183. A Demonstrated Example of Competing D and I_d Mechanisms for Dimethylformamide Exchange on the Octakis(dimethylformamide)-erbium(III) Ion

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Summary

Dimethylformamide exchange on $[Er(DMF)_8]^{3+}$ is shown to take place *via* two competing dissociative-type mechanisms: D and I_d. It is concluded that a mechanistic crossover occurs along the series Tb–Yb and this behaviour is contrasted with the changeover observed for the solvent exchange on the first-row transition metal ions.

Introduction. – The kinetics and mechanisms of dimethylformamide (DMF) exchange on $[Ln(DMF)_8]^{3+}$ species (Ln = Tb – Yb) have been recently investigated by variable-pressure and -temperature NMR spectroscopy [1-3]. From these studies it is apparent that the mode of exchange becomes more dissociative from Tb to Yb in accordance with predictions based on simple steric considerations. Kinetic observations for Tb- and Tm-systems in CD_3NO_2-diluent were compatible with results in neat DMF and indicated dissociative interchange (I_d) and dissociative (D) [4] mechanisms for Tb and Tm, respectively [3]. In the cases of $[Ln(DMF)_8]^{3+}$ where Ln = Dy – Er intermediate behaviour is expected, manifesting itself either as a mechanistic crossover or changeover [5]. Our study seeks to confirm the suggestion of mechanistic heterogeneity for the $[Er(DMF)_8]^{3+}$-ion [3].

Experimental. – $[Er(DMF)_8](ClO_4)_3$ was prepared as described in [3]. DMF *(Fluka, puriss.)* was purified by fractional distillation at reduced pressure. CD_3NO_3 *(Ciba-Geigy)* was used as received. All liquid reagents were stored over previously activated 4-Å molecular sieves. Solutions were prepared by weight in a glove box (water < 1 ppm) and incorporated a 1% *w/w* benzene reference. ^1H-NMR spectra were run at 200-MHz on a *Bruker CXP-200* spectrometer with a deuterium lock. Sample temperatures were measured before and after spectral accumulation by substituting the sample with a calibrated Pt-resistance [6].

Results and Discussion. – ^1H-NMR spectra of solutions of $[Ln(DMF)_8](ClO_4)_3$ (Ln = Tb, Er and Tm) and DMF in CD_3NO_2 exhibit a single exchange broadened

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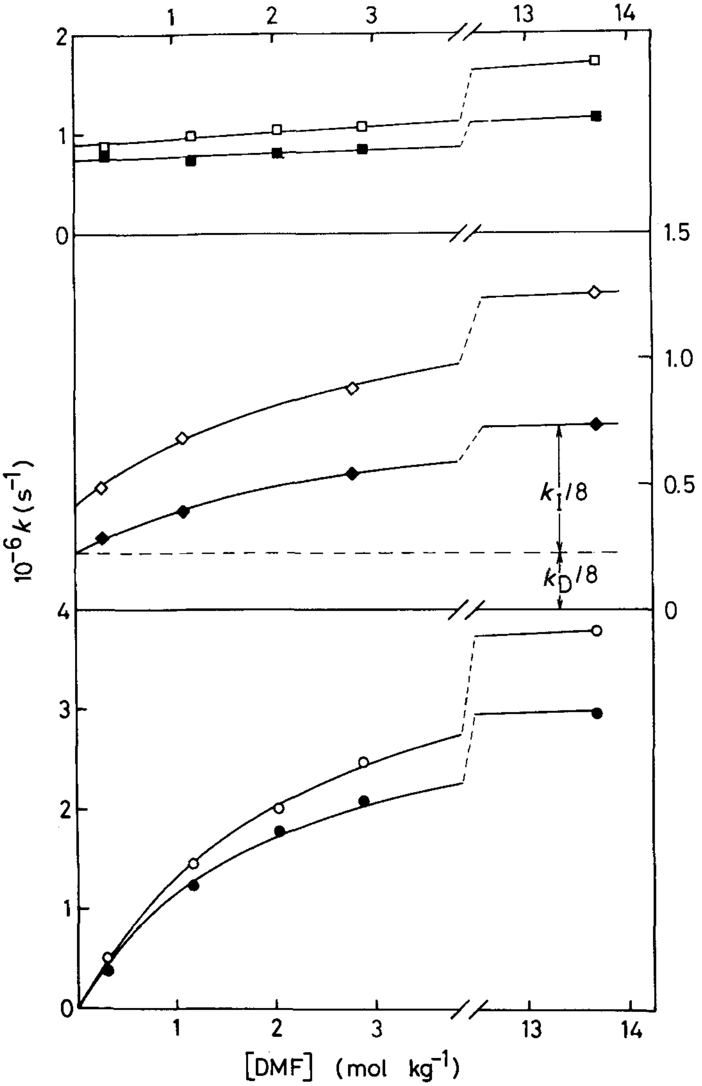

Figure. *Plots of* k *vs.* *[DMF] for Tm* (upper plot), *Er* (centre) *and Tb* (bottom) *systems in CD_3NO_2* (●, 231 K; ○, 239 K; ◆, 234 K; ◇, 244 K; ■, 242 K; □, 248 K. The solid lines are from least-squares fits as in *Table 1* and [3])

formyl resonance in the temperature range of 230–250 K. Kinetic information, obtained by use of a *Swift* and *Connick* analysis, is taken from [3] for Tb and Tm, and has been measured following a similar procedure for Er *(Table 1)*. The *Figure* depicts the observed variation of the exchange rate constant k ($= 1/\tau_m$, the inverse mean life-time of DMF in the first coordination sphere) with free dimethylformamide concentration. The respective rate laws for Tb and Tm in the diluent CD_3NO_2 are consistent with the postulated [3] I_d- and D-mechanisms based on

Table 1. *Formyl Proton Relaxation Rates* ($1/T_{2r}$), *Chemical Shifts* ($\Delta\omega_r$), *Exchange Rate Constants* (k_I and k_D), *and Encounter Complex Equilibrium Constant* (K_{os}) *for Solutions of* $[Er(DMF)_8](ClO_4)_3$ *and DMF in the Diluent* CD_3NO_2 *at 200 MHz*

Mol-% DMF[a]	[DMF] free[b]	$10^{-3}/T_{2r}$[c] [s^{-1}]	$10^{-3}\,\Delta\omega_r$ [rad s^{-1}]	$10^{-5}\,k$ [s^{-1}]	$10^{-5}\,k_I$[d] [s^{-1}]	K_{os}[d] [mol^{-1} kg]	$10^{-5}\,k_D$[d] [s^{-1}]
T = 234 K:							
2	0.27	14.5	52.5	2.85	49 ± 4	0.37 ± 0.12	18 ± 3
8	1.08	11.0	58.5	3.92			
18.5	2.78	8.29	63.1	5.44			
100	13.7	6.58	70.6	7.35			
T = 244 K:							
2	0.27	6.74	48.4	4.88	84 ± 4	0.30 ± 0.06	34 ± 3
8	1.08	5.25	51.2	6.88			
18.5	2.73	4.44	53.9	8.79			
100	13.7	3.55	59.3	12.6			

[a] $[DMF]_t/([DMF]_t + [CD_3NO_2])$ in %.

[b] In mol/kg of solvent (total DMF + CD_3NO_2), excluding the reference (1% benzene).

[c] $T = 234$ K, $1/T_{2m} = 1602\ s^{-1}$, $\Delta\omega_m = 6.09 \times 10^4$ rad s^{-1}; $T = 244$ K, $1/T_{2m} = 1488\ s^{-1}$; $\Delta\omega_m = 5.11 \times 10^4$ rad s^{-1}.

[d] Obtained by least-squares fit to $8\,k = k_I\,K_{os}[DMF]/(1 + K_{os}[DMF]) + k_D$.

Table 2. *Kinetic Parameters for DMF-Exchange on* $[Ln(DMF)_8]^{3+}$ *in DMF*[a])

Ln	ΔH^* [kJ · mol^{-1}]	ΔS^* [J · K^{-1} mol^{-1}]	ΔV^* [cm^3 · mol^{-1}]
Tb	14.1	−58	5.2
Er	23.6	−30	5.4
Tm	33.2	9.9	7.4

[a] From [3].

the activation parameters in neat DMF *(Table 2)*. However, due to the nonzero intercept, the data for Er indicate simultaneous operation of I_d- and D-mechanisms. On account of the dissociative nature of both mechanisms, the apparent ΔV^* is not expected to be markedly pressure- or temperature-dependent [5]. This expectation is in contrast to that observed, for example, for simultaneous I_d and I_a water exchange on Fe^{3+} [7]. According to the operational definitions of *Langford* and *Gray*, the distinction between D- and I_d-mechanism is based on the evidence, or absence thereof, for an intermediate of reduced coordination number. In the former case *(Equations 1–3)* an intermediate is formed by bond cleavage at a rate k_D,

$$[\mathrm{Ln(DMF)_8}]^{3+} \overset{k_D}{\rightleftharpoons} \{\mathrm{Ln(DMF)_7}\}^{3+} + \mathrm{DMF} \tag{1}$$

$$\{\mathrm{Ln(DMF)_7}\}^{3+} + {}^*\mathrm{DMF} \xrightarrow{\text{fast}} [\mathrm{Ln(DMF)_7}({}^*\mathrm{DMF})]^{3+} \tag{2}$$

$$-d[\mathrm{Ln(DMF)_8^{3+}}]/([\mathrm{Ln(DMF)_8^{3+}}]dt) = 8\,k = k_D \tag{3}$$

whereas in the latter case *(Equations 4–6)* a dissociatively activated interchange takes place at a rate k_I between one inner-sphere and one outer-sphere ligand in an

$$[\mathrm{Ln(DMF)_8}]^{3+} + {}^*\mathrm{DMF} \xrightleftharpoons{K_{os}} [\mathrm{Ln(DMF)_8^{3+}} \ldots {}^*\mathrm{DMF}] \tag{4}$$

$$[\mathrm{Ln(DMF)_8^{3+}} \ldots {}^*\mathrm{DMF}] \xrightarrow{k_I} [\mathrm{Ln(DMF)_7({}^*DMF)^{3+}} \ldots \mathrm{(DMF)}] \tag{5}$$

$$-d[\mathrm{Ln(DMF)_8^{3+}}]/([\mathrm{Ln(DMF)_8^{3+}}]dt) = 8k = k_I K_{os}[\mathrm{DMF}]/(1 + K_{os}[\mathrm{DMF}]) \tag{6}$$

encounter complex. For a neutral ligand, such as DMF, the encounter complex formation constant, K_{os}, is expected to be low and close to unity [3] [8] and this compares favourably with the observed values *(Table 1)*.

This mechanistic crossover is in contrast to the changeover occurring for solvent exchange on the first-row transition metal ions. For these six coordinate ions, the exchange pathway is unique, with a nucleophilic attack of the entering ligand at a face of the octahedron and a smooth mechanistic changeover along the series from an expanded transition state for Ni^{2+} (ΔV^* positive, $\mathrm{I_d}$-mechanism) to a compressed transition state for V^{2+} (ΔV^* negative, $\mathrm{I_a}$-mechanism) [7]. Unlike the d-orbitals of these 3d-metal ions, the directional properties of the inner f-orbitals of the lanthanides are of no mechanistic consequences meaning that only the ionic radius need to be taken into account.

For the small Tm-ion the only feasible exchange pathway is the dissociation of a DMF molecule to form a seven-coordinate intermediate. With increasing ionic radius a second exchange pathway becomes competitive: the dissociative interchange (ΔV^* positive) of two solvent molecules in a nine-coordinate transition state. Both pathways are operative for Er, but for the larger Tb the $\mathrm{I_d}$-pathway becomes much more favourable and the D-pathway is no longer observed. For the even larger Nd-ion a solvento-equilibrium $[\mathrm{Nd(DMF)_8}]^{3+}/[\mathrm{Nd(DMF)_9}]^{3+}$ is observed at low temperatures. It is therefore reasonable to predict an $\mathrm{I_a}$- or A-mechanism for DMF-exchange on the Nd^{3+}-octasolvate. This $\mathrm{I_a}$- or A-mechanism could arise from a smooth changeover of the $\mathrm{I_d}$-pathway first observed for Er across the series.

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