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Aminopolycarboxylates of Rare Earths.
X. ^{1}H-NMR Spectroscopic Study of the Mechanism of Dissociation of Ethylenediamine-N,N,N',N'-tetraacetate Complexes of Cerium(III) and Yttrium(III)

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The ^{1}H-NMR signal of the carboxy methylene protons in Ceedta$^-$ or Yedta$^-$ is an AB multiplet. On formation of the protonated complexes in solutions with lower pH, the multiplet signals are broadened. By means of line-shape analysis, the pH-dependence of the average lifetime (τ) before exchange of the carboxy methylene protons H_A and H_B was determined (at various temperatures in the case of Ceedta$^-$). The dependence of the rate of the AB exchange process ($1/\tau$) on the H^+ ion concentration can be described by a similar relation as for the rate of the proton-catalyzed dissociation of the complexes. On the basis of the rate constants it is assumed that the proton-catalyzed AB exchange process of the carboxy methylene protons in Ceedta$^-$ and Yedta$^-$ occurs via *formation of the same intermediates as in the proton-catalyzed dissociation of Ceedta$^-$ and Yedta$^-$. The rate-determining step is also the same in the AB exchange and in the dissociation of the complexes; this is probably the formation of an intermediate containing one free protonated iminodiacetate group.*

Introduction

^{1}H-NMR spectroscopic examinations can yield valuable information on the structures of complexes of polyfunctional aminopolycarboxylate ligands, *e.g.* the various ethylenediamine-N,N,N',N'-tetraacetate (edta^{4-}) complexes, and on the lability of the metal–ligand bonds [1–4]. From the variations in the multiplet signals as functions of temperature or H$^+$ ion concentration, conclusions may be drawn concerning the rates and mechanisms of the ligand-exchange reactions and the intramolecular transformations [2, 5–7].

Very detailed studies have been made of the kinetics of the metal ion-exchange reactions of the edta complexes of the rare earth (III) ions (Lnedta$^-$) [8–14]. These reactions predominantly occur through proton-catalyzed dissociation of the complexes in the pH interval 2–5, and a relatively small role is played by reactions involving direct attack by the exchanging metal ions. The effect of H$^+$ ions in promoting the dissociation of the complexes is interpreted by the protonation and the faster dissociation of the protonated complexes. The structures of the protonated complexes LnHedta in aqueous solution are not known exactly, but it is probable that the number of coordinated donor atoms decreases on protonation.

The results of ^{1}H-NMR spectroscopic studies of the complexes Lnedta$^-$ reveal that the ethylenediamine methylene protons always give a singlet signal because of the symmetry of the complex, while (with the exception of Laedta$^-$) the carboxy methylene protons give an AB quartet signal [4, 15, 16]. The explanation given for the occurrence of the AB multiplet signal is that the average lifetime of the metal-nitrogen bonds is longer than the reciprocal of the difference in the shifts of the AB protons, and the carboxy methylene groups are situated adjacent to an asymmetric nitrogen atom, which eliminates the magnetic equivalence of the geminal protons [1, 2]. At the same time, the four carboxy methylene groups of edta are equivalent, which is a result of the symmetry of the complex and the short lifetime, very frequent breaking and reformation of the metal–carboxylate oxygen bonds.

In our experience the AB quartet signal of the carboxy methylene protons is broadened by decrease

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of the pH of the Lnedta$^-$ solutions, *i.e.* by the formation of the protonated complexes LnHedta^0. The broadening of the signals points to an increase in the rate of intramolecular transformation occurring in the complex, which results in the carboxy methylene protons exchanging positions. Since the dissociation of the protonated complexes plays the determining role from the aspect of the metal ion-exchange reactions of the complexes Lnedta$^-$, we have carried out a ^{1}H-NMR spectroscopic study of the pH-dependence of the rate of transformation involving the exchange of positions by the carboxy methylene protons in the complexes Ceedta$^-$ and Yedta$^-$. From comparisons of the rates of the proton-catalyzed dissociation of the complexes and the rates of AB exchange, conclusions may be drawn regarding certain elementary steps in the proton-catalyzed dissociation.

Experimental

The KCeedta (0.02 mol dm^{-3}) and KYedta (0.01 mol dm^{-3}) solutions used in the experiments were prepared from $CeCl_3$ and YCl_3 (Fluka) of 99.9% purity and from K_2H_2edta (Reanal) of the highest analytical purity. The concentrations of the $CeCl_3$ and YCl_3 solutions were determined with K_2H_2-edta solution with xylenol orange as indicator, and the concentration of the K_2H_2edta solution with standard $CuCl_2$ solution with murexide as indicator.

The protonation constants of Ceedta$^-$ and Yedta$^-$ were taken into account and the ^{1}H-NMR spectra were recorded in 99.5% D_2O solution in a pD interval in which the concentrations of the protonated complexes CeHedta and YHedta were always less than 3%, when the complexes underwent a negligible extent of decomposition.

The pH was measured with a Radiometer pHM-26 pH-meter, with a combined electrode. The pD value was calculated from the measured pH value *via* the relation pD = pH –0.41 [17].

^{1}H-NMR spectra were recorded on a Varian-XL-100/15 FT NMR instrument, with t-butanol as internal standard. The customary inversion recovery method [19] was used to measure the longitudinal relaxation times (T_1). In the perturbation mixing experiments the length of the selective decoupling pulse was 10 ms.

Results and Discussion

With the increase of the H$^+$ ion concentration in the solutions of the complexes Ceedta$^-$ and Yedta$^-$, the signals of the carboxy methylene protons become progressively broader. Figure 1. presents two characteristic spectra of the complex Yedta$^-$ in solution in D_2O.

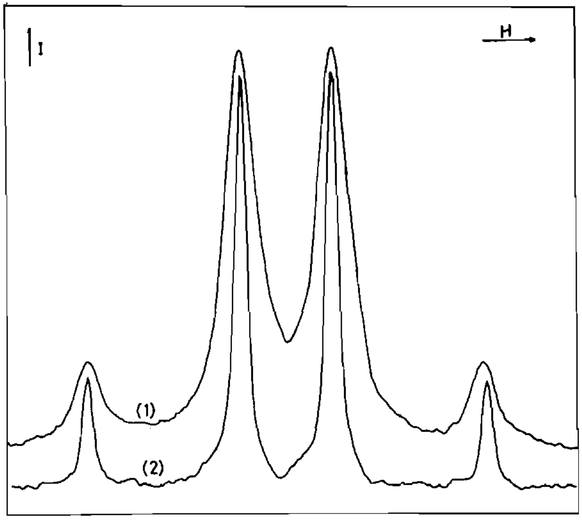

Fig. 1. Spectrum of carboxy methylene protons in Yedta$^-$. pD = 1.97 (1) and pD = 5.72 (2); t = 28 °C.

The broadening of the AB multiplet signals with the decrease of the pH can be interpreted by the increase in the rate of exchange of the carboxy methylene protons, and by the decrease in the average lifetime of the metal–nitrogen bonds. The average lifetime (τ) of the carboxy methylene protons H_A and H_B in the different environments before exchange can be calculated by analysis of the signal function describing the multiplet. The intensity of the AB quartet signal as a function of the frequency can be written in terms of the coupling constant J_{AB}, the chemical shift difference $\Delta\nu_{AB}$, the transversal relaxation time T_2, the centre ν_0 of the multiplet signal, and the average lifetime τ before the AB exchange [18].

From spectra recorded at 28 °C in neutral medium, the values of J_{AB} and $\Delta\nu_{AB}$ for the complex Yedta$^-$ are 16.7 Hz and 20.5 Hz. In the range of slow exchange (in neutral medium) the value of T_2 was calculated from the width of the signals:

$$W_{1/2}\cdot\pi = \frac{1}{T_2^*} = \frac{1}{T_2} + \Delta H$$

where $W_{1/2}$ is the natural line-width, T_2^* and T_2 are the apparent and the true transversal relaxation times, and ΔH is the line broadening caused by the inhomogeneity of the magnetic field. For Yedta$^-$, $W_{1/2}$ = 1.7 Hz and T_2 = 0.19 s (at 28 °C and pD = 6.11).

For Ceedta$^-$ the values of J_{AB} and $\Delta\nu_{AB}$ are 16.2 Hz and 134.1 Hz. The paramagnetism of Ce means that, in comparison to the natural line-width, the increase resulting from the exchange is small in the

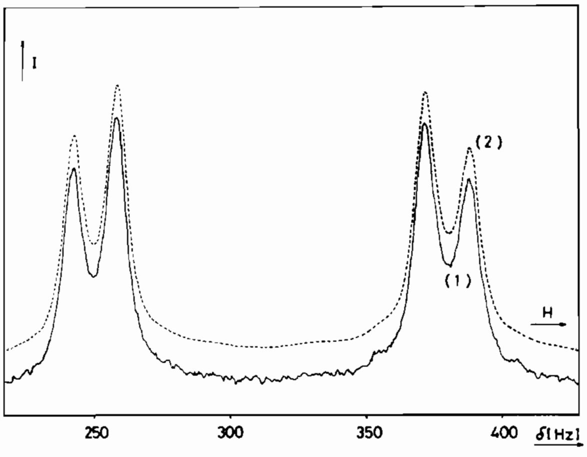

Fig. 2. Measured (1) and calculated (2) spectrum of carboxy methylene protons in Ceedta$^-$. pD = 3.53; t = 50 °C.

case of Ceedta$^-$, and its determination is not very accurate. Accordingly, the relaxation parameters necessary for the calculations were also determined by an independent method. Since $T_1 = T_2$ in the examined system, from an experimental aspect it appeared most obvious to measure the longitudinal relaxation (T_1) of the carboxy methylene protons. The resulting T_1 values exhibited good agreement with the T_2 values determined from the line-width. On this basis, signal width values of $W_{1/2}$ = 4.0, 3.7, 3.2 and 2.7 Hz at 28, 50, 75 and 100 °C, respectively, were used in the further calculations. The $1/\tau$ values were calculated by means of a FORTRAN programme *via* the relation given by Heidberg *et al.* [18]. 200–250 frequency-intensity data pairs were read off each spectrum and, in the knowledge of the T_2 and J_{AB} values, the estimated value of $\Delta\nu_{AB}$ was refined and the weighted square sum of the differences in the measured and calculated intensities was minimized.

In order to obtain further confirmation of the calculations, we carried out measurements for the direct determination of the rate of exchange by an independent method. The double resonance procedure known as perturbation mixing [24] was used for this purpose. Here one of the protons (A) of the AB system was polarized with a selective decoupling pulse π, and the spreading of the spin polarization to the resonance of the other (B) proton was measured after the passage of a variable mixing time t. In the knowledge of the relaxation time T_1, the rate constant of the exchange can be calculated directly from the dependence of the amplitude of the B proton signal on t. The rate constant values obtained by the two means agreed within the limits of experimental error (<10%). An experimental and a calculated spectrum are shown in Fig. 2.

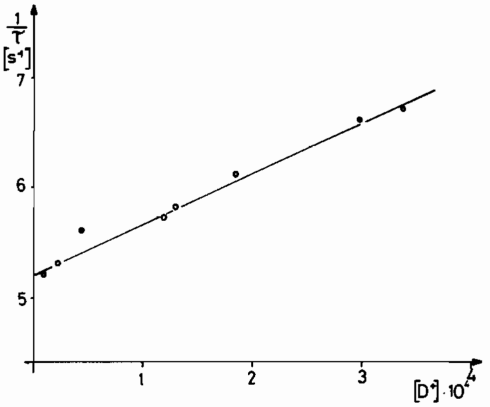

Fig. 3. Rate of AB exchange process of carboxy methylene protons in Ceedta$^-$. t = 28 °C.

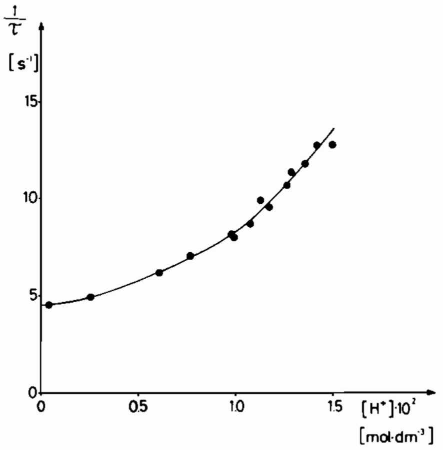

Fig. 4. Rate of AB exchange process of carboxy methylene protons in Yedta$^-$. t = 28 °C.

The exchange of the protons H_A and H_B is connected with the intramolecular transformation of the complex, and is therefore a first-order process kinetically. The average lifetime of the A and B protons before exchange can thus be expressed in terms of the total concentration of the complexes, $[\text{Lnedta}]_t$, and the rate of the AB exchange (v_i): $\tau = [\text{Lnedta}]_t/v_i$, from which the rate of exchange is

$$v_i = \frac{1}{\tau}\,[\text{Lnedta}]_t \qquad (1)$$

The term $1/\tau$ in eqn. (1) can be regarded as the pseudo first-order rate constant of the exchange process.

$1/\tau$ values obtained by line-shape analysis for Ceedta$^-$ and Yedta$^-$ at 28 °C and at various pD values are presented in Figs. 3 and 4.

TABLE I. Rate Constants Characterizing the AB Exchange Rates of the Carboxy Methylene Protons in Ceedta$^-$ and Yedta$^-$ and their Proton-Catalyzed Dissociation.

	t [°C]	Ceedta	Yedta
k_{i0} [s^{-1}]	28	5.2 ± 0.2	4.5 ± 0.2
k_{d0} [s^{-1}]	25	$2 \cdot 10^{-4}$ [21]	$1 \cdot 10^{-4}$ [21]
k_{i1} [$M^{-1} s^{-1}$]	28	$(4.2 \pm 0.3) \cdot 10^3$	90 ± 7
k_{d1} [$M^{-1} s^{-1}$]	25	$2.9 \cdot 10^3$ [22]	30 [23]
k_{i2} [$M^{-2} s^{-1}$]	28		$(2.9 \pm 0.2) \cdot 10^4$
k_{d2} [$M^{-2} s^{-1}$]	25		$5.2 \cdot 10^5$ [23]

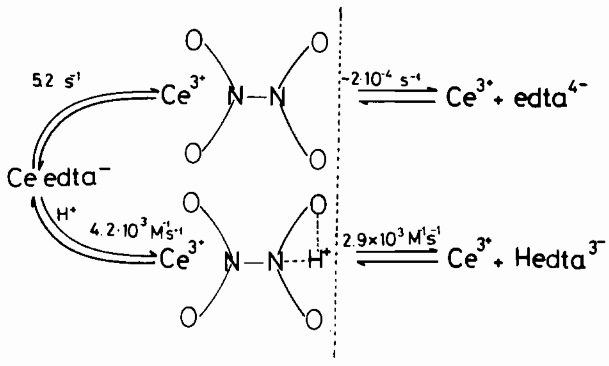

Fig. 5. Assumed course of AB exchange and dissociation of Ceedta$^-$.

The data in Fig. 3 indicate that the rate of AB exchange of the methylene protons in Ceedta$^-$ is linearly proportional to the H$^+$ ion concentration:

$$\frac{1}{\tau} = k_{i0} + k_{i1}[H^+] \qquad (2)$$

From the data in Fig. 4, the rate of AB exchange of the methylene protons in Yedta$^-$ depends on a more complex function of the H$^+$ ion concentration:

$$\frac{1}{\tau} = k_{i0} + k_{i1}[H^+] + k_{i2}[H^+]^2 \qquad (3)$$

Relations (2) and (3) describing the AB exchange rates of the methylene protons in Ceedta$^-$ and Yedta$^-$ correspond to the rate equations for the metal ion-exchange reactions of the complexes, involving their proton-catalyzed dissociation. The rates of the proton-catalyzed dissociation of Ceedta$^-$ and Yedta$^-$ are $v_d = k_{obs}[\text{Lnedta}]_t$, where the pseudo first-order rate constant k_{obs} for Ceedta$^-$ is [20]

$$k_{obs} = k_{d0} + k_{d1}[H^+] \qquad (4)$$

while that for Yedta$^-$ is [23]

$$k_{obs} = k_{d0} + k_{d1}[H^+] + k_{d2}[H^+]^2 \qquad (5)$$

k_{d0}, k_{d1} and k_{d2} are the rate constants of dissociation of the non-protonated, the monoprotonated and the diprotonated complexes, respectively.

The rate constants k_{i0}, k_{i1} and k_{i2} calculated from the data in Figs. 3 and 4 are to be found in Table I, together with the rate constants from eqns. (4) and (5).

The similarity between eqns. (2) and (4), and (3) and (5), describing the dependences of $1/\tau$ and k_{obs} on the H$^+$ ion concentration, shows that there must be a close connection between the AB exchange process and the dissociation of the complexes. The exchange of the protons H_A and H_B is accompanied by inversion of the nitrogen atom, which can presumably occur only after the metal–nitrogen bond breaks; this must be preceded by rupture of the two carboxylate oxygen–metal bonds [1, 2]. Before the AB exchange takes place, therefore, one of the iminodiacetate (imda) groups of the edta^{4-} ligand becomes free, and the rate constants k_{i0}, k_{i1} and k_{i2} express the frequency of cessation of coordination of the imda group. From eqns. (2) and (3), the constants k_{i0}, k_{i1} and k_{i2} are presumably characteristic of the rates of AB exchange involving formation of the complexes Lnedta$^-$, LnHedta and LnH$_2$edta, respectively.

A comparison of the rate constants in Table I reveals the similarity of k_{i1} and k_{d1} for both Ceedta$^-$ and Yedta$^-$. Accordingly, we assume that the proton-catalyzed AB exchange and the proton-catalyzed dissociation of the complexes proceed via formation of the same intermediates. Figure 5 illustrates the assumed course of the AB exchange and the dissociation *via* the 'semi-dissociated' intermediate in the case of Ceedta.

The rate of formation of the 'semi-dissociated' intermediate is higher than the values of k_{i0} or k_{i1} if inversion of the nitrogen atom occurs several times before the re-coordination of the free imda group. (If the inversion of the nitrogen atom takes places very many times, the rate of formation

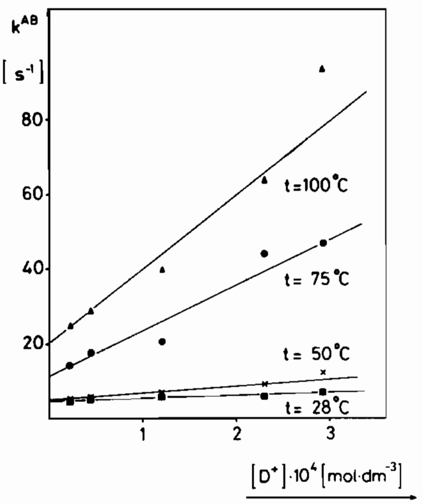

Fig. 6. Temperature-dependence of rate of AB exchange of carboxy methylene protons in Ceedta$^-$.

of the intermediate is twice the rate of AB exchange).

Figure 5 indicates that the rate of spontaneous dissociation of the complex (k_{d0}) is several orders lower than the rate of spontaneous AB exchange (k_{i0}). This can be interpreted in that the re-coordination of the free imda group is not inhibited, and thus its rate may be substantially higher than the rate of dissociation of the other imda group. At the same time, the rate of the proton-catalyzed dissociation of the complex is roughly the same as the rate of the proton-catalyzed exchange. Hence, we assume that the rate-determining step in the proton-catalyzed dissociation of the complex is the formation of the 'semi-dissociated' protonated intermediate.

The AB multiplet signal of the methylene protons in Ceedta was also studied as a function of pH at various temperatures. The $1/\tau$ values found are depicted in Fig. 6.

The rate constants k_{i1} at 28, 50, 75 and 100 °C, respectively, are 4.2×10^3, 1.8×10^4, 1.2×10^5 and 1.9×10^5 mol^{-1} dm^3 s^{-1}; the activation energy calculated from these values is 53 ± 5 kJ mol^{-1}. The value thus obtained for the activation energy of the AB exchange process agrees well with the value of 50.2 ± 3.3 kJ mol^{-1} found for the proton-catalyzed dissociation of Ceedta$^-$ by kinetic study of the isotope-exchange reactions in the Ceedta$^-$–Ce^{3+} system [9]. The agreement of the activation energies also shows that the AB exchange and the proton-catalyzed dissociation of the complex proceed *via* formation of the same intermediate, and the rate-determining step is the formation of a species with the same structure in the two processes.

Comparison of the rate constants k_{i0} and k_{i1} for the AB exchange of the methylene protons in Yedta$^-$ with the rate constants k_{d0} and k_{d1} for dissociation of the complex (Table I) leads to analogous conclusions as in the case of Ceedta$^-$. At the same time, it is surprising that $k_{d2} > k_{i2}$: the AB exchange presumably involving formation of the diprotonated complex is slower than its dissociation. It is difficult to explain this finding, for conclusions on the formation of the diprotonated complex can be drawn only from kinetic data, and thus information is not available on its structure and the sites of protonation (which can occur on different functional groups).

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