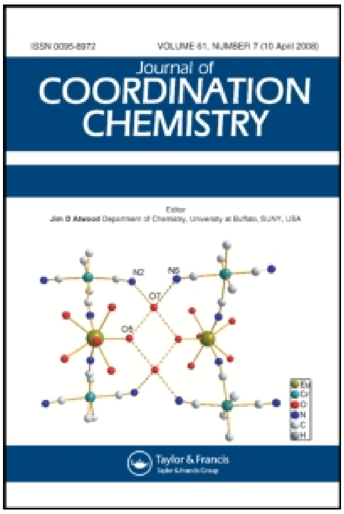

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SHORT COMMUNICATION

The Effect of Pressure on the Exchange Reactions Between the Diaminocyclohexanetetraacetate Complexes of Trivalent Cerium, Europium, Terbium and Free Erbium Ions

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A number of reports in the literature[1] are concerned with exchange reactions between aminopolycarboxylate (A) complexes of trivalent lanthanide (Ln) ions and free metal ions (M) of the type:

$$\mathrm{LnA + M \rightleftharpoons MA + Ln}$$

In most cases ethylenediaminetetraacetate (EDTA) or *trans*-1,2,-diaminocyclohexanetetraacetate (DCTA) were used as multidentate ligands.

Several mechanisms are discussed for the exchange reactions. They can be divided in those assuming a dissociation of the original complex followed by the formation of a complex with the free metal ion and those considering a direct attack on the original complex by the free metal ion.[1,2] Since the exchange reactions were found to be catalyzed by hydrogen ions, the dissociation path is generally favoured. Yet there are still different opinions on the kind of influence of the hydrogen ions and hence on the rate determining step within the series of bond dissociation processes resulting finally in the total unwrapping of the original complex.

Some authors[3] proposed a mechanism in which the protonation of the original complex is rate determining. However, this in not very probable considering our knowledge about the very fast rates of neutralisation reactions. According to structural studies[4] of solid HLaEDTA.7 H_2O and KLaEDTA.8 H_2O complexes the protonation occurs at one of the carboxylate groups of the ligand and this results in a lengthening of the La–O–bond. Proton magnetic resonance studies[5] have shown that the metal–(carboxylate)–oxygen bonds have short life times which probably become even shorter upon protonation. During this process the site of the dissociating carboxylate group is taken by a water molecule. The longer life times of the metal–nitrogen bonds support the idea that the cleavage of these bonds, which may occur simultaneously with or after completion of further carboxylate group dissociations, resembles the rate determining step of the exchange process. Whether the individual dissociation step at a coordination site is of dissociative, associative or interchange nature remains unknown.

Recently it became evident[6] that the volume of activation, derived from the pressure dependence of the rate constant of a reaction, offers useful criteria for the discussion of mechanisms.[7] We have, therefore, selected three exchange reactions of fairly simple kinetic behaviour and studied their pressure dependence. These reactions are the exchange of Ce(III)–, Eu(III)–, and Tb(III)–ions in their respective DCTA – complexes by Er(III) – ions. The course of the reactions was followed spectrophotometrically at 302, 238, and 241 nm using a ZEISS PMQ II photometer. The cuvette compartment of the photometer was also part of a high pressure apparatus.[8] All measurements were carried out at

25.0 ± 0.1°C. The ionic strength of the solutions was maintained at 0.1 M using potassium chloride as an inert salt. The reactions were studied at pH values 5.22 and 5.37 for the Ce–, 3.80 and 4.02 for the Eu– as well as 3.53 and 3.75 for the TbDCTA complexes. No buffer was applied since the pH value of the solutions was practically constant during the course of the reactions. Employing a 20-fold excess of the free metal ions over the complex concentration the rate law simplifies to:

$$\frac{d[LnDCTA]}{dt} = k_{obs}[LnDCTA]$$

with $k_{obs.} = k_2[H^+]$ as was shown previously.[1,9,10] The rate constants k_2 obtained at six different pressures and the volumes of activation calculated therefrom according to the relation

$$\frac{d(\ln k_2)}{dP} = -\frac{\Delta V^{\ddagger}_{exp}}{RT}$$

are summarized in Table I. The rate constants obtained at normal pressure agree well with the results of other studies.[1,9,10]

The relative reproducibility of the rate constants reached ±5%; the uncertainty of the volumes of activation amounts to ±1.0 ml mol^{-1}.

The course of the selected exchange reactions can be depicted by the following scheme which is in accordance with the general discussion of the exchange mechanisms given above:

$$[Ln(DCTA)(H_2O)_n]^- + H^+_{aq} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$[Ln(DCTAH)(H_2O)_n] + Er^{3+}_{aq}$$

$$k_{-2} \upharpoonleft\!\downharpoonright k_2$$

$$[Ln(DCTAH)(H_2O)_{n+1}] + Er^{3+}_{aq}$$

$$k_{-3\ldots x-1} \upharpoonleft\!\downharpoonright k_{3\ldots x-1}$$

$$[Er(DCTAH)(H_2O)_{n+1}] + Ln^{3+}_{aq}$$

$$\underset{k_{-x}}{\overset{k_x}{\rightleftharpoons}} [Er(DCTA)(H_2O)_n]^- + H^+_{aq}$$

Depending on the concept of the mechanism, i.e. the placing of the rate determining step, different volume contributions to the overall volume of activation, $\Delta V^{\ddagger}_{exp}$, are to be expected. An estimation of these contributions can be made by comparison with volumes measured for similar processes and reported in the literature. Among these especially the volume effect of about +10 ml mol^{-1} that derives from the neutralisation of a carboxylate group should be mentioned.[11] The dissociation of a carboxylate group involves a cleavage of a metal–oxygen bond whereas the addition of a water molecule to the complex represents the reverse of this, a formation of a metal–oxygen bond. As a rule bond making occurs to a larger extent than bond stretching during the formation of the transition state for a reversible process.[11] Therefore small to moderately positive contributions to $\Delta V^{\ddagger}_{exp}$ are to be expected for the dissociation of a protonated carboxylate group and somewhat larger, but negative, values for the association of a water molecule to the inner coordination sphere. Consequently, an interchange of carboxylate and water during the rate determining step should result in a small, but negative, $\Delta V^{\ddagger}$ contribution. In the case of the dissociation of an unprotonated carboxylate group a substantial negative contribution arising from the electrostriction of the solvent due to the developing charges must also be taken into account.

TABLE I

Rate constants k_2 (M^{-1} sec.$^{-1}$) and volumes of activation $\Delta V^{\ddagger}_{exp}$ (ml mol^{-1}) of the exchange reactions

Pressure	Complexes					
(atm)	CeDCTA		EuDCTA		TbDCTA	
	k_2	$\Delta V^{\ddagger}_{exp}$	k_2	$\Delta V^{\ddagger}_{exp}$	k_2	$\Delta V^{\ddagger}_{exp}$
1	135	−3.2	2.62	−2.2	0.52	−4.7
250	146	−2.9	2.76	−2.2	0.56	−3.9
500	154	−2.5	2.92	−2.1	0.64	−3.0
750	164	−1.8	3.07	1.7	0.66	−1.8
1000	169	−1.1	3.15	−1.2	0.68	−1.1
1500	174	−0.6	3.30	−0.7	0.72	−0.9

For a slow reaction of the proton with the original anionic complex one should thus expect a $\Delta V^{\ddagger}_{exp}$, value of about +10 ml mol^{-1} which is in contrast with the findings. On the other hand if one assumes a fast protonation preequilibrium, $\Delta V^{\ddagger}_{exp}$ consists of an equilibrium contribution, ΔV, and a volume of activation, $\Delta V^{\ddagger}$. With the known values of $\Delta V = +10$ ml mol^{-1} and our $\Delta V^{\ddagger}_{exp}$ of −2 to −4 ml mol^{-1} a substantial negative value for $\Delta V^{\ddagger}$ of about 12 to 14 ml mol^{-1} must therefore be involved. Such negative contribution can not stem from the cleavage of one metal–oxygen bond, as this process would result in a smaller $\Delta V^{\ddagger}$ value. It is more probable that the rate determining step of the reactions investigated consists of successive breaking of additional metal ligand bonds, presumably the dechelation of one of the iminodiacetate groups of the ligand.[9] In the case of the formation of a noncoordinated iminodiacetate group the contribution of the electrostriction of the solvent to the negative $\Delta V^{\neq}$ value can be also significant. The explanation of the negative $\Delta V^{\neq}$ values is also possible assuming the formation of a transition complex similar to that found by Nyssen and Margerum in the reaction of La^{3+} with $H_2 DCTA^{2-}$.[9] In this species the ligand is probably coordinated only by its carboxylate groups and the metal ion is outside of the coordination cage of the $H(DCTA)^{3-}$.[9] In the case of the formation of this transition complex the cleavage of the metal–ligand bonds and the developing partial charges which give rise to the coordination of additional water molecule(s) can result in the negative $\Delta V^{\neq}$ values.

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