26. Volumes of Activation for Dimethylsulfoxide and *N*, *N*-Dimethylformamide Exchange with Hexasolvates of Aluminium (III) and Gallium (III) Ions in Deuterionitromethane Solution[1])

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Summary

High-pressure ^{1}H-NMR. has been used to determine volumes of activation ($\Delta V^{\neq}$) for solvent exchange with $[M(S)_6]^{3+}$ ion (M = Al(III), Ga(III); S = dimethylsulfoxide (DMSO) and *N,N*-dimethylformamide (DMF)) in $[^2H]_3$-nitromethane solution. For Al(III), $\Delta V^{\neq} = +15.6 \pm 1.4$ (S = DMSO, 358.5 K) and $\Delta V^{\neq} = +13.7 \pm 1.2$ cm^{3}mol^{-1} (S = DMF, 354.5 K), whilst for Ga(III), $\Delta V^{\neq} = +13.1 \pm 1.0$ (S = DMSO, 334.6 K) and $\Delta V^{\neq} = +7.9 \pm 1.6$ cm^{3}mol^{-1} (S = DMF, 313.8 K). Variable temperature studies over a temperature range of 107.2 K (Al(III)) and 101.1 K (Ga(III)) were carried out for solvent exchange with $[M(DMF)_6]^{3+}$ ions in $[^2H]_3$-nitromethane solution, using stopped-flow NMR. and conventional line-broadening, and gave $\Delta H^{\neq} = 88.3 \pm 0.9$ and 85.1 ± 0.6 kJ mol^{-1}, and $\Delta S^{\neq} = 28.4 \pm 2.7$ and 45.1 ± 1.9 JK^{-1}mol^{-1} for Al(III) and Ga(III) ions respectively. All of these results are consistent with dissociative modes of activation.

Introduction. - High-pressure NMR. measurements have proved to be a unique tool for mechanism assignments of solvent-exchange reactions on labile metal-ions [1-5]. We have shown that for the first-row labile divalent transition-metal ions, only the later members of the series substitute *via* an I_d-mechanism, while the earlier members show an associative I_a-behaviour, with the changeover occurring around Fe(II) [1] [5]; this is in disagreement with the earlier belief that substitution reactions on all octahedral divalent ions occur *via* a dissociative activation mode [6]. For solvent exchange with inert trivalent transition-metal ions and their complexes, using for example, isotopic dilution techniques, both positive and negative values of $\Delta V^{\neq}$ have been found. For example, the solvent exchange reactions $[Cr(S)_6]^{3+}$ (S = H_2O, DMSO, DMF), and $[M(NH_3)_5(S)]^{3+}$ (S = H_2O, M = Cr, Rh, Ir; S = DMF,

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[1]) High-pressure NMR. kinetics, part 10. For part 9 see [1].

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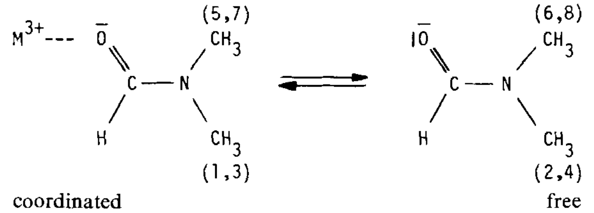
M = Rh) [7] [8] exhibit negative values $\Delta V^{\neq}$ which are usually interpreted in terms of I_a-mechanisms, whereas solvent exchange or anation reactions of $[Co(NH_3)_5(S)]^{3+}$ and $[RhCl_{6-n}(H_2O)_n]^{n-3}$ (n = 1, 2) ions are known to proceed by a dissociative interchange, I_d, mechanism [7-9]. Measurement of $\Delta V^{\neq}$ for the aquation of $[Cr(NCS)_6]^{3+}$ ion also indicates and I_d-mechanism [10], whereas in the case of aquation of $[Co(CN)_5X]^{3-}$ ions ($X = N_3^-$, halides) and the anation of $[Co(CN)_5OH_2]^{2-}$ ion, the $\Delta V^{\neq}$ values support the extreme dissociative D-mechanism [11]. However, the predominance of associative mechanisms for most other trivalent metal ion complexes has been suggested [12].

Although there have been numerous variable temperature studies of solvent exchange with the labile Al(III) and Ga(III) ions [13-20], so far, measurements of volumes of activation $\Delta V^{\neq}$ have not been published [7]. Recently, we reported enthalpies $\Delta H^{\neq}$ and entropies $\Delta S^{\neq}$ of activation for dimethylsulfoxide exchange with $[M(DMSO)_6]^{3+}$ (M = Al(III), Ga(III)) ions in $[^2H]_3$-nitromethane solution [20]. The reactions were studied over a wide temperature range (> 100 K) using both stopped-flow NMR. and conventional NMR. line-broadening, and the values of $\Delta S^{\neq}$ found to be $+22.3 \pm 3.7$ and $+3.5 \pm 1.6$ J $K^{-1} mol^{-1}$ for Al(III) and Ga(III) respectively. These positive $\Delta S^{\neq}$ values are consistent with a dissociative activation mode, although a distinction between I_d- and D-mechanisms was not possible. Also, the small positive value of $\Delta S^{\neq}$ for DMSO exchange with $[Ga(DMSO)_6]^{3+}$ ion did not conclusively establish a dissociative activation mode in this case. We have now extended our studies of these systems to high pressures to determine

Table 1. a) *Probability matrix for the* N,N-*dimethylformamide exchange reaction* (8 methyl sites only)



	1	2	3	4	5	6	7	8
1	-1	1	0	0	0	0	0	0
2	p_1/p_2	$-p_1/p_2$	0	0	0	0	0	0
3	0	0	-1	1	0	0	0	0
4	0	0	p_3/p_4	$-p_3/p_4$	0	0	0	0
5	0	0	0	0	-1	1	0	0
6	0	0	0	0	p_5/p_6	$-p_5/p_6$	0	0
7	0	0	0	0	0	0	-1	1
8	0	0	0	0	0	0	p_7/p_8	$-p_7/p_8$

with: $p_1 = p_3 = p_5 = p_7$, $p_2 = p_4 = p_6 = p_8$, and $\sum_{i=1}^{8} p_i = 1$.

b) *Methyl chemical shifts* δ, in Hz, *and* ^4J *(methyl-formyl) coupling constants*, in Hz, *at 298 K*

Free DMF:	$\delta(2,4) = 170.3$	$\delta(6,8) = 161.6$	$^4J(2,4) = 0.4$	$^4J(6,8) = 0.6$
$[Al(DMF)_6]^{3+}$:	$\delta(1,3) = 188.8$	$\delta(5,7) = 179.8$	$^4J(1,3) = 0.6$	$^4J(5,7) = 0.9$
$[Ga(DMF)_6]^{3+}$:	$\delta(1,3) = 188.1$	$\delta(5,7) = 179.1$	$^4J(1,3) = 0.7$	$^4J(5,7) = 0.9$

values of $\Delta V^{\neq}$, and report the results of this work together with determinations of $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta V^{\neq}$ for *N, N*-dimethylformamide exchange with $[M(DMF)_6]^{3+}$ ion (M = Al(III), Ga(III)).

Experimental and data treatment. - DMSO was dried and $[M(DMSO)_6](ClO_4)_3$ (M = Al, Ga) were prepared as described previously [20].

$[M(DMF)_6](ClO_4)_3$ (M = Al, Ga, In) were prepared by dissolving the hydrated salts (10^{-3} mol) in DMF (20 ml) and this solution was dehydrated by stirring with 5% excess triethylorthoformate for 1 h under dry N_2. Precipitation occurs during this last step. The volume of the solution was reduced by vacuum evaporation, the white cristalline product was collected by filtration under N_2 and washed with dry ether (5 × 10 ml). The compounds gave satisfactory C, H, N, Cl and M analyses. The water content of the complexes, as determined by *Karl-Fischer* titration, was always less than 0.05 mol of water per mol of salt. DMF *(Fluka, puriss)* and $[^2H]_3$-nitromethane *(Ciba-Geigy AG)* were stored over 4 Å molecular sieves before use. Nitromethane was distilled twice over P_2O_5 and stored over molecular sieves.

^{1}H-FT-NMR. line-broadening measurements were performed on a *Bruker* WP-60 spectrometer. 10-1000 scans (8 k data points, sweep width 720 Hz) were used. For the variable temperature measurements $[^2H]_3$-nitromethane was used as internal lock and inhomogeneity corrections were estimated from the signal of normal nitromethane. Temperatures were measured (±0.5 K) with a calibrated platinum resistance thermometer in an identical tube to the sample, by substitution after each experiment. The variable pressure experiments were performed with a high pressure probe-head, using non-spinning capillary sample tubes, and similar to that described previously [21]. The temperature stability over periods of several hours, as measured by an *in situ* platinum resistance was better than ±0.2 K [22].

The line-broadening results for the DMSO-exchange reactions were treated by a complete line shape analysis to obtain the exchange rate constants, by a method outlined previously [20]. For the DMF exchange reactions the spectra are more complex, with eight exchanging sites for the methyl groups only, and a modified version of the program ECHGNC [23] was used, which includes non-linear least square fit to the experimental spectra[3]). The spectra are calculated on the basis of the *Kubo-Sack* stochastic theory, using *Bloch*'s modified equations. The utilised exchange probability matrix, representing the fraction of nuclei exchanging between the different sites is given in *Table 1*. The program allows the adjustment of the populations, chemical shifts and relaxation times for the different sites and the rate constant k_{ex} for the solvent exchange. At low temperature these parameters were obtained by line-shape analysis, whereas at higher temperatures only the rate constant k_{ex} was obtained in this way. The temperature dependence of the chemical shifts was very small and the pressure dependence was negligible over the range studied.

Stopped-flow NMR. experiments were carried out at *Warwick* at 90 MHz with a *Bruker* WH-90 spectrometer as described previously [20].

The pseudo-first-order reaction rate constant for solvent exchange k_{ex} is related to the residence time τ_m of the solvent in the coordinated site by equ. (1). The variable temperature results were fitted to equ. (2) to obtain $\Delta H^{\neq}$ and $\Delta S^{\neq}$. The variable pressure results were analyzed using equ. (3) and $\Delta V_0^{\neq}$, $\Delta\beta^{\neq}$ and $k_0 (k_0 = k_{ex}$ when P = 0) were treated as parameters to be optimized with a nonlinear least-squares fitting procedure. Given errors are standard deviations.

$$k_{ex} \equiv 1/\tau_m \tag{1}$$

$$\ln(k_{ex}) = \ln(k_B T/h) + \Delta S^{\neq}/R - \Delta H^{\neq}/RT \tag{2}$$

$$\ln(k_{ex}) = \ln k_o - P\Delta V^{\neq}/RT + P^2\Delta\beta^{\neq}/2RT \tag{3}$$

Results. - The variable temperature results for the DMF exchange on $[M(DMF)_6]^{3+}$ ions (M = Al, Ga) are collected in *Table 2*. Eight methyl resonances are observed under conditions of slow solvent exchange, four each from the bound

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[3]) A listing of this program, written in FORTRAN by Dr. *J. Wenger* is available upon request.

Table 2. *Temperature T (K) dependence of the rate constants* k_{ex} (s^{-1}) *for the DMF exchange reactions on* $[M(DMF)_6]^{3+}$ *ions* (M = Al, Ga) *by SF-NMR. and NMR. line-broadening in nitromethane solutions*

$[Al(DMF)_6]^{3+}$		$[Ga(DMF)_6]^{3+}$	
T	k_{ex}	T	k_{ex}
SF-NMR.		SF-NMR.	
258.8	$(3.2\pm0.2)\ 10^{-4}$	244.9	$(6.8\pm0.1)\ 10^{-4}$
268.8	$(11.2\pm0.4)\ 10^{-4}$	254.9	$(42.1\pm1.2)\ 10^{-4}$
278.8	$(51.4\pm1.6)\ 10^{-4}$	264.7	$(230\pm8)\ 10^{-4}$
288.8	$(180\pm5)\ 10^{-4}$	274.5	$(930\pm40)\ 10^{-4}$
301.7	$(720\pm30)\ 10^{-4}$	NMR. line-broadening[b])	
NMR. line-broadening[a])		303.6	3.4 ± 0.1
330.6	2.2 ± 0.1	308.9	5.0 ± 0.1
335.8	3.8 ± 0.1	314.4	11.0 ± 0.2
340.9	5.8 ± 0.1	320.0	18.5 ± 0.3
345.7	10.5 ± 0.1	325.1	33.0 ± 0.3
351.1	17.0 ± 0.2	330.5	54.0 ± 0.4
355.9	26.5 ± 0.2	335.6	90.0 ± 0.6
361.2	41.5 ± 0.2	340.8	140.0 ± 1.0
366.0	64.0 ± 0.3	346.0	230.0 ± 2.1

[a]) $[Al(DMF)_6^{3+}] = 0.1$ m, $[DMF] = 0.6$ m.

[b]) $[Ga(DMF)_6^{3+}] = 0.035$ m, $[DMF] = 0.19$ m.

Table 3. *Pressure P* (MPa) *dependence of the rate constant* k_{ex} (s^{-1}) *for the solvent exchange reactions on* $[M(S)_6]^{3+}$ *ions* (M = Al, Ga; S = DMSO, DMF) *in nitromethane solutions*

$[Al(DMSO)_6]^{3+}$		$[Al(DMF)_6]^{3+}$		$[Ga(DMSO)_6]^{3+}$		$[Ga(DMF)_6]^{3+}$	
P	k_{ex}	P	k_{ex}	P	k_{ex}	P	k_{ex}
1.5	76.9 ± 0.9	5.0	30.0 ± 1.0	0.1	47.4 ± 0.5	0.1	14.3 ± 0.2
2.5	76.1 ± 0.7	10.0	28.0 ± 0.9	20.0	43.5 ± 0.4	5.0	14.2 ± 0.2
20.0	74.0 ± 0.7	20.0	28.0 ± 0.9	40.0	39.0 ± 0.4	10.0	14.1 ± 0.2
40.0	65.7 ± 0.6	40.0	25.0 ± 0.8	60.0	36.0 ± 0.3	20.0	13.8 ± 0.3
60.0	56.8 ± 0.5	60.0	24.0 ± 0.7	80.0	33.7 ± 0.3	40.0	12.6 ± 0.1
80.0	55.6 ± 0.5	80.0	21.0 ± 0.6	100.0	32.2 ± 0.3	60.0	12.6 ± 0.1
100.0	51.8 ± 0.4	100.0	21.0 ± 0.6	120.0	32.6 ± 0.3	79.5	11.5 ± 0.1
120.0	46.0 ± 0.2	120.0	20.0 ± 0.6	140.0	30.2 ± 0.2	100.0	11.1 ± 0.1
140.0	43.3 ± 0.2	140.0	18.5 ± 0.5	160.0	29.0 ± 0.2	120.0	10.9 ± 0.1
150.0	44.0 ± 0.4	160.0	18.0 ± 0.5	180.0	27.6 ± 0.2		
180.0	39.4 ± 0.2	180.0	17.5 ± 0.5	200.0	26.8 ± 0.2		
200.0	38.7 ± 0.3	200.0	17.0 ± 0.5				
T = 358.5 K $[Al(DMSO)_6^{3+}] = 0.011$ m $[DMSO] = 0.103$ m in CD_3NO_2		T = 354.5 K $[Al(DMF)_6^{3+}] = 0.050$ m $[DMF] = 0.300$ m in $CH_3NO_2/CD_3NO_2 = 1/3$ Int. ref. = 6% C_6H_{12}		T = 334.6 K $[Ga(DMSO)_6^{3+}] = 0.011$ m $[DMSO] = 0.099$ m in CD_3NO_2		T = 313.8 K $[Ga(DMF)_6^{3+}] = 0.050$ m $[DMF] = 0.300$ m in $CH_3NO_2/CD_3NO_2 = 1/3$ Int. ref. = 6% TMS	

and free solvent molecules. The temperature NMR. line-broadened spectra could be analyzed with the probability matrix given in *Table 1*. The four methyl signals (1, 3, 5, 7 for the bound and 2, 4, 6, 8 for the free DMF) are from the two non-equivalent methyl groups, *trans* and *cis*, each split due to ^4J coupling with the formyl protons. The coupling constants for free DMF are 0.4 Hz for the methyl group *trans*

Table 4. *Enthalpies* $\Delta H^{\ddagger}$ (kJ mol^{-1}), *entropies* $\Delta S^{\ddagger}$ (J K^{-1}mol^{-1}), *volumes* $\Delta V^{\ddagger}$ (cm^{3}mol^{-1}), *and compressibility coefficients of activation* $\Delta\beta^{\ddagger}$ (cm^{3}mol^{-1}MPa^{-1}) *and rate constants* k_{ex}(s^{-1}) *for DMSO and DMF exchange reactions with trivalent metal ions on their complexes* (at 298.2 K unless specified)

Complex ion	k_{ex}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta V^{\ddagger}$	$10^2\ \Delta\beta^{\ddagger}$
$[\mathrm{Al(DMSO)_6}]^{3+}$	0.30 ± 0.02	82.6 ± 1.2	$+22.3 \pm 3.7$	$+15.6 \pm 1.4$ a)	$+4.8 \pm 1.4$
$[\mathrm{Al(DMF)_6}]^{3+}$ l)	0.05 ± 0.01	88.3 ± 0.9	$+28.4 \pm 2.7$	$+13.7 \pm 1.2$ b)	$+5.4 \pm 1.2$
$[\mathrm{Ga(DMSO)_6}]^{3+}$	1.87 ± 0.05	72.5 ± 0.5	$+3.5 \pm 1.6$	$+13.1 \pm 1.0$ c)	$+5.5 \pm 0.9$
$[\mathrm{Ga(DMF)_6}]^{3+}$ m)	1.72 ± 0.10	85.1 ± 0.6	$+45.1 \pm 1.9$	$+7.9 \pm 1.6$ d)	$+2.6 \pm 2.7$
$[\mathrm{Cr(DMSO)_6}]^{3+}$	3.2×10^{-8}	96.7 ± 2.1	-64.4 ± 6.3	-11.3 ± 1.0 e)	negligible
$[\mathrm{Cr(DMF)_6}]^{3+}$	5.5×10^{-8}	97.1 ± 0.9	-58.4 ± 2.8	-6.3 ± 0.2 f)	negligible
$[\mathrm{Co(NH_3)_5(DMSO)}]^{3+}$	2.7×10^{-6} g)	123 ± 2	$+61 \pm 6$	$+10.0 \pm 1.2$ h)	negligible
$[\mathrm{Co(NH_3)_5(DMF)}]^{3+}$	1.12×10^{-6} i)	113.4 ± 1.2	$+21.6 \pm 3.8$	$+3.2 \pm 0.1$ j)	negligible
$[\mathrm{Rh(NH_3)_5(DMF)}]^{3+}$	2.44×10^{-6} i)	99.1 ± 2.0	-19.8 ± 6.0	-1.4 ± 0.2 k)	negligible

a) 358.5 K, this work. b) 354.5 K, this work. c) 334.6 K, this work. d) 313.8 K, this work. e) 348.2 K, D.L. Carle and T.W. Swaddle, Canad. J. Chemistry *51*, 3795 (1973). f) 338.3 K, S.T.D. Lo and T.W. Swaddle, Inorg. Chemistry *14*, 1878 (1975). g) Calculated at 298.2 K from data of S.T.D. Lo, E.M. Oudeman, J.C. Hansen and T.W. Swaddle, Canad. J. Chemistry *54*, 3685 (1976) h) 308.2 K, see g. i) 298.2 K, calculated from [8]. j) 328.6 K, [8]. k) 318.0 K, [8]. l) From SF-NMR. data only $k_{\mathrm{ex}} = 0.05$, $\Delta H^{\ddagger} = 81.1 \pm 1.9$, $\Delta S^{\ddagger} = +2.2 \pm 6.8$, and from line-broadening data $k_{\mathrm{ex}} = 0.05$, $\Delta H^{\ddagger}\ 93.2 \pm 1.0$, $\Delta S^{\ddagger} = +42.8 \pm 3.1$. m) From SF-NMR. data only $k_{\mathrm{ex}} = 2.57$, $\Delta H^{\ddagger} = 91.2 \pm 1.6$, $\Delta S^{\ddagger} = +68.9 \pm 6.1$ and from line-broadening data $k_{\mathrm{ex}} = 1.67$, $\Delta H^{\ddagger} = 85.6 \pm 1.4$, $\Delta S^{\ddagger} = +46.5 \pm 4.3$.

to the carbonyl group and 0.6 Hz for the *cis* one; these values increase by 0.3 Hz upon complexation *(Table 1)*. It is well known that as the temperature is raised, internal rotation about the (carbonyl C)–N bond allows for interchange of the *cis* and *trans* methyl groups. For pure DMF this gives methyl peak line-broadening of 0.9 Hz at 366 K [24]. Work at this high temperature showed no significant methyl peak line-broadening either of DMF diluted in nitromethane, nor of an $[\mathrm{Al(DMF)_6}]^{3+}$ nitromethane solution. The intramolecular rotation is therefore too slow to affect our intermolecular solvent exchange study. The activation parameters obtained by line-broadening experiments for $[\mathrm{M(DMF)_6}]^{3+}$ (*Table 4,* footnotes 1 and m) can be compared with those obtained by *Movius & Matwiyoff* in pure DMF: for M=Al4), $\Delta H^{\ddagger} = 74.0$ kJ mol^{-1}, $\Delta S^{\ddagger} = -9.6$ J K^{-1} mol^{-1} and for M=Ga [18], $\Delta H^{\ddagger} = 61.0$ kJ mol^{-1}, $\Delta S^{\ddagger} = -34.7$ J K^{-1} mol^{-1}. The differences may be explained by the simplified analysis in the earlier work which neglected the ^4J coupling and used the so-called slow exchange approximation and can only be partly due to the diluent nitromethane used in our work. The accuracy of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be improved by extending the temperature range over which rate data are obtained. Using stopped-flow FT-NMR. we could add low temperature data and in this way extend the temperature range to more than 100 K. The variable temperature results are collected in *Table 2* and represented in the *Figure.* The pressure dependence of the rate constant for the solvent exchange reactions on $[\mathrm{M(S)_6}]^{3+}$ ions (M=Al, Ga; S=DMSO, DMF) in nitromethane solutions are given in *Table 3.*

The complete set of activation parameters, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ are collected in *Table 4,* together with results for other DMSO and DMF solvates of trivalent metal ions for comparison.

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4) From [17], a correction to k_{ex} by a factor of 6 has been made.

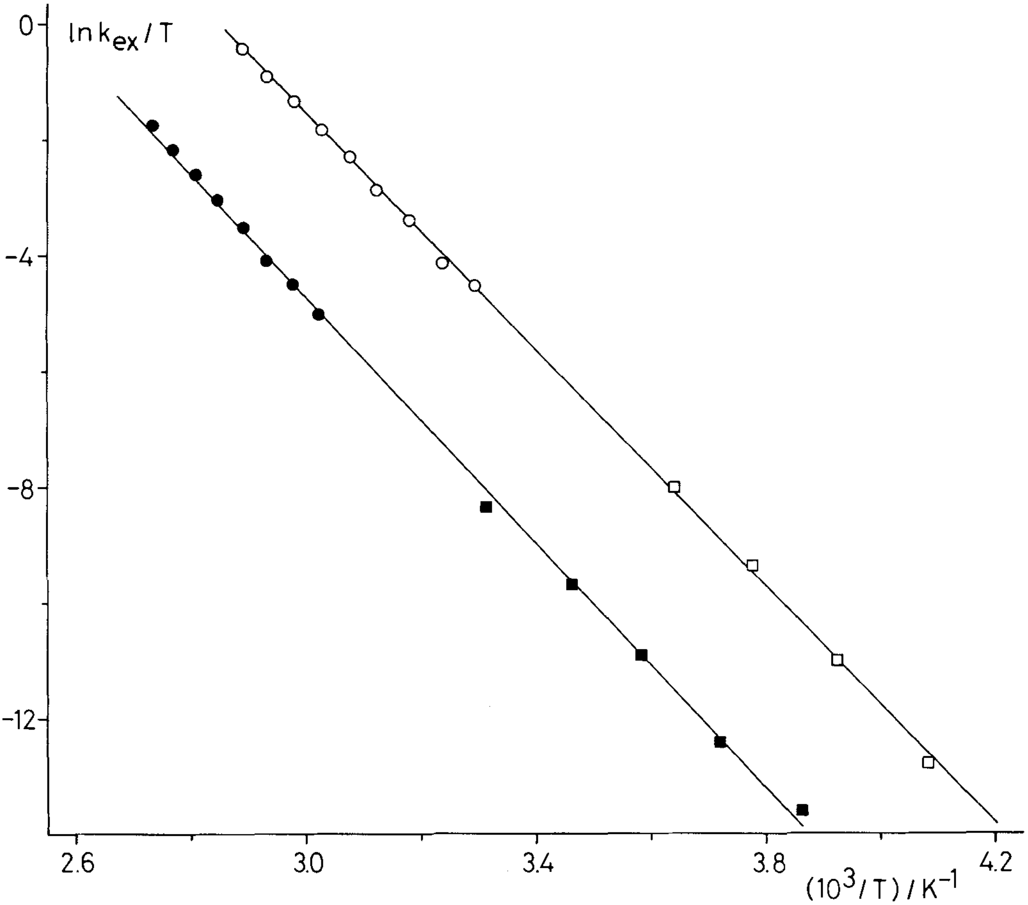

Figure. *Ln*(k_{ex}/T) *as a function of* 1/*T for* [*Al*(*DMF*)$_6$]$^{3+}$ (●, ■) *and for* [*Ga*(*DMF*)$_6$]$^{3+}$ (○, □) *from line-broadening* (circles) *and SF-NMR.* (squares).

Kinetic measurements of the exchange reaction of DMF on $[In(DMF)_6]^{3+}$ ion in nitromethane solution, at all temperatures studied, always fell within the NMR. time-scale fast exchange limit. Following arguments previously put forward for the exchange of DMSO on $[In(DMSO)_6]^{3+}$ ion [20], we conclude that the DMF exchange also follows an I_a-mechanism.

Discussion. - Recent studies of complex formation reactions of $[M(H_2O)_6]^{3+}$ ions have been interpreted in terms of a dissociative mechanism when M = Al [25], and an associative mechanism when M = Ga [26], V [27] and Ti [28]. However, for the water exchange with the $[Ga(H_2O)_6]^{3+}$ ion a positive value of $\Delta S^{\neq}$, +42 J $K^{-1}mol^{-1}$ [6a], has been added to the formerly negative published value of −92 J $K^{-1}mol^{-1}$ [13a]. Unfortunately these values of $\Delta S^{\neq}$ were determined at very high molarities ($[Ga(H_2O)_6]^{3+} \simeq 2$ moldm^{-3}) in the presence of *ca.* 0.2 moldm^{-3} of a shift reagent ($Co(H_2O)_6^{2+}$) [13a] or of *ca.* 0.6 moldm^{-3} of a relaxation reagent

($Mn(H_2O)_6^{2+}$) [13b]; these studies are of limited value for comparison with rate data for complex formation reactions obtained at much lower molarities. Further work will be necessary before the mechanism for water exchange with gallium(III) ion in aqueous media is definitely established.

In non-aqueous solvents, the mechanistic picture is clearer. Values of $\Delta S^{\ddagger}$ are positive for $[Al(S)_6]^{3+}$ and $[Ga(S)_6]^{3+}$ ions (S=DMSO, DMF, $(CH_3O)_3PO$ [16]) and the significantly positive values of $\Delta V^{\ddagger}$ in *Table 4* are entirely in accord with dissociative modes of activation for both of these metal ions. Comparison of the values of $\Delta V^{\ddagger}$ with those for analogous solvates of chromium(III) is particularly striking, and there can be little doubt that there is a switch from associative behaviour for solvent exchange with most chromium(III) solvates, to dissociative behaviour for aluminium(III) and gallium(III) ions.

The reason for this mechanistic difference is less certain, but a mechanistic changeover along the first row transition divalent metal ion series from Mn^{2+}, I_a, to Ni^{2+}, I_d, has also been reported. This changeover was discussed in terms of two possible effects [1] [5]. The *first* is a simple ion size argument originally introduced to explain the difference in mechanism between the very small low spin Co^{3+}, I_d or D, (0.53 Å)⁵) and Cr^{3+}, I_a, (0.62 Å) [12]. Under such an argument, the smaller the ion, the less able it is to accommodate a seventh solvent molecule in the transition state. Thus Al^{3+} (0.53 Å) should behave like low spin Co^{3+}, Ga^{3+} (0.62 Å) should show some associative behaviour and In^{3+} (0.80 Å) should be highly associative. For the extreme cases of Al^{3+} and In^{3+}, the predictions are in accord with experimental facts, while for Ga^{3+} the discrepancy may be tempered by two possibilities: differences between compilations of ionic radii or differences in electronic configuration. The *second* possible effect used to explain the changeover from Mn^{2+} to Ni^{2+} is based on the availability of suitable lowlying vacant (or partially vacant) orbitals capable of accepting a lone pair of electrons from the incoming solvent molecule. For an octahedral solvate, in the absence of π-bonding, the t_{2g}-orbitals are nonbonding and the e_g-orbitals σ-antibonding. The t_{2g}-orbitals which point between adjacent ligands are in a position to overlap with the incoming solvent molecule lone-pair in an associative process. For example, the e_g-orbitals never change their occupancy from Mn^{2+} to Ni^{2+} and the tendency towards less and less associative behaviour for the methanol exchange on $[M(MeOH)_6]^{2+}$ is related to the increasing occupancy of the t_{2g}-orbitals. This is exemplified by the $\Delta V^{\ddagger}$ values ($cm^3 mol^{-1}$) for this reaction: Mn (−5.0), Fe (+0.4), Co (+8.9) and Ni (+11.4) [5]. Early members of the first row transition metal ions (Sc^{3+}, Ti^{3+}, V^{3+}, Cr^{3+}) have empty or only partially filled t_{2g}-orbitals and are thus expected to react associatively. For the Ga^{3+}-ion, the 3d-orbitals are full and the empty 4d-orbitals are too high in energy to be involved in significant overlap. In the case of the Al^{3+}-ion, the empty 3d-orbitals are also too high in energy. For both Al^{3+} and Ga^{3+}, the electronic configuration argument is in accord with the observed dissociative behaviour. This argument also explains well the dissociative nature of the low-spin Co^{3+}-ion, due to its t_{2g}^{6} electronic configuration.

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⁵) The most recent and comprehensive set of radii for metal ions is that of *Shannon & Prewitt* [30].

From the electronic configuration point of view, one would predict an identical behaviour for the $t_{2g}{}^6$-ions Co^{3+} and Rh^{3+}. It is clearer from *Table 4* that Rh^{3+}, unlike Co^{3+}, is showing associative behaviour. This must clearly be a size effect and one therefore expects that, when comparing ions with isoelectronic configuration down a column of the periodic table, the tendency towards an associative mechanism should increase. This is clearly borne out by our results on going from Al^{3+} to Ga^{3+}, and even more to In^{3+} where an I_a-mechanism is observed.

The values of $\Delta V^{\neq}$ observed for Al^{3+} and Ga^{3+} ions *(Table 4)* are significantly smaller than the molar volume (V^0) of DMSO and DMF molecules which are *ca.* 71 and 73 $cm^3 mol^{-1}$ respectively. For a D-mechanism (reactions (4) and (5)), the volume of activation is given approximately by equ. (6), neglecting any second-sphere solvation

$$[M(S)_6]^{3+} \xrightarrow{\text{slow}} [M(S)_5]^{3+} + S \tag{4}$$

$$[M(S)_5]^{3+} + {}^{*}S \longrightarrow [M(S)_5{}^{*}S]^{3+} \tag{5}$$

effects, where $V^0(X)$ represents the molar volume of species X (M = metal ion, S = solvent). In aqueous solution, it is usually assumed that

$$\Delta V^{\neq} = V^0_{MS5} + V^0_S - V^0_{MS6} \tag{6}$$

$V^0_{MS6} \simeq V^0_{MS5}$ and then $\Delta V^{\neq} \simeq V^0_S$, the molar volume of the released solvent molecule [29]. This is probably a reasonable hypothesis for a small solvent molecule like water (molar volume *ca.* 18 $cm^3 mol^{-1}$) [29], but as V^0_S increases, the assumption that $V^0_{MS6} \simeq V^0_{MS5}$ will become less likely, and one might expect $\Delta V^{\neq}$ to be less than V^0_S in general. For an I_d-mechanism (reactions (7) and (8)) one must postulate $K_0[S] \gg 1$ to account for the observed [8] independence of k_{ex} with [S], and $\Delta V^{\neq}$ will be associated with k_I, the interchange rate constant. With this

$$[M(S)_6]^{3+} + {}^{*}S \underset{\text{rapid}}{\overset{K_0}{\rightleftarrows}} \{[MS_6]^{3+}, {}^{*}S\} \tag{7}$$

$$\{[MS_6]^{3+}, {}^{*}S\} \xrightarrow{k_I} [M(S)_5{}^{*}S]^{3+} + S \tag{8}$$

mechanism, $\Delta V^{\neq}$ will be expected to be significantly less than V^0_S, but positive. The values of $\Delta V^{\neq}$ observed for Al^{3+} and Ga^{3+} are nearer to values one might expect for an I_d-mechanism, but since no values of $\Delta V^{\neq}$ are available for known D-mechanisms involving these solvents, one cannot categorically rule out this alternative possibility at the present time, especially as the observed values of $\Delta V^{\neq}$ are somewhat larger than those observed for $[Co(NH_3)_5(S)]^{3+}$ ions (S = DMSO, DMF, *Table 4*) which are known to react with an I_d-mechanism [7] [12].

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