Effects of Electrolytic Dissociation upon Rates of Reactions. Part 11.[1] Metal Ion Catalysed Rates of Aquation of Penta-ammineoxalatocobalt(III)

Pauzi B. Abdullah and Cecil B. Monk
Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, Dyfed SY23 1NE

Association constants (K_{ML}) of ion pairs formed between a series of divalent metal ions [including magnesium, and also lanthanum(III) ions] (M^{n+}) and the divalent anion (L^{2-}) of the complex penta-ammineoxalatocobalt(III) have been calculated from spectrophotometric u.v. absorbance measurements under virtually static conditions at 50 and 60 °C with ionic strength $I = 0.5$ mol dm^{-3}. Some of these constants have also been estimated from e.m.f. measurements of a glass electrode/calomel electrode cell under the same conditions. Rate coefficients of aquation ($k_{obs.}$) of the cobalt(III) species in the metal salt solutions at 60 °C and $I = 0.5$ mol dm^{-3} were determined from timed u.v. absorbance changes. From the $k_{obs.}$ and K_{ML} data, rate coefficients (k_3) of the metal-oxalato ion pairs were estimated. The figures for the transition metals of the first series (manganese, cobalt, nickel, copper, and zinc) and for magnesium indicate an approximate linear relationship between the K_{ML} and k_3 values; in terms of this, the k_3 values for cadmium, lead, and lanthanum are of a lower order. There is a broad similarity between these features and those reported by others for various metal ion catalysed reactions, such as the rates of decarboxylation of 3-oxoglutaric acid.

The aquation of penta-amminecarboxylatocobalt(III) ions is subject to catalysis by both hydrogen ions and many metal ions. Studies such as those of Dash and Nanda [2,3] show that ion pairing between unprotonated forms of the cobalt(III) species and metal ions can account for increased sensitivity to aquation, so the pK values of the protonated cobalt(III) ions are an important factor. This arises from a need to suppress the self hydrolysis of metal ions by using slightly acidic media. Thus with the dicarboxylato types the pK_{D1} (first dissociation constant) value of the monoprotonated oxalato form is about 2, so that useful concentrations of the unprotonated complex can be realised in dilute acidic solutions. This is not so with other known dicarboxylato complexes of cobalt(III), which have pK_{D1} values of about 4.[4]

Dash and Nanda [2] utilised this feature of the oxalato complex to make extensive studies of its metal ion catalysed rates of aquation and of the corresponding association equilibria of the metal–oxalato complex ion pairs (both by spectrophotometry). Their analysis of the kinetic data was based on the expression (i), where k_0 is the rate coefficient of aquation of the unprotonated complex, k_1 is that of the singly protonated complex, k'_2 is described as that of an activated complex formed between the singly protonated complex and the H$^+$ ion, k_3 is that of the metal ion–oxalato complex ion pair, K_{D1} is the dissociation constant of the hydrogenoxalato complex, K_{ML} is the association constant of the metal ion–oxalato (L^{2-}) ion pair, and [H$^+$] and [M^{n+}] represent concentrations of these two cations at zero time of reaction.

$$k_{obs.} = \frac{k_0K_{D1}/[H^+] + k_1 + k'_2[H^+] + k_3K_{ML}K_{D1}[M^{n+}]/[H^+]}{1 + K_{D1}/[H^+] + K_{D1}K_{ML}[M^{n+}]/[H^+]} \quad \text{(i)}$$

The expression (i) was treated as a two-parameter equation in k_3K_{ML} and K_{ML}. These were computed from linear plots of $1/(k_{obs.} - k'_{obs.})$ against $1/[M^{n+}]$. The term $k'_{obs.}$ refers to the value of $k_{obs.}$ when $[M^{n+}] = 0$. Nanda and Dash [3] also used $[M^{n+}] = [M^{n+}]_{total}$ and $[H^+] = [HClO_4] + [\text{complex}]$. The derived parameters were then refined by linear least mean squares analysis to get the minimum value of $k_{calc.} - k_{obs.}$.

Since K_{ML} and k_3 are interdependent, improved precision would result from independent assessments of K_{ML}, and in a later paper Nanda and Dash [3] did this by obtaining absorbance changes at a low enough temperature to provide almost static conditions. Some of their K_{ML} results, even allowing for temperature differences, are markedly different from those deduced from the kinetic data,[2] and there is some scatter among the K_{ML} values from different runs with the same metal ion.

We have therefore repeated some of the work, and have also extended it to other metal ions so that comparisons could be made with other metal ion catalysed reaction rates where general relationships between k_3 and K_{ML} or M^{n+} concentrations have been noted. Also on the practical side, we have used the more convenient method of measuring timed absorbance decreases to obtain $k_{obs.}$, whereas Nanda and Dash [3] transferred timed samples to cold acid, treated these samples with cation exchange resin, and titrated the freed oxalate in the filtrates from this with $KMnO_4$. In addition, estimates of some K_{ML} values and that of K_{A1} [the association constant of penta-ammine(hydrogenoxalato)cobalt(III)] have been derived from e.m.f. measurements of a cell containing glass and calomel electrodes.

Experimental

Penta-ammineoxalatocobalt(III) perchlorate was prepared by a published method.[1,5] Perchlorates of metal ions (including lithium for maintaining constant ionic strength) were made from the corresponding carbonates or oxides and perchloric acid. The concentrations (apart from the lithium perchlorate) were found by titrations with ethylenediaminetetra-acetate (edta);[6] those of the lithium stock solutions were determined by treatment with hydrogen ion exchange resin and titration with standard sodium hydroxide.

Spectrophotometric measurements were obtained with a Pye-Unicam SP 8-200 instrument fitted with temperature control and probe, programme control unit, and printer. For rate studies, readings were taken at 5—30 min intervals according to the speed of reaction. A 50 cm^3 sample of each solution was taken, and after the cells had been filled the rest was kept at 70—80 °C until the final readings were constant. This took account of any absorbance by the metal ions. The reference cells contained water.

The e.m.f. cell for obtaining pK_{A1} and pK_{ML} values can be represented as: glass electrode/$[Co(NH_3)_5(Hox)][ClO_4]_2$ (C_1),

Table 1. Example of the determination of the association constants of monoprotonated penta-ammineoxalatocobalt(III) from e.m.f. measurements; $I = 0.5$ mol dm^{-3}; $2.303RT/F$ at 50 °C = 0.064 116 V; correction to C_2 values to obtain constant $E°$(cell) was -64×10^{-5} mol dm^{-3}; $E°$(cell) $= -0.373\,54 \pm 0.000\,04$ V; $K_{A1} = 122 \pm 2$ dm^3 mol^{-1}

10^5C_1/ mol dm^{-3}	10^5C_2/ mol dm^{-3}	-10^5E(cell)/ V	$-10^5E°$(cell)/ V	K_{A1}
	196	18 887	37 349	
	287	20 356	37 358	
	374	21 272	37 356	
	457	21 928	37 352	
181	457	22 629		123
396	457	23 202		120
661	457	23 703		120
935	457	24 070		125

$HClO_4$ (C_2), $M(ClO_4)_n$ (C_3), $LiClO_4$ to $I = 0.5$ mol dm^{-3}/calomel electrode (ox = oxalate, n = 2 or 3).

The calomel electrode contained 0.1 mol dm^{-3} $KClO_4$ instead of a saturated solution, to prevent $KClO_4$ crystal formation at the calomel electrode liquid junction. The starting solution was 0.5 mol dm^{-3} $LiClO_4$ (200 cm^3) containing $HClO_4$ (*ca.* 0.005 mol dm^{-3}). E.m.f. measurements were made with a digital voltmeter system described elsewhere.[7,8] The ensuing procedures are described in the Results section.

Results and Discussion

Association Constants.—Cation association with the oxalato complex decreases u.v. absorbance at a specific wavelength. If such absorbances are measured before changes due to aquation occur, these decreases can be used to calculate the association constants of the ion pairs formed between the metal ions and penta-ammineoxalatocobalt(III).[3] We have used this method of calculation here, and the results are summarised in Table 1, together with those of Nanda and Dash [3] and those which Dash and Nanda [2] deduced from their kinetic studies. The two sets of results for nickel and copper given by these authors differ considerably. An examination of their 'static' figures for nickel(II) (for which they cite 139 dm^3 mol^{-1} at 28 °C) gives 75 ± 1 dm^3 mol^{-1} for the second of their two runs. This is in closer accord with 51.5 dm^3 mol^{-1} at 55 °C which they derived from kinetics, and with the answers obtained from the present work. On the other hand a wide difference between the K_{ML} value (148 dm^3 mol^{-1} at 55 °C) which they obtained from kinetic runs with copper(II) and their 'static' average of 473 dm^3 mol^{-1} at 28 °C is not resolved by inspection of their three runs carried out by the latter method. Our own work suggests that their figure from the kinetics is much too small.

As to the other metal ions we have used in common with the above authors, namely zinc(II), cobalt(II), and manganese(II), there is good general agreement in the results. Other sources of data are required for comparisons with our studies using lead(II), cadmium(II), lanthanum(III), and magnesium(II). These are referred to later.

E.m.f. measurements with our cell have given independent answers for K_{A1} [the association constant of penta-ammine(hydrogenoxalato)cobalt(III)] and for K_{ML} of the zinc(II), nickel(II), cobalt(II), and lead(II) ion pairs. To calculate K_{A1}, the expressions used were (ii)—(iv), in which C_1 and C_2 are stoicheiometric concentrations of the complex salt and perchloric acid, respectively, and x is the concentration of hydrogenoxalato complex.

$$E(\text{cell}) = E°(\text{cell}) - (RT/F)\ln[\text{H}^+] \qquad \text{(ii)}$$

$$K_{A1} = x/[(C_1 - x)(C_1 + C_2 - x)] \qquad \text{(iii)}$$

$$x = C_1 + C_2 - [\text{H}^+] \qquad \text{(iv)}$$

Values of $E°$(cell) were calculated from the e.m.f.s of dilute perchloric acid and lithium perchlorate ($I = 0.5$ mol dm^{-3}), using $[H^+] = C_2$ in equation (ii). Several additions of acid were made but the corresponding $E°$(cell) values changed systematically with increases in C_2. This is attributed to H^+ ion exchange and/or adsorption by the glass of the cell and electrodes. A similar feature was observed by Hills and Ives [9] in their work with the mercury(I) chloride electrode in the same acid concentrations as we used, namely 0.001—0.005 mol dm^{-3}. We found that by subtracting a small fixed concentration for the C_2 values of a particular run the average deviation in the $E°$(cell) values was reduced to a reasonable level.

After the last addition of perchloric acid, several successive amounts of complex were stirred into solution. From the e.m.f. values and the average $E°$(cell) value, $[H^+]$ was found from equation (ii), x from (iv), and hence K_{A1} from (iii). A sample run is shown in Table 1. The average K_{A1} values from several runs are 120 ± 2 dm^3 mol^{-1} at 50 °C, and 132 ± 4 at 60 °C (both at $I = 0.5$ mol dm^{-3}). These agree well [1] with 125 ± 5 from 'static' spectrophotometric shifts and 115 ± 5 from spectrophotometric studies of rates of aquation (both answers are for 60 °C and $I = 0.5$ mol dm^{-3}).

For a K_{ML} determination the initial solution consisted of complex (C_1) and perchloric acid (C_2) in 0.5 mol dm^{-3} lithium perchlorate. The values of E(cell) and K_{A1} were used to calculate x of equation (iii) (in its quadratic form) and hence $E°$(cell) was found by way of equations (ii) and (iv). Several successive additions of stock solution of metal perchlorate (concentration equivalent to $I = 0.5$ mol dm^{-3}) were made and the resulting E(cell) values yielded a set of K_{ML} figures. For this purpose equations (ii) and (iv) gave $[H^+]$ and x for applications in equations (v)—(viii).

$$[\text{Co(NH}_3)_5(\text{ox})^+] = x/([\text{H}^+]K_{A1}) \qquad \text{(v)}$$

$$[\text{Co(NH}_3)_5(\text{ox})^+, \text{M}^{n+}] = C_1 - x - [\text{Co(NH}_3)_5(\text{ox})^+] \qquad \text{(vi)}$$

$$[\text{M}^{n+}] = C_3 - [\text{Co(NH}_3)_5(\text{ox})^+, \text{M}^{n+}] \qquad \text{(vii)}$$

$$K_{ML} = [\text{Co(NH}_3)_5(\text{ox})^+, \text{M}^{n+}]/[\text{Co(NH}_3)_5(\text{ox})^+][\text{M}^{n+}] \qquad \text{(viii)}$$

The average K_{ML} values are shown in Table 2. They agree well with those obtained in the present work by the 'static' spectrophotometric method (Table 2).

Rate Coefficients.—Values of $k_{obs.}$ were calculated by means of the linear least mean squares method in which $Y = \ln(A_{obs.} - A_\infty)$ and X = time. The rate coefficients of aquation (k_3) of the $[Co(NH_3)_5(ox)]^+$, M^{n+} ion pairs were calculated from equation (ix) and the k_0, k_1, and k'_2 values given in a previous study.[1] The concentrations of the three complex species at zero time were found by use of equations (v)—(viii).

$$k_{obs.}C_1 = k_0[\text{Co(NH}_3)_5(\text{ox})^+] + k_1[\text{Co(NH}_3)_5(\text{Hox})^{2+}] + k'_2[\text{H}^+] + k_3[\text{Co(NH}_3)_5(\text{ox})^+, \text{M}^{n+}] \qquad \text{(ix)}$$

The values of K_{ML} and of k_3 for the first series of transition metal ions, as noted previously,[2] follow the Irving–Williams order [10] for the stability constants of many metal ion association complexes involving chelating ligands. A wider comparison which covers all the metal ions in the present work [except lead(II)] is provided by the figures of Prue [11] for the metal ion catalysed decarboxylation of 3-oxoglutarate.

Table 2. Association constants of ion pairs formed between metal(II) ions and penta-ammineoxalatocobalt(III) from measurements under almost static conditions; concentrations in mol dm^{-3}; $I = 0.5$ mol dm^{-3}

Metal ion	T/°C	10^4C_1	10^3C_2	10^2C_3	K_{ML}
	Spectrophotometry at 300 or 310 nm				
Zinc	50	4.82	4.83	0.45 to 4.50	46 ± 2
Zinc	60	4.82	4.86	0.45 to 4.50	49 ± 3
Nickel	50	4.56	4.33	0.79 to 9.83	66 ± 3
Nickel	60	4.65	4.23	0.49 to 3.70	65 ± 3
Cobalt	50	4.95	4.23	0.67 to 8.35	48 ± 3
Cobalt	60	4.69	4.86	2.00 to 6.68	38 ± 5
Manganese	50	4.82	4.23	0.86 to 6.45	14 ± 3
Manganese	60	4.82	4.23	0.86 to 10.76	14 ± 2
Copper	50	5.12	4.23	0.08 to 1.18	508 ± 6
Copper	60	4.65	4.23	0.06 to 0.60	380 ± 20
Lead	50	4.42	3.78	0.10 to 1.97	165 ± 17
Lead	60	4.95	4.12	0.99 to 7.46	129 ± 9
Cadmium	60	4.57	4.86	0.94 to 9.42	21 ± 4
Magnesium	60	6.25	4.73	3.40 to 13.60	6.1 ± 0.3
Lanthanum(III)	60	6.11	4.73	0.25 to 2.52	169 ± 9
	E.m.f. measurements				
Zinc	50	111.0	5.42	0.19 to 1.84	51 ± 3
Zinc	60	164.0	5.07	0.54 to 2.87	54 ± 1
Nickel	50	71.9	4.72	0.82 to 2.55	60 ± 3
Cobalt	60	164.0	2.54	0.19 to 1.92	35 ± 1
Manganese	50	100.3	4.72	1.56 to 3.50	11 ± 0.2
Lead	50	106.0	3.80	0.48 to 1.80	164 ± 5
Lead	60	165.0	5.07	0.48 to 1.80	132 ± 4
Cadmium	60	81.0	4.73	1.56 to 3.96	14 ± 0.5

Prue's version of the mechanism of decarboxylation in the presence of metal ions is as follows. 3-Oxoglutarate loses CO_2 in two stages. The first results from bond rearrangement and this leads to loss of CO_2 and formation of an enolate anion. If the activated complex (from which the second molecule of CO_2 is lost) closely resembles this anion it might be expected to form metal chelates with association constants similar to those of the corresponding malonates. Prue[11] obtained values of k_3 by application of equation (x), where

$$k_{obs.}C_1 = k_2[A^{2-}] + k_1[HA^-] + k_3[A^{2-}][M^{n+}] \quad \text{(x)}$$

A^{2-} represents 3-oxoglutarate and $[A^{2-}][M^{n+}]$ is proportional to [MA]. He showed that a plot of log k_3 against log K_{MA} (malonate chelates) is almost linear for the first series of transition metals together with magnesium and cadmium, while the point for lanthanum lies well below this plot. The present results (summarised in Table 4) give a similar picture. Our figures for cadmium and lead lie below the main line of a log k_3/log K_{ML} plot (the cadmium point in Prue's plot is also slightly low). This may arise from the relatively larger sizes of these two cations, resulting in slightly less weakening of the bond where aquation occurs. The low effect of lanthanum in both reactions may be related to the chelate or ion pair having a charge of +1 whereas the divalent metal series are electrically neutral.

Table 3. Metal(II) ion catalysed rates of penta-ammineoxalatocobalt(III) at 60 °C and $I = 0.5$ mol dm^{-3}; concentrations in mol dm^{-3}

10^4C_1	10^3C_2	10^3C_3	$10^6k_{obs.}$/s^{-1}	10^5k_3/s^{-1}
		Zinc		
4.43	10.80	43.9	8.55	1.4
4.43	10.80	65.8	10.15	1.5
4.43	10.80	87.7	10.95	1.5
25.9	22.00	87.7	10.30	1.7
		Nickel		
32.5	10.60	12.7	7.55	2.15
32.5	10.60	25.4	9.65	1.95
32.5	10.60	38.0	11.25	1.95
32.5	10.60	50.7	12.2	1.9
4.05	10.80	11.0	8.05	2.25
		Cobalt		
4.03	5.40	66.8	9.20	1.5
32.2	10.60	33.4	7.35	1.55
32.2	10.60	50.1	8.35	1.5
32.2	10.60	66.8	8.55	1.4
		Manganese		
28.2	7.56	50.0	5.85	1.2
28.2	7.56	65.0	6.20	1.2
28.2	7.56	75.0	6.55	1.25
28.2	7.56	90.0	6.75	1.2
		Copper		
38.4	10.80	21.1	86.5	10.2
38.4	10.80	30.2	92.0	10.4
38.4	10.80	45.3	98.5	10.5
32.2	21.20	21.1	70.0	9.8
32.2	21.20	30.2	79.0	9.9
		Lead		
29.6	7.56	39.5	13.9	1.85
29.6	7.56	59.2	15.9	1.95
11.53	5.67	9.85	8.05	1.9
11.53	5.67	68.1	16.4	1.95
		Cadmium		
24.6	7.56	50.0	5.35	0.85
24.6	7.56	65.0	5.60	0.85
24.6	7.56	75.0	5.80	0.90
24.6	7.56	90.0	6.25	0.90
		Magnesium		
9.95	4.73	42.4	4.08	0.65
9.95	4.73	84.8	4.73	0.62
9.95	4.73	106.0	5.06	0.71
9.95	4.73	127.0	5.42	0.79
		Lanthanum(III)		
10.53	4.73	2.52	5.80	1.25
10.53	4.73	5.03	7.48	1.4
10.53	4.73	7.51	8.42	1.45
10.53	4.73	10.05	8.95	1.4

An alternative view of the mechanism is that metal chelates are formed with 3-oxoglutarate and for an analogous reaction, the decarboxylation of oxalacetic acid which also loses carbon dioxide in two stages, Gelles *et al.*[12,13] attempted to distinguish between the possible forms of the activated complex generated in the presence of calcium, manganese, nickel, and copper(II) ions. The first possibility is that there is interaction between metal ion and oxalacetate before the first stage of decarboxylation, and the second is that the interaction is with the species left after this first stage. If the latter interaction is the one which actually occurs, it should be similar to that in metal oxalate complexes. Gelles *et al.* attempted to resolve the issue by determining the association constants K_{ML} and K_{MHL} of the metal ion oxalacetate chelates, and plotted the K_{ML} values and published figures for the corresponding oxalates against log k_3 values. The plot involving

Table 4. Average values of association constants of metal(II) ion–penta-ammineoxalatocobalt(III) ion pairs, and their rate coefficients of aquation

Metal ion	K_{ML}/dm^3 mol^{-1}	10^5k_3/s^{-1}
Zinc	50,[a] 39,[b] 64 [c]	1.5,[a] 0.71 [b]
Nickel	62,[a] 52,[b] 139,[c] 76 [d]	2.0,[a] 1.54 [b]
Cobalt	37,[a] 25,[b] 48 [c]	1.5,[a] 1.46 [b]
Manganese	12,[a] 4.6,[b] 15 [c]	1.2,[a] 0.46 [b]
Copper	380,[a] 148,[b] 473 [c]	10.2,[a] 8.38 [b]
Lead	130 [a]	1.9 [a]
Cadmium	18 [a]	0.9 [a]

[a] Present work at 60 °C, $I = 0.5$ mol dm^{3}. [b] Ref. 2, 55 °C, $I = 0.3$ mol dm^{-3}. [c] Ref. 3, 28 °C, $I = 0.3$ mol dm^{-3}. [d] Ref. 3, recalculated.

K_{ML} (oxalates) is approximately linear, while that involving K_{ML} (oxalacetates) shows that the reactivities of the nickel and copper(II) activated complexes are lower than expected from a linear free energy relationship.

However several factors render this interpretation uncertain. Thus the K_{ML} and K_{MHL} determinations of the oxalacetates were made at varying ionic strengths in order to establish the values at zero ionic strength, whereas the rate coefficients, $k_{obs.}$, were obtained in media of $I = 0.1$ mol dm^{-3}. Conversion of K_{ML} and K_{MHL} to $I = 0.1$ mol dm^{-3} involves significant activity coefficient expressions. The existence of K_{MHL} chelates and of enolic and ketonic forms, both of which can form chelates, also obscures a precise analysis. Later work by others,[14] particularly on metal–enzyme catalysis of the decarboxylation of oxalacetate, is considered to favour the view that activation arises from the formation of 1 : 1 M : oxalacetate chelates. This is in line with the generally held view that ion pair or chelate formation between metal ions and the original reactant(s) accounts for enhanced reaction rates. It is clearly desirable, as in the present work, to obtain independent assessments of the ion pairs or chelates formed by the reactants under conditions as close as possible to those used in obtaining the kinetic data.

Acknowledgements

We thank the S.E.R.C. for a grant (to C. B. M.) for the purchase of the spectrophotometer, and the National University of Malaysia for study leave and financial support (for P. B. A.).

References

1 Part 10, D. Smith, M. F. Amira, P. D. Abdullah, and C. B. Monk, *J. Chem. Soc., Dalton Trans.*, 1983, 337.
2 A. C. Dash and R. K. Nanda, *Inorg. Chem.*, 1974, **1**, 655.
3 R. K. Nanda and A. C. Dash, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1595.
4 A. C. Dash and R. K. Nanda, *J. Inorg. Nucl. Chem.*, 1976, **38**, 119.
5 J. C. Bailar, jun., *Inorg. Synth.*, 1953, **4**, 171.
6 ' Complexometry with EDTA and Related Reagents,' ed. T. S. West, B.D.H. Chemicals, Poole, 1969.
7 R. P. Henry, J. E. Prue, F. J. C. Rossotti, and R. J. Whewell, *Chem. Commun.*, 1971, 868.
8 C. B. Monk and M. F. Amira, *J. Chem. Soc., Faraday Trans. 1*, 1978, 1170.
9 G. J. Hills and D. J. G. Ives, *J. Chem. Soc.*, 1951, 318.
10 H. Irving and R. J. P. Williams, *Nature*, 1948, **162**, 746.
11 J. E. Prue, *J. Chem. Soc.*, 1952, 1331.
12 E. Gelles and R. W. Hay, *J. Chem. Soc.*, 1958, 3673.
13 E. Gelles and A. Salama, *J. Chem. Soc.*, 1958, 3683, 3689.
14 M. Birus and D. Leussing, *Inorg. Chem.*, 1982, **31**, 437.

Received 7th September 1982; *Paper* 2/1546