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Variable Pressure Spectrophotometric Equilibrium and ^{139}La NMR Kinetic Studies of Lanthanum(III) Ion Complex Formation with 2,6-Dicarboxy-4-hydroxypyridine in Aqueous Solution[†]

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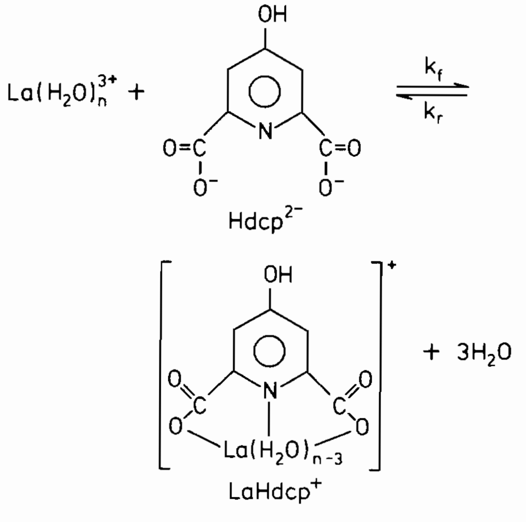
The rate constants for complex formation reactions of trivalent lanthanide aqua-ions are generally very fast, and consequently often difficult to measure. Reactions with multidentate ligands, however, can be slower when chelation is the rate-controlling process. The present work is a variable pressure study of the dissociation of the monocomplex of La^{3+} with a tridentate ligand, 2,6-dicarboxy-4-hydroxypyridine (eqn. (1)) by ^{139}La NMR lineshape analysis. The ^{139}La NMR method as applied to kinetic measurements has been described in a previous publication [1]. Using the spectrophotometrically determined equilibrium constant for this reaction, the rate constant and activation parameters for complex formation can then be derived.



(1)

Experimental

$La(ClO_4)_3$ and 2,6-dicarboxy-4-hydroxypyridine (H_3dcp) solutions were prepared as decribed previously [1].

^{139}La NMR spectra were obtained on a Bruker AM400 spectrometer with an ^{17}O high-pressure probe [2] modified to work at the ^{139}La resonance frequency. Variable pressure NMR measurements were recorded at 275.7 K and 339.5 K up to 200 MPa. The concentrations were $C_{LaHdcp} = 0.0788$ M and $C_{La} = 0.0894$ M [1].

Spectrophotometric data were obtained on a Perkin-Elmer Lambda 7 spectrophotometer. The equilibrium constant at 298.2 K was determined from spectra at different concentrations ($C_{Hdcp} = 1.8 \times 10^{-6}$ M and $2.0 \times 10^{-6} \leqslant C_{La} \leqslant 1.0 \times 10^{-4}$ M). The variable temperature (273.7 to 325.8 K) and pressure (up to 200 MPa at 298 K) measurements were carried out at 285 nm ($\epsilon_{LaHdcp} = 2987$ cm^{-1} M^{-1} and $\epsilon_{Hdcp} = 8900$ cm^{-1} M^{-1}, $l = 5$ cm) with a solution of $C_{Hdcp} = 1.8 \times 10^{-6}$ M and $C_{La} = 2.0 \times 10^{-6}$ M ($I = 1 \times 10^{-3}$ M $NaClO_4$). The variable pressure study was made in a high-pressure optical cell built in our laboratory [3].

Results and Discussion

In the slow exchange limit chosen for the NMR experiment, the measured transverse relaxation rate of the aquated lanthanum(III) ion, $1/T_{2,La}$, is given by eqn. (2). The effect of pressure on the dissociation rate constant k_r and on the quadrupolar relaxation rate $1/T_{2Q,La}$ is given by eqns. (3) and (4) respectively.

$$1/T_{2,La} = k_r + 1/T_{2Q,La} \tag{2}$$

$$k_r = k_{r,0} \exp(-\Delta V_r^{\ddagger} P/RT) \tag{3}$$

$$1/T_{2Q,La} = (1/T_{2Q,La})_0 \exp(-\Delta V_{Q,La}^{\ddagger} P/RT) \tag{4}$$

The $k_{r,0}$ and $(1/T_{2Q,La})_0$ parameters are defined as the zero pressure values. The data (Fig. 1) were analyzed using eqns. (2) to (4) ($k_{r,0}{}^{339.5}$, $(1/T_{2Q,La})_0{}^{257.7}$, $\Delta V_r^{\ddagger}$ and $\Delta V_{Q,La}^{\ddagger}$ as adjustable parameters) with a value of 8.7 s^{-1} at 275.7 K (taken from ref. 1) for the k_r term in eqn. (2), which amounts to less than 1% of $1/T_{2,La}$ at that temperature, and a value of 272 s^{-1} at 339.5 K [1] for the $1/T_{2Q,La}$ term, which is in turn a minor contribution of the measured relaxation rate (~20%).

The stability constant K^{298} was obtained from data collected at several wavelengths between 255 and 315 nm and calculated with a minimizing computer program [4]. Its temperature dependence was analyzed with K^{298} (or ΔS°) and ΔH° as adjusted parameters, and the variable pressure data were fitted to eqn. (5), with K_0 and ΔV° as variables (Table 1).

$$\ln K = \ln K_0 - \Delta V^{\circ} P/RT \tag{5}$$

[†] Part 39 of the series 'High-Pressure NMR Kinetics'; for part 38 see ref. 2.

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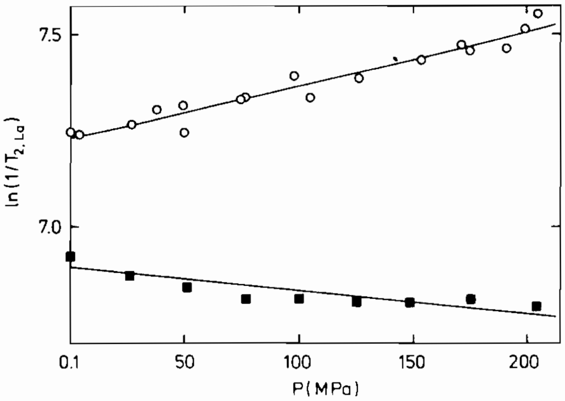

Fig. 1. Observed ^{139}La NMR transverse relaxation rates $1/T_{2,\mathrm{La}}$ as a function of pressure at 275.7 K (■) and 339.5 K (○).

TABLE 1. Pressure and Temperature Dependencies of the Stability Constant K

P (MPa)[a]	T (K)	$10^6 \times K$ (M^{-1})
	273.7	6.3
	288.5	4.5
	298.2	3.9
	310.5	3.6
	325.9	3.2
0.1		3.9
25		3.1
50		3.5
75		2.6
100		2.0
125		2.1
175		1.6
200		1.5

[a] At 298 K.

TABLE 2. Kinetic, Thermodynamic and NMR Parameters

$\log K^{298}$ (M^{-1})	6.58 ± 0.09[a]
k_r^{298} (s^{-1})	207 ± 51[b]
k_f^{298} ($M^{-1}\ s^{-1}$)	8×10^8[c]
ΔH° (kJ mol^{-1})	-9.4 ± 1.5
$\Delta H_r^\ddagger$ (kJ mol^{-1})	38.3 ± 3.1[b]
$\Delta H_f^\ddagger$ (kJ mol^{-1})	29[c]
ΔS° (J K^{-1} mol^{-1})	$+95 \pm 5$
$\Delta S_r^\ddagger$ (J K^{-1} mol^{-1})	$+72 \pm 8$[b]
$\Delta S_f^\ddagger$ (J K^{-1} mol^{-1})	+23[c]
ΔV° (cm^3 mol^{-1})	$+12.1 \pm 1.5$
$\Delta V_r^\ddagger$ (cm^3 mol^{-1})	-4.9 ± 0.3
$\Delta V_f^\ddagger$ (cm^3 mol^{-1})	+7[c]
$1/T_{2\mathrm{Q,La}}^{298}$ (s^{-1})	550 ± 83[b]
$1/T_{2\mathrm{Q,LaHdcp}}^{298}$ (s^{-1})	20000 ± 800[b]
$E_{\mathrm{Q,La}}$ (kJ mol^{-1})	26.4 ± 5.8[b]
$E_{\mathrm{Q,LaHdcp}}$ (kJ mol^{-1})	16.3 ± 1.6[b]
$\Delta V_{\mathrm{Q,La}}^\ddagger$ (cm^3 mol^{-1})	$+1.5 \pm 0.4$

[a] Quoted errors correspond to one standard deviation.
[b] Taken from ref. 1.
[c] Derived from equilibrium and dissociation reaction kinetics data.

Table 2 summarizes the kinetic, thermodynamic and NMR parameters. The kinetic parameters of the complex formation reaction may be discussed according to the Eigen-Wilkins mechanism, which considers ion-pairing to occur in a fast pre-equilibrium before the rate-determining interchange of water for the ligand, with rate constant k_I [5]. The stability constant of the ion-pair complex can be evaluated using the Fuoss model, which yields a value of $K_{os} = 1700\ M^{-1}$ ($r = 500$ ppm) [6]. The deduced value of $5 \times 10^5\ s^{-1}$ for k_I ($= k_f/K_{os}$) is small compared to the water exchange rate constant on La^{3+} ($10^8\ s^{-1} \leqslant k_{ex} \leqslant 10^9\ s^{-1}$ [7]). This suggests that chelation is rate determining in forming the complex, as was previously observed with a similar ligand [8]. The electrostrictive and chelation–dechelation contributions to $\Delta V_f^\ddagger$ and $\Delta V_r^\ddagger$ are, however, hard to evaluate. The large expansion ($\Delta V^\circ = +12.1\ cm^3\ mol^{-1}$) well reflects the strong electrostriction decrease due to charge neutralization in forming the complex. The activation volumes are of opposite signs and small with respect to the ΔV°, precluding decisive mechanistic conclusions, as would be possible in more clear-cut cases.

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