Stability Constants and Rate Coefficients for Decarboxylation of Lanthanide Oxalacetates

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Stability constants β_{101} of ML and β_{102} of ML_2 (M = lanthanide, L = oxalacetate) for most of the series La to Yb have been calculated from the electromotive force values of a glass electrode–calomel electrode cell at $I = 0.5$ mol dm^{-3} and 25 °C. Rate coefficients for decarboxylation, k_{ML} and k_{ML_2}, have been calculated from UV spectrophotometric data obtained at $I = 0.5$ mol dm^{-3}. The stability-constant values follow the usual pattern for moderately strong complexes, *i.e.* increasing from La to Yb with a slight dip around Gd and Ho, but this pattern is not found in the rate coefficients. Those for k_{ML} decrease from Ce to Eu, rise again for Gd and Ho and then decrease again from Ho to Yb. The ratio of k_{ML_2} to k_{ML} is about 2 to 3:1 except for La, Ce and Yb. With La and Ce the k_{ML_2} values, like the β_{102} values, are zero or very small while the ratio for the strong ytterbium complex is about 10:1. Some interpretations for the above trends are made.

Some years ago, Gelles, Nancollas and Clayton[1,2] reported estimates of association constants and rates of decarboxylation of a few lanthanide oxalacetates. They found that the association constants are large and this generates fast rates of decarboxylation. An approximately linear relationship between the rate coefficients k and the association constants K_{ML} was noted[2] for the diamagnetic ions La^{3+}, Y^{3+} and Lu^{3+}. The data for Gd^{3+} and Dy^{3+} are higher than predicted, the extra acceleration being attributed to the paramagnetism of these ions caused by unpaired 4f electrons. Another correlation, suggested by Gelles and Nancollas,[1] is that the K_{ML} values are linearly related to $1/r$ where r is the crystallographic radius. This is based on data for La, Gd, Dy and Lu.

The association-constant calculations were based on electromotive force (e.m.f.) measurements using a glass electrode–calomel cell calibrated with standard buffers. Timed e.m.f. values of the lanthanide oxalacetate solutions were extrapolated to zero time to compensate for drifts due to decarboxylation. The precision was estimated as ±0.1 mV and the numerical analysis to obtain K_{ML} and K_{ML_2} involved a graphical procedure. For the kinetic studies timed measurements of CO_2 in a manometric apparatus[1,2] were obtained. The present association-constant determinations, which involve most of the lanthanides from La to Yb, are based on e.m.f. measurements with a previously described DVM system[3] that reads to ±0.01 mV

Table 1 Stability constant data for lanthanide oxalacetates at $I = 0.5$ mol dm^{-3} and 25 °C. Concentrations in mol dm^{-3}: c_1, oxalacetic acid; c_2, NaOH; c_3, $HClO_4$; c_4, MCl_3

10^3c_1	10^3c_2	10^3c_3	10^3c_4	10^4X	$10^{-4}Y$	$\bar{n}$
Lanthanum						
11.29	0	0.70	6.02	2.59	0.133	0.138
20.84	6.64	0	3.91	7.25	0.117	0.265
20.56	16.27	0	3.84	30.90	0.135	0.561
Cerium						
10.87	0	0	11.53	2.13	0.177	0.148
12.36	6.51	0	5.88	6.80	0.202	0.342
11.26	9.70	0	5.84	12.21	0.239	0.495
12.79	12.86	0	5.80	21.5	0.297	0.632
Praseodymium						
18.52	0	0	8.58	2.48	0.311	0.249
15.25	6.12	0	8.48	4.38	0.357	0.375
16.52	9.13	0	8.43	6.17	0.396	0.461
15.63	9.7	0	7.22	7.72	0.471	0.518
Neodymium						
16.13	0	7.26	11.78	1.05	0.478	0.184
17.86	0	4.01	8.60	1.59	0.498	0.253
16.81	0	0	12.06	1.81	0.505	0.275
17.17	6.12	0	8.19	4.06	0.632	0.472
Samarium						
17.4	0	11.98	5.43	0.92	0.84	0.249
23.43	0	8.12	5.52	1.49	0.98	0.362
22.36	0	0	5.47	3.06	1.51	0.578
17.6	3.23	0	5.44	4.12	1.75	0.651
Europium						
8.32	0	0	8.82	1.28	0.97	0.332
15.72	0	6.16	4.58	1.48	1.08	0.380
15.57	0	0	4.64	1.97	1.24	0.461
17.01	0	0	4.88	2.93	1.51	0.570
Gadolinium						
9.05	0	0	12.83	1.10	0.763	0.262
8.75	0	0	6.89	1.66	0.870	0.361
16.82	0	0	4.59	2.99	1.21	0.533
14.65	6.23	0	6.80	4.43	1.54	0.643
Holmium						
12.03	0	3.67	10.22	1.06	0.90	0.285
11.07	0	0	10.33	1.33	0.98	0.342
17.93	0	4.60	5.46	1.71	1.11	0.413
16.09	0	0	4.62	2.92	1.31	0.545
Erbium						
21.29	0	0	11.17	1.59	1.79	0.490
16.16	0	0	5.71	2.11	2.03	0.565
21.60	10.67	0	9.62	5.60	3.57	0.782
18.53	0	0	4.60	6.20	3.90	0.801
Ytterbium						
12.12	0	0	11.97	0.77	3.82	0.496
18.47	0	0	9.75	1.50	4.90	0.662
12.69	0	1.95	4.93	2.12	5.33	0.715
14.26	0	0	4.93	3.52	7.42	0.808

Table 2 Rate coefficients for decarboxylation of lanthanide oxalacetates by spectrophotometry at $I = 0.5$ mol dm^{-3} and 37 °C

M^{III}	10^3c_1/ mol dm^{-3}	10^3c_3/ mol dm^{-3}	10^4c_4/ mol dm^{-3}	10^4k_{obs}/ s^{-1}	M^{III}	10^3c_1/ mol dm^{-3}	10^3c_3/ mol dm^{-3}	10^4c_4/ mol dm^{-3}	10^4k_{obs}/ s^{-1}
La	5.42	4.90	15.1	3.29	Eu	5.02	0.98	7.78	11.36
	4.86	0.49	30.1	10.20		5.02	2.45	7.78	9.17
	4.86	0.98	30.1	9.42		5.02	4.90	7.78	6.24
	4.86	1.96	30.1	8.00		5.02	7.35	7.78	4.48
Ce	5.10	0.98	155.8	39.2	Gd	4.96	0.98	13.94	19.13
	5.10	7.35	155.8	19.8		4.96	2.45	13.94	16.10
	5.03	4.90	18.45	5.57		4.96	3.43	13.94	13.27
	5.03	9.80	18.45	3.32		4.96	5.83	13.94	9.23
Pr	7.40	0	21.77	13.14	Ho	5.08	1.96	9.80	15.24
	7.40	2.45	21.77	9.17		5.08	3.43	9.80	12.54
	7.40	4.90	21.77	7.12		5.08	7.35	9.80	7.87
	7.40	7.35	21.77	5.53		5.08	9.80	9.80	6.02
Nd	4.92	0.98	11.29	10.59	Er	5.79	1.96	6.36	10.30
	4.92	2.45	11.29	8.31		5.79	3.43	6.36	8.60
	4.92	4.90	11.29	5.89		5.79	4.90	6.36	7.33
	4.92	9.80	11.29	3.43		5.79	5.88	6.36	6.67
Sm	4.18	0.98	6.17	9.01	Yb	4.99	2.45	7.80	17.25
	4.18	1.96	6.17	7.44		4.99	4.90	7.80	12.57
	4.18	2.94	6.17	6.41		4.99	7.35	7.80	9.51
	4.18	3.92	6.17	5.62		4.99	9.80	7.80	7.00
						5.28	6.32	7.95	28.9

Table 3 Summary of stability constants, rate coefficients for decarboxylation and standard deviations for lanthanide oxalacetates at $I = 0.5$ mol dm^{-3}

M^{III}	$10^3\beta_{101}$/ dm^3 mol^{-1}	$10^6\beta_{102}$/ dm^6 mol^{-2}	10^3k_{ML}/ s^{-1}	$10^2k_{ML_2}$/ s^{-1}
La	1.28 ± 0.08	0	10.2 ± 0.2	0
Ce	1.62 ± 0.01	0.63 ± 0.01	13.8 ± 0.2	0
Pr	2.31 ± 0.18	2.94 ± 0.33	12.8 ± 0.6	2.4 ± 0.5
Nd	4.16 ± 0.02	5.27 ± 0.24	8.9 ± 0.1	3.0 ± 0.1
Sm	5.65 ± 0.15	25.7 ± 0.6	7.1 ± 0.6	1.9 ± 0.2
Eu	5.93 ± 0.39	31.7 ± 1.9	7.1 ± 0.3	2.4 ± 0.1
Gd	4.93 ± 0.13	23.7 ± 0.5	10.0 ± 1.2	2.9 ± 0.4
Ho	6.98 ± 0.41	21.5 ± 2.2	13.1 ± 0.1	3.0 ± 0.1
Er	10.7 ± 0.26	45.2 ± 0.6	9.6 ± 0.3	2.5 ± 0.1
Yb	28.3 ± 1.7	128.6 ± 7.8	4.3 ± 0.3	4.5 ± 0.1

while the kinetic data were derived from timed UV spectrophotometry.[4,5]

Results and Discussion

Some typical experimental data and resultant calculations are shown in Tables 1–3. The treatments are extensions of those described previously[5] for some transition-metal oxalacetates. Values of β_{10n} [equation (1), where c_1 is the total oxalacetate

$$\beta_{10n} = [ML_n]/([M][L]^n) \qquad n = 1 \text{ or } 2 \tag{1}$$

$$k_{obs}c_1 = k_0[H_2L] + k_1[HL] + k_2[L] + k_{ML}[ML] + k_{ML_2}[ML_2] \tag{2}$$

concentration] were calculated from e.m.f. data *via* linear least mean squares [equations (3) and (4)] after obtaining $\bar{n}$ and [L]

$$X = (2 - \bar{n})[L]/(1 - \bar{n}) \tag{3}$$

$$Y = \bar{n}/\{[L](1 - \bar{n})\} \tag{4}$$

as described previously.[5] In plots of x against y the 'intercept' gave β_{101} and the 'slope' gave β_{102}. Values of k_{ML} and of k_{ML_2} were likewise obtained by linear least mean squares from the kinetic data obtained by spectrophotometry *via* equations (5) and (6).

$$X' = (k_{obs}c_1 - k_0[H_2L] - k_1[HL] - k_2[L])/[ML] \tag{5}$$

$$Y' = [ML_2]/[ML] \tag{6}$$

To use these expressions one starts with $[ML] = 0$, $[ML_2] = 0$, $[HL]_s = 0$ (a temporary value of [HL]) and $[H]_1$ (a guessed temporary value of [H]) in equations (7)–(15)

$$[L] = (C - [H])/(2\beta_{021}[H]^2 + \beta_{011}[H]) \tag{7}$$

$$[HL] = \beta_{011}[H][L] \tag{8}$$

$$[H_2L] = \beta_{021}[H]^2[L] \tag{9}$$

$$[HL] = c_1 - [L] - [H_2L] - [ML] - 2[ML_2] \tag{10}$$

$$[ML] = \beta_{101}(c_4 - [ML_2])[L]/(1 + \beta_{101}[L]) \tag{11}$$

$$[ML_2] = \beta_{102}[L]^2(c_4 - [ML])/(1 + \beta_{102}[L]^2) \tag{12}$$

$$[H] = C - 2[H_2] - [HL] \tag{13}$$

$$[H] = ([H] + [H]_1)/2 \tag{14}$$

$$[HL]_s = [L] \tag{15}$$

together with $C = 2c_1 + c_3 - c_2$ where c_3 and c_2 refer to added concentrations of HCl and of NaOH, while c_4 is the total concentration of lanthanide salt, $M(ClO_4)_3$. Iteration is employed until the absolute value of $[HL]_s - [L]$ is $< 10^{-6}$ mol dm^{-3} with[5] $\beta_{011} = 5.40 \times 10^3$ dm^3 mol^{-1} and $\beta_{021} = 8.63 \times 10^5$ dm^6 mol^{-2}. A lower limit to $[HL]_s - [HL]$ has little effect upon the outcome.

The figures for β_{102} in Table 3 increase from La to Eu, decrease for Eu and Gd then increase from Ho to Yb. A somewhat similar pattern occurs for the β_{102} values except that those for Gd and Ho dip below the general trend. These patterns are similar to those found for a number of moderately strong lanthanide complexes such as those of glycolate[6] and acetate.[7] Such irregular patterns lie between those for weakly associating ligands such as sulphate* and those for strongly associating ligands such as ethylenediaminetetraacetate (edta).[9] The association constants of the sulphates from La to Yb are almost constant at ≈5000 mol dm^{-3} and so are the mobilities of the cations (≈70 for La to ≈65 mol dm^{-3} for Lu at 25 °C). This suggests that the complexing involves the hydrated forms of the cations. In contrast, the β_{101} values of the edta complexes are strongly related to the crystallographic radii of the cations. These decrease from La to Lu while β_{101} increases. There is a small decrease from linearity around the region of Gd. Several reasons for this dip have been proposed such as the electronic configurations of the 4f electrons and covalent contributions to the bonding. With moderately associating ligands such as glycolate[6] and the present one there are distinct dips at Gd while the general patterns, in terms of the above remarks, suggest that association involves partial penetration of the cation hydration shells.

With regard to the rate coefficients k_{ML} and k_{ML_2} (shown in Table 3), apart from La and Ce which have little or no tendency to form ML_2, k_{ML_2} is about twice k_{ML}. This appears to be the first time this feature has been found. There is a decrease in k_{ML} from Pr to Eu, whereas the β_{101} values increase. This trend also occurs with Gd. The lower β_{101} compared with that of Eu is marked by an increase in k_{ML}. In a similar vein the increase in β_{101} from Ho to Yb produces decreases in k_{ML}. Such trends are less apparent on comparing the β_{102} and k_{ML_2} values but there are small signs for example with the series Nd to Er. It is suggested that, although complexing between the lanthanides and oxalacetate strongly enhances the rate of decarboxylation, there are opposing factors. The rate of release of CO_2 is increased by weakening of the carboxylate bond but this is opposed by the stabilising process which causes metal–ligand bonding.

Experimental

Oxalacetic acid (Aldrich, 96%) was recrystallised as before.[5] Stock solutions of lanthanide chlorides were made from the oxides or chlorides (Aldrich) and analysed by gravimetric determinations of AgCl.

E.m.f. measurements to ±0.01 mV for the stability-constant calculations were made with a previously described[3] DVM system. An initial solution consisted of oxalacetic acid (c_1), NaOH (c_2), HCl (c_3) and $NaClO_4$ to $I = 0.5$ mol dm^{-3}. It was allowed to reach equilibrium at 25 °C. About 1 h was needed and the molar ratio of NaOH:oxalacetic acid was kept below 0.35:1 to keep drifts due to decarboxylation to <0.01 mV min^{-1}. An aliquot of stock MCl_3 was then added and the e.m.f. read at 1 min intervals. It took about 20 min before drifts due to decarboxylation became linear with time. The linear portion was then extrapolated to zero time.

UV measurements were made with the previously described[4] kinetic version of a Philips Analytical SP8-200 spectrophotometer.

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* Unpublished calculations based on conductance studies.[8]