron; SXO, semixylene orange; MTB, methylthymol blue. ^b k₁ = K_{os}k_i (cf. eq 8). ^c Calculated with the Fuoss equation. ^d P-J, pressure jump; T-J, temperature jump; S-F, stopped flow; Spec, spectrophotometry. ^e k_i, overall forward rate constant, cannot be directly compared with any one pathway. ^f Calculated by ref 14. [‡] At 25 °C unless indicated otherwise.

Ni²⁺),³⁰ water exchange on the small Al³⁺ and Ga³⁺ can be considered to proceed via dissociative interchanges, I_d. In contrast, the larger Sc³⁺ and In³⁺ exchange according to an associative mechanism, although it is more difficult to decide whether I_a or A mechanisms are operative, since both are compatible with the observed second-order rate laws, and there is no known limiting ΔV[‡] for the nonaqueous solvents used. Nevertheless, the similarity of the ΔV[‡] values with the volume of reaction for the addition of TMP to Nd(TMP)₆³⁺ (r_i = 98 pm), ΔV[‡] = -23.8 cm³ mol⁻¹,³⁴ suggests a common A mechanism for both ions. These results illustrate the relationship between the increasing size of the central ion and the mechanism: dissociative, associative, and finally even a solvation equilibrium between a six- and seven-coordinated solvated metal ion.

There is still some controversy over the interpretation of complex formation on hexaquaaluminum(III) in aqueous solution, with both associative^{7–12} and dissociative^{13–15} mechanisms proposed.

Therefore the available rate constants will be reexamined in the light of the water-exchange results. Hydrolyzed species and protonated ligands must be accounted for in complexation studies on Ga³⁺, and Scheme I shows the reaction scheme with all the pathways generally considered in aqueous solution. Dimeric and polymeric hydrolysis products can be ignored¹⁶ at the metal ion concentrations and pH levels present in the reported complex formation studies, of which the available rate constants are listed in Table IV, along with the water-exchange rate constants found in this study. According to the Eigen–Wilkins mechanism for substitution,³⁵ the observed second-order forward rate constant, k_i, is given by eq 8, where K_{os,i} is the outer-sphere association

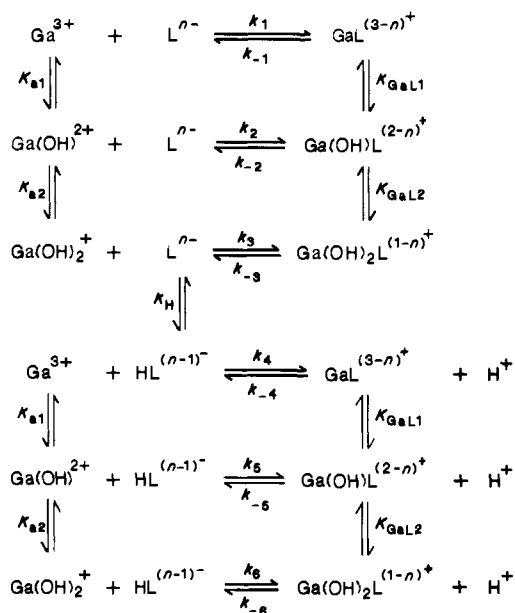
$$k_i = K_{os,i} k_{1,i} \quad (8)$$

constant and k_{1,i} is the rate constant for the outer-sphere–inner-sphere interchange reaction. K_{os} is usually estimated by the Fuoss equation,³⁶ and the ionic strength can be accounted for by

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Scheme 1. Pathways Considered for Complexation of Ga^{3+} , $\text{Ga}(\text{OH})^{2+}$, and $\text{Ga}(\text{OH})_2^+$ Cations^a


^a The vertical equilibria are all rapid in comparison with the rates of complex formation.

the Davies equation.³⁷ This was the case for the reactions under study, and the estimated values are listed in Table IV.

For a dissociative interchange mechanism, the rate constants, $k_{1,i}$, should all be similar and reasonably close to the water-exchange rate constant.⁴⁰ At first glance this does not seem to be the case in Table IV, but the discrepancies can be explained. Complexation by substituted salicylates,⁹⁻¹¹ the main evidence so far for a supposed associative mechanism, has been discussed by ref 14 and found to be inconclusive due to the problems of proton ambiguity. It was proposed that the reaction proceeds principally via pathways 5 and 6, involving the hydrolyzed metal ion and the protonated ligand. Thus this system does not provide any information as to the mechanism of complex formation on $\text{Ga}(\text{H}_2\text{O})_6^{3+}$. Inspection of the rate constants for the three differently charged ligands, TROP,¹⁵ PCV⁻,¹² and TIR²⁻,¹⁵ has shown that k_1 values for all three are very similar. If it can be assumed⁴¹ that for large ions a negatively charged group removed from the eventual coordination site is unimportant for the calculation of K_{os} , then, for all three ligands, $K_{os} \approx 0.3 \text{ M}^{-1}$ and k_1 ranges from 50 to 220 s^{-1} . Thus the first-order rate constants for the three ligands are all within an order of magnitude of the water-exchange rate constant and point toward dissociative activation. The first-order rate constants for SO_4^{2-} (ref 8 and 13) and SCN^- (ref 14) do not resemble the water-exchange value, but here again the choice of K_{os} is critical.

In conclusion, by the proper choice of K_{os} , the first-order rate constants for complex formation on $\text{Ga}(\text{H}_2\text{O})_6^{3+}$ are within approximately an order of magnitude of the water-exchange rate constant. However, the Fuoss equation was derived for primitive model electrolytes,⁴² and its application to real systems is difficult.

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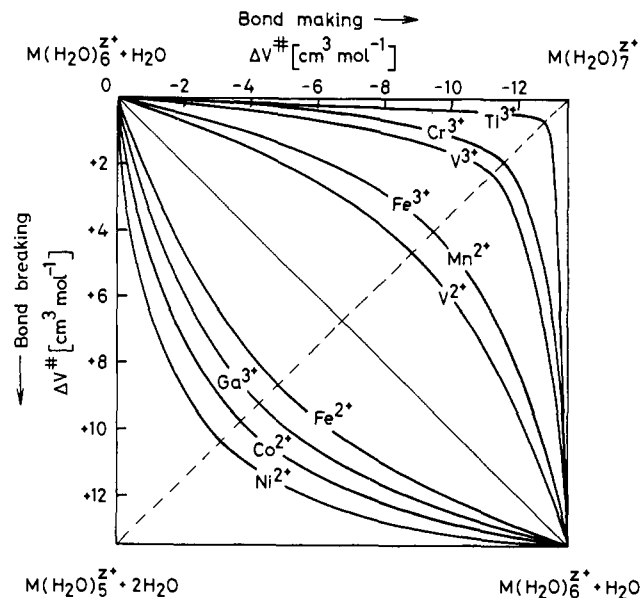


Figure 4. Bond-making and bond-breaking contributions to the volume of activation for water exchange on $\text{M}(\text{H}_2\text{O})_6^{z+}$ (after ref 53).

Thus, even though the complex formation rate constants can be interpreted as being indicative of dissociative activation, the problems in extracting true rate constants make definitive assignment impossible on this basis alone. The activation volume, on the other hand, is an unambiguous mechanistic diagnostic when the observed ΔV^\ddagger can be separated into the intrinsic component, due to changes in bond lengths and angles, and the electrostrictive component, due to changes in solvent electrostriction when ions or dipoles are formed or neutralized at the transition state. This is the case in a variable-pressure study of complex formation on Ga^{3+} with tropolone.¹⁵ Since the ligand is uncharged, the electrostrictive component is negligible in a polar solvent like water, and the observed activation volume of $+4.0 \pm 1.3 \text{ cm}^3 \text{ mol}^{-1}$ indicates that complex formation on Ga^{3+} is dissociatively activated. Furthermore, the observed activation volume complements our value of $+5.0 \text{ cm}^3 \text{ mol}^{-1}$ for water exchange on $\text{Ga}(\text{H}_2\text{O})_6^{3+}$, and together they provide firm evidence for dissociative activation of both water exchange and complex formation on this species.

The kinetic and activation parameters for water exchange on di- and trivalent high-spin first-row transition-metal hexaqua ions are listed in Table V. The activation volumes for the divalent ions show a definite trend across the period, passing gradually from negative (associative activation) to positive (dissociative activation), with the changeover occurring after the d^5 configuration, Mn^{2+} . This changeover has been explained in terms of the variation in ionic radius and of the filling of the d orbitals.⁶

In a similar fashion, the observed ΔV^\ddagger values for the trivalent ions become gradually more positive going across the period. The only observable trivalent hexaqua ion after d^5 , Ga^{3+} (d^{10}), provides the key evidence that a changeover in water-exchange mechanism also occurs for the trivalent hexaqua ions. As in the case of the divalent ions, the errors in ΔS^\ddagger determination⁵ preclude the implication of any clear-cut mechanistic trend, and the changeover in solvent-exchange mechanism across the period can only be concluded from examination of the activation volumes.

This systematic mechanism trend can be visualized, following Swaddle,⁵³ with the aid of a two-dimensional More-O'Ferrall type

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Table V. Kinetic and Activation Parameters for Water Exchange on Di- and Trivalent High-Spin First-Row Transition-Metal Hexaaqua Ions

electronic configuration	t_{2g}^1	t_{2g}^2	t_{2g}^3	$t_{2g}^3 e_g^2$	$t_{2g}^4 e_g^2$	$t_{2g}^5 e_g^2$	$t_{2g}^6 e_g^2$	$t_{2g}^6 e_g^4$
$M(H_2O)_6^{3+}$	Ti^{3+b}	V^{3+c}	Cr^{3+d}	Fe^{3+e}				Ga^{3+f}
r, pm^a	67	64	61	64				62
k_{ex}^{298}, s^{-1}	1.8×10^5	5.0×10^2	2.4×10^{-6}	1.6×10^2				4.0×10^2
$\Delta H^\ddagger, kJ mol^{-1}$	43.4	49.4	108.6	64.0				67.1
$\Delta S^\ddagger, J K^{-1} mol^{-1}$	+1.2	-27.8	+11.6	+12.1				+30.1
$\Delta V^\ddagger, cm^3 mol^{-1}$	-12.1	-8.9	-9.6	-5.4				+5.0
$M(H_2O)_6^{2+g}$			V^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	
r, pm^a			79	83	78	74	69	
k_{ex}^{298}, s^{-1}			87	2.1×10^7	4.4×10^6	3.2×10^6	3.2×10^4	
$\Delta H^\ddagger, kJ mol^{-1}$			61.8	32.9	41.4	46.9	56.9	
$\Delta S^\ddagger, J K^{-1} mol^{-1}$			-0.4	+5.7	+21.2	+37.2	+32.0	
$\Delta V^\ddagger, cm^3 mol^{-1}$			-4.1	-5.4	+3.8	+6.1	+7.2	

^a Reference 32. ^b Reference 3. ^c Reference 19. ^d Reference 20. ^e References 21 and 43. ^f This work. ^g Reference 6.

Table VI. Selection of First Hydrolysis Constants for $Ga(H_2O)_6^{3+}$

temp, °C	ionic strength, $I(M)$	pK_{a1}	$[Ga^{3+}], M$	method ^a	ref
25	0.1(NaClO ₄)	3.50			14
25	0.5(NaClO ₄)	3.69	4×10^{-4}		14
25	1.5(NaClO ₄)	4.15	to	pot	14
10	0.5(NaClO ₄)	4.17	1×10^{-2}		14
15	0.50 M(NaClO ₄)	3.01			15
25	0.50 M(NaClO ₄)	2.89	3×10^{-3}	Spec	15
35	0.50 M(NaClO ₄)	2.89			15
45	0.50 M(NaClO ₄)	2.52			15
20	1.0(NaClO ₄)	3.6		Cat	44
25	0.1(NaClO ₄)	2.87			45
25	0.5(NaClO ₄)	2.30	2×10^{-5}	Spec	45
25	1.0(NaClO ₄)	1.78			45
25	0.1(NaCl)	2.9	1×10^{-5}		
			to	Spec	46
			2×10^{-5}		
25	0.01(GaX ₃) ^b	2.9	0.01	Pot	16 ^c
25	0.02(GaX ₃) ^b	3.0	0.02		16
25	0.05(GaX ₃) ^b	3.17	0.05		16

^a Pot = potentiometric titration; Spec = spectrophotometric method; Cat = cation exchange. ^b GaX₃, X = Cl⁻, Br⁻, NO₃⁻. ^c Calculated from the data of ref 47.

plot (Figure 4). The sum of the coordinates of each point along a trajectory represents the change in volume to reach that point. The volume of activation is obtained at the intersection with the dashed diagonal. It should be noted, however, that this square representation implies that the activation volumes for the two limiting mechanisms be represented by the same absolute value at the corners. In this diagram, we have chosen as ΔV^\ddagger values for A and D mechanisms those yielded by Swaddle's semiempirical treatment, which fortuitously come out as approximately equal. Looking closer at Figure 4, though, the possibility cannot be excluded that the extreme value for a dissociative process might be less than those proposed by Swaddle's model.

B. $Ga(H_2O)_5OH^{2+}$. The experimentally determined rate constant for water exchange on the monohydroxy pentaqua ion, k_2 , is the product of the first-order rate constant, k_{OH} , and the first hydrolysis constant for $Ga(H_2O)_6^{3+}$, K_{a1} (eq 3). Thus K_{a1} must be known in order to determine k_{OH} . Unfortunately, the

hydrolysis of aqueous Ga^{3+} solutions is quite complicated,¹⁶ and a variety of hydrolysis constants have been reported, of which a selection is given in Table VI. Some pK_{a1} values were determined by using indirect spectrophotometric methods with colored ligands,^{45,46} and they are not considered due to the uncertainties of this method.¹⁶ Our kinetic study was carried out at high ionic strengths, I between 4.7 ($\approx 3.9 M$) and 7.5 m ($\approx 6.0 M$), and no equilibrium constants have been determined in such concentrated solutions. Since the available data indicate that pK_{a1} increases with increasing ionic strength, it was decided to consider only those values obtained at high I , i.e., pK_{a1} between 3.6⁴⁴ and 4.15.¹⁴ It is interesting to note that these high pK_{a1} values fit very well with those obtained from a semiempirical model for cation hydrolysis.⁴⁸ By use of the chosen pK_{a1} range, the first-order rate constant for water exchange on $Ga(H_2O)_5OH^{2+}$ was estimated: $k_{OH} = (0.6-2.0) \times 10^5 s^{-1}$.

In a similar fashion, the observed activation volume, ΔV_2^\ddagger , is the sum of the activation volume for water exchange on $Ga(H_2O)_5OH^{2+}$, ΔV_{OH}^\ddagger , and the reaction volume for the hydrolysis of Ga^{3+} , ΔV^0 . No reaction volume data are available for Ga^{3+} , but an estimation of ΔV^0 can be made using the semiempirical equation for limiting activation volumes³³ to give $\Delta V^0 \approx +1.5 cm^3 mol^{-1}$. This lies within the range 0.8-3.0 $cm^3 mol^{-1}$ found for Fe^{3+} ($r_i = 64 pm$).^{21,49,50} Therefore an estimation of ΔV_{OH}^\ddagger is $\approx +6.2 cm^3 mol^{-1}$. These estimations, along with the activation parameters and rate constants for water exchange on two other hexaaqua and monohydroxy pentaqua ions, are listed in Table VII. Two principal features are apparent: the higher reactivity (by a factor of 75-750) and larger dissociative character (more positive activation volumes) for water exchange on the monohydroxy species. These differences may be due to the strong bonding between the metal center and the hydroxy group which will weaken the remaining metal-water bonds (probably the trans one). The complex thus becomes more labile and more prone to dissociative activation than the hexaaqua ion.

Conclusion

The positive activation volume for the water exchange on $Ga(H_2O)_6^{3+}$ establishes that the reaction is dissociatively activated. This conclusion could not be reached on the basis of complex formation data alone due to the problem of proton ambiguity. The

Table VII. Rate Constants and Activation Parameters for Water Exchange on Some Hexaaqua and Monohydroxy Pentaqua Ions

M^{3+}	mechanism	k^{298a}	k_{OH}/k_1	$\Delta H^\ddagger, kJ mol^{-1}$	$\Delta S^\ddagger, J K^{-1} mol^{-1}$	$\Delta V^\ddagger, cm^3 mol^{-1}$	pK_{a1}	ref
Cr^{3+}	I_a	$2.46 \times 10^{-6} s^{-1}$	75	108.6	+11.6	-9.6	4.1 ^b	20
$Cr(OH)^{2+}$	I	$1.4 \times 10^{-8} m s^{-1}$		148.9	+10.7	-1.1		
Fe^{3+}	I_a	$1.8 \times 10^{-4} s^{-1}$		110.0	+55.6	+2.7		
$Fe(OH)^{2+}$	I_a	$1.6 \times 10^2 s^{-1}$	750	64.0	+12.1	-5.4	2.9 ^c	21 and 43
	I_d	$1.5 \times 10^2 m s^{-1}$				+7.8		
	I_d	$1.2 \times 10^5 s^{-1}$		42.4	+5.3	+7.0		
Ga^{3+}	I_d	$403 s^{-1}$	150-500	67.1	+30.1	+5.0	3.6-4.15 ^d	this work
$Ga(OH)^{2+}$	I_d	$14 m s^{-1}$		110.9	+149.2	+7.7		
	I_d	$(0.6-2.0) \times 10^5 s^{-1}$		58.9		+6.2		

^a In order: k_1, k_2, k_{OH} ($=k_2/K_{a1}$). The same order is used for the corresponding activation parameters. ^b Reference 52. ^c Reference 53. ^d References 14 and 44, see text.

assignment of dissociative water exchange on $\text{Ga}(\text{H}_2\text{O})_6^{3+}$ provides the evidence necessary to show that gradual changeover in substitution mechanism, from associative to dissociative interchange, across the period of the first-row trivalent high-spin transition-metal ions already observed in nonaqueous solvents⁶ is also operative in water.

Estimations of the rate constant and activation volume for water exchange on $\text{Ga}(\text{H}_2\text{O})_5\text{OH}^{2+}$ indicate that this species is much more reactive and has more dissociative character than the hexaqua ion, as is the case for other pairs of trivalent hexaqua and monohydroxy pentaqua ions.

Acknowledgment. This work was financially supported by the Swiss National Science Foundation (Grant No. 2.854-0.85).

Registry No. $\text{Ga}(\text{H}_2\text{O})_6^{3+}$, 19521-89-2; $\text{Ga}(\text{H}_2\text{O})_5\text{OH}^{2+}$, 12519-06-1; H_2O , 7732-18-5.

Supplementary Material Available: Temperature and pressure dependence of transverse relaxation rates (Tables S1 and S2), correlation coefficient matrices of the computer fits (Tables S3 and S4), and kinetic and quadrupolar contributions to the transverse relaxation rates (Table S5) (11 pages). Ordering information is given on any current masthead page.

Theoretical Study of the Cyclopropane Ring Opening by Palladium(II) Complexes

Margareta R. A. Blomberg,*† Per E. M. Siegbahn,† and Jan-Erling Bäckvall†

Contribution from the Institute of Theoretical Physics, University of Stockholm, S-113 46 Stockholm, Sweden, and the Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden. Received November 19, 1986

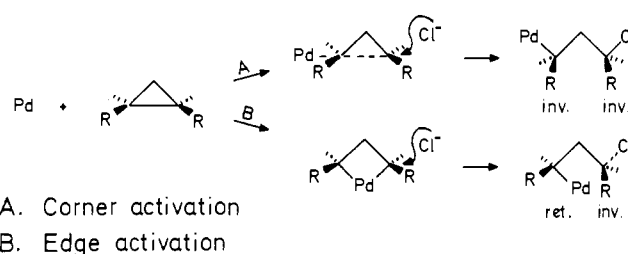
Abstract: CASSCF and contracted CI calculations have been performed on the ring opening of cyclopropane by different palladium(II) compounds (PdCl_2 , PdCl_4^{2-} , and PdCl^+). Two reaction mechanisms were studied, corner activation and edge activation. The results are compared to a previous study of the reaction of the ligand-free palladium(0) atom with cyclopropane, and, as expected, it was found that the addition of the chloride ligands changes the reaction barriers drastically. For palladium(0) only the edge activation has a low activation energy. For the palladium(II) complexes only the corner activation by PdCl^+ has a low activation energy, estimated to be about 5 kcal/mol. For PdCl_2 and PdCl_4^{2-} very high barriers (25–45 kcal/mol) are found for both corner and edge activation. The energy differences between the complexes investigated are found to be directly related to the excitation energies of the atomic states of palladium involved. The atomic state of palladium involved in a complex is determined by the actual number of covalent bonds, and the actual charge of palladium. The atomic state is reflected in the calculated 4d population of palladium. The results obtained in this paper lead to a new view on the ring opening of cyclopropane by palladium(II): corner activation, rather than the usually accepted edge activation, is predicted to be the most favorable reaction pathway.

I. Introduction

The interaction between transition metals and small strained-ring hydrocarbons often leads to the cleavage of one of the C–C bonds. In recent experimental studies of chloropalladation of the cyclopropane ring in (+)-2-carene, two different products were obtained.¹ The two products have different stereochemistry at the active carbons, and different C–C bonds have been cleaved. It was proposed¹ that the main difference in the reaction mechanisms leading to the two products is that one of them involves a corner activation of the cyclopropane ring by palladium (see Scheme I, reaction A) and the other an edge activation (see Scheme I, reaction B). The results from this experimental study inspired the present theoretical investigation of the edge and the corner mechanisms for the activation of cyclopropane by palladium(II) complexes.

In a previous theoretical paper² the corner and the edge palladation of cyclopropane by palladium(0) were studied. However, most of the experimentally studied cyclopropane ring-opening reactions involving platinum metals were performed with palladium(II) and platinum(II). The purpose of the present paper is therefore to perform a similar theoretical study on palladium(II). In the above mentioned experimental study¹ of chloropalladation of cyclopropane the reactant was $\text{PdCl}_2(\text{MeCN})_2$, and it is natural to use PdCl_2 as a model for palladium(II) complexes. This complex yields high barriers for both the edge and the corner

Scheme I. Ring Opening of Cyclopropane by Palladium



mechanism of the cyclopropane ring opening. Two other complexes, PdCl_4^{2-} and PdCl^+ , which are both present in a solution of the PdCl_2 polymer were therefore also investigated.

Our goal has been to estimate reaction barriers for the two reaction mechanisms for cyclopropane ring opening, and for this purpose we have calculated the most interesting parts of the potential energy surfaces. The activated complex between cyclopropane and the metal is different for the two reaction mechanisms. In the case of corner activation the activated complex has a biradical structure, and in the case of edge activation the

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*University of Stockholm.

†Royal Institute of Technology.