Inorganica Chimica Acta, *99* (1985) 207–216

Prediction of Stability Constants.
I. Protonation Constants of Carboxylates and Formation Constants of their Complexes with Class A Metal Ions

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Received August 7, 1984

Abstract

Methods recently developed for the estimation of stability and protonation constants of ligands for which no data currently exist are now applied to aliphatic organic mono-, di-, and tricarboxylic acids and their complexes with basic metal ions such as the alkali(I) and alkaline earth(II) metal ions, the lanthanide(III) ions, the actinide(III and IV) ions, and the dioxoactinide(VI) ions. The results consist of selected measured values, and estimated values, of the protonation and formation constants of 18 structural types of carboxylate ligands. Variations of stability constants with ionic strength are determined for various charge types, extending the data for potential application to environment systems, sea water, and biological fluids. The complexes of the alkali metal ions and of the alkaline earth ions showed variations in stability constants that are interpreted with the aid of ionic models of these complexes. The lanthanide complexes showed increases in stability constant increments through the first half of the series, followed by a change to a lower slope, and in some cases to a negative slope, at or just before gadolinium(III). Data currently available for the actinides are limited, but a few estimated constants are presented. More data are needed to establish definite trends.

Introduction

Of the 50,000 organic compounds manufactured in the U.S.A., toxicity data are available on less than one per cent, although most of them eventually find their way into the environment. The situation is further complicated by the fact that some of these compounds complex metal ions that are present in environmental systems, or added through contamination, and the toxicities of the complexes formed vary greatly with the nature of the metal ion and ligand. Further complications arise through the normal processes such as hydrolysis, air oxidation (via microbial and enzyme-catalyzed bio-oxidation, direct metal ion-catalyzed oxidation, and photocatalyzed oxidation) that convert organic pollutants to complexing agents for metal ions.

The mandatory first step in estimating toxicities of these complex environmental systems is to determine the distribution of metals among the large number of ligands present, a process that requires a knowledge of the stability constants involved. This requires in turn a critical evaluation of the literature on this subject to identify the reliable equilibrium data, and for the estimation (or experimental determination) of those that have not been measured previously. It is obvious that for the vast majority of complexes that may be formed (10^5–10^6) direct measurement is impossible and estimated values must be employed.

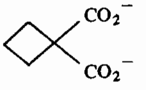
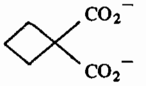
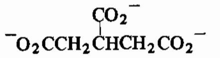
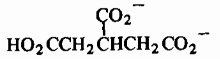
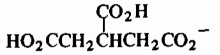
The theoretical and empirical methods of estimating stability constants, including the use of linear free energy relationships, have recently been reviewed and compared in some detail [1]. A viable procedure consisting of extrapolations and interpolations based on the most reliable data that are now available, has also been suggested [1].

Relatively complete, but non-critical compilations of stability constant data [2–4] have been produced over the past twenty five year period for organic and inorganic complexes formed in aqueous solution. More recently critically selected data [5] have become available thus providing constants that may be considered to provide a suitable base for the estimation of stability constants of complexes that have not yet been measured. For ligands where sufficient reliable data are available the observable trends may now be employed for the estimation of new constants, in accordance with previously recommended procedures [1].

This paper describes the first application of these estimation procedures to an important class of environmental organic compounds, the carboxylic acids. Carboxylates are the largest single class of complexing donor groups in the environment, and are present as the result of degradative processes involving naturally-occurring bioorganic substances. Carboxylates are also produced from organic pollu-

0020-1693/85/$3.30

TABLE I. Log Stability Constants for Class A Metal Ion Carboxylates at 25.0 °C and 0.10 M Ionic Strength. Values with [ ] are

	H^+	$Na^{+\,a}$	Be^{2+}		$Mg^{2+\,b}$	Sc^{3+}				Y^{3+}	
	Log K_1	Log K_1	Log K_1	Log β_2	Log K_1	Log K_1	Log β_2	Log β_3	Log β_4	Log K_1	Log β_2
HCO_2^-	3.6 ± 0.0[i]	[−0.4]	[1.3]	[2.2]	0.5	[1.8]	[3.1]			1.1	
RCO_2^-	4.7 ± 0.1	−0.4	1.6	2.4	0.6 ± 0.0	[3.2]	[5.3]			1.8 ± 0.1	3.2 – 0.1
$^-O_2CCO_2^-$	3.8 ± 0.0	0.5	4.0 ± 0.1	5.8 ± 0.2	2.7 ± 0.1	7.5	12.0	15.1	16.6	5.5	9.3
$^-O_2CCH_2CO_2^-$	5.3 ± 0.0	0.3	5.4 ± 0.1	9.0 ± 0.4	2.1	6.5	10.8	13.9		4.4	7.0
$^-O_2CCHRCO_2^-$	5.5 ± 0.1	[0.3]	[4.5]	[7.5]	1.7 – 0.1	[5.8]	[9.7]			[4.1]	[6.9]
	5.5 ± 0.0	[0.3]	[5.5]	[9.2]	2.1	[5.7]	[9.5]			[4.0]	[6.7]
$^-O_2CC(CH_3)_2CO_2^{-\,f}$	5.7 ± 0.0	[0.3]	[4.2]	[7.0]	1.6	[5.8]	[9.7]			[3.5]	[5.8]
	5.8 ± 0.0	[0.3]	[4.5]	[7.5]	[1.7]	[6.0]	[10.0]			[4.2]	[7.0]
$^-O_2CCR_2CO_2^{-\,g}$	7.1 ± 0.1	[0.3]	[4.7]	[7.8]	[1.8]	[6.2]	[10.3]			[4.4]	[7.3]
$^-O_2CCH_2CHRCO_2^-$	5.3 ± 0.1	−0.1	3.3 ± 0.2	4.9	1.2	[4.8]	[8.0]			3.1	4.9
$^-O_2C(CH_2)_nCO_2^-$	5.1 ± 0.1	[−0.1]	[2.9]	[4.8]	1.1	4.8	[8.0]			3.3	[5.5]
 $^-O_2CCH_2CH(CO_2^-)CH_2CO_2^-$	5.8 ± 0.0	[0.3]	4.3	[7.2]	2.1	[6.2]	[10.3]			[4.4]	[7.3]
$HO_2CCH_2CO_2^-$	2.6 ± 0.0	[−0.8]	[2.6]	[4.3]	1.0	[2.5]	[4.2]			[1.5]	[2.5]
$HO_2CCHRCO_2^{-\,h}$	2.9 ± 0.1	[−0.8]	[2.6]	[4.3]	1.0	[2.5]	[4.2]			[1.5]	[2.5]
$HO_2CCH_2CHRCO_2^-$	3.9 ± 0.1	[−0.6]	1.6	[2.7]	0.5	[2.5]	[4.2]			[1.5]	[2.5]
$HO_2C(CH_2)_nCO_2^-$	4.2 ± 0.1	[−0.4]	[1.6]	[2.7]	[0.6]	[2.5]	[4.2]			[1.5]	[2.5]
 $HO_2CCH_2CH(CO_2^-)CH_2CO_2^-$	4.5 ± 0.0	[0.1]	2.9	[4.6]	1.2	[4.2]	[7.0]			[2.9]	[4.8]
 $HO_2CCH_2CH(CO_2H)CH_2CO_2^-$	3.5 ± 0.0	[−0.2]	[2.1]	[3.5]	0.8	[2.5]	[4.2]			[1.5]	[2.5]

[a] Internal trends for alkali metal complexes are in Table III. [b] Internal trends for alkaline earth complexes are in Table IV. trends for hexavalent lanthanides are in Table VII. [f] Also including cyclohexane-1,1-dicarboxylic acid. [g] Also including cyclomethylmalonic acid. [i] The ±, + and – numbers with measured constants are not errors; they represent the existence of other

tants through biological and chemical oxidations of terminal groups of hydrocarbons or hydrocarbon derivatives. The selection of the various types of carboxylates for study is restricted to those for which some initial data are available, those that show very little difference in behavior are represented by a single parent ligand. Those that show differences in metal ion affinity as the result of the number and arrangement of carboxylate groups are considered separately. In all, stability constants for eighteen distinctly different carboxylate ligands have been compiled and/or estimated.

Because carboxylates are intermediate between type A and B donors, but are somewhat closer to the former, this first investigation involves the most basic or 'hard' type A metal ions, a category that includes alkali metals, the alkaline earths, the lanthanides, and the actinides.

Experimental

Critical Data Selection

Selected data used as a base for estimation purposes were taken from Critical Stability Constants, Volumes 1–5 [5], and from the data compiled thus far for volume 6 [6]. The carboxylate constants collected and evaluated for the latter are complete through the end of the calendar year 1982. The methods employed in the selection of critical data have been described [1], and may be found in the introductory chapters of the volumes cited in ref. 5.

Estimation Procedure

The procedure employed for the estimation of new stability constants has been described previously [1] and is given here only in outline form. The method involves the use of dependable measured estimated (see Text); R = Short Chain Alkyl except where indicated by Footnotes.

La^{3+} [c]		Am^{3+} [d]		Th^{4+}				NpO_2^+		UO_2^{2+} [e]		
Log K_1	Log β_2	Log K_1	Log β_2	Log K_1	Log β_2	Log β_3	Log β_4	Log K_1	Log β_2	log K_1	Log β_2	Log β_3
1.1		[1.4]	[2.3]	3.5	5.9	7.5		[0.8]		2.1 ± 0.0	3.3 ± 0.0	
1.9 – 0.1	2.9 ± 0.2	2.3 ± 0.0	3.8	4.3 ± 0.0	7.8 ± 0.2	10.2 ± 0.4	11.7 ± 0.5	[1.1]		2.7 – 0.1	4.9 ± 0.3	6.9 ± 0.6
4.7	7.8	5.3 ± 0.1	9.0 ± 0.2	8.9 ± 0.1	17.5	23.9		3.9	6.5	6.4 ± 0.0	10.9 ± 0.3	
3.7 ± 0.0	5.9 – 0.1	[4.3]	[7.2]	7.5	12.8	16.3		3.0		5.8 ± 0.0	9.9 ± 0.1	
3.5 – 0.1	5.8 ± 0.2	[3.9]	[6.5]	[6.7]	[11.2]			[3.4]		6.0	10.0	
3.4	5.5	[3.8]	[6.3]	[6.5]	[10.8]			[3.4]		[6.0]	[10.0]	
3.5	5.8	[3.9]	[6.5]	[6.7]	[11.2]			[3.4]		6.0	9.9	
[3.6]	[6.0]	[4.0]	[6.7]	[6.9]	[11.5]			[3.6]		[6.4]	[10.7]	
3.7 – 0.1	6.0 ± 0.0	[4.0]	[6.7]	[6.9]	[11.5]			[3.8]		6.8	11.5	
3.0	4.6	[3.6]	[6.0]	7.0	[11.7]			1.9		4.3 ± 0.0	[7.2]	
3.0	[5.0]	[3.6]	[6.0]	[7.0]	[11.7]			1.4		4.0 ± 0.1	[6.7]	
3.7	[6.2]	5.6	[9.3]	[7.1]	[11.8]			[3.1]		[5.6]	[9.3]	
1.5	[2.5]	[1.8]	[3.0]	[3.7]	[6.2]			[1.0]		[2.4]	[4.0]	
[1.5]	[2.5]	[1.8]	[3.0]	[3.7]	[6.2]			[1.0]		[2.4]	[4.0]	
1.5	2.7	[1.8]	[3.0]	3.9	7.1			[1.0]		2.4 ± 0.1	[4.0]	
[1.5]	[2.5]	[1.8]	[3.0]	[3.7]	[6.2]			0.9		2.3 ± 0.2	[3.8]	
2.5	[4.2]	5.0	[8.3]	[4.8]	[8.0]			[2.1]		[3.8]	[6.3]	
[1.5]	[2.5]	[1.8]	[3.0]	[3.7]	[6.2]			[1.0]		[2.4]	[4.0]	

[c] Internal trends for trivalent lanthanides are in Table V. [d] Internal trends for trivalent actinides are in Table VI. [e] Internal propane-1,1-dicarboxylic acid. [h] Also including monoprotonated cyclobutane-1,1-dicarboxylic acid and monoprotonated di-data in the literature, as in refs. [5] and [6].

constants as a base, and comparison of the measured constants available as a function of composition and structure, with allowance for differences in reaction conditions such as temperature and ionic strength. The selection of the new values is made only when constants for sufficiently similar complexes are available. The extrapolations are made in a linear fashion (*i.e.*, by the use of ratios of constants for stepwise structural or constitutional changes).

The broad range of metal ions involved in this study, together with the complications arising from considerable structural variations in the ligands, made it advisable to round off the log stability constants to one decimal point, and the more accurately known experimental values were therefore rounded off to one decimal point for consistency. A case may be made for keeping two significant figures in the log values for limited groups of complexes involving small structural variations but for the purpose of this research the single decimal in the log value seems more reasonable.

Conditions

The log stability constants must be expressed at uniform conditions of temperature and ionic strength in order to make valid comparisons between formation constants of complexes of various ligands. Although data have been reported at various ionic strengths and temperatures, the majority of the measurements have been made at 0.10 M ionic strength and 25.0 °C, and these conditions were therefore chosen for the primary comparisons made in this paper. Reliable constants measured at other temperatures were corrected to 25.0 °C by using ΔH° values for the complex under consideration, or, if not available, ΔH° values for similar com-

TABLE II. Variation of Stability Constants with Ionic Strength and Charge Relative to 0.1 M Ionic Strength.

Ionic strength		M^+					M^{2+}				
		0.0	0.5	1.0	2.0	3.0	0.0	0.5	1.0	2.0	3.0
L^-	$\log K_1$	+0.2	−0.1	−0.1	0.0	+0.2	+0.4	−0.2	−0.2	−0.1	0.0
	$\log \beta_2$	+0.3	−0.1	0.0	+0.3	+0.6	+0.6	−0.4	−0.4	−0.3	0.0
L^{2-}	$\log K_1$	+0.4	−0.2	−0.2	−0.1	0.0	+0.8	−0.4	−0.4	−0.4	[−0.3]
	$\log \beta_2$	+0.6	−0.4	−0.4	−0.3	0.0	+1.2	−0.8	−0.8	[−0.7]	[−0.5]
L^{3-}	$\log K_1$	+0.6	−0.3	−0.3	−0.3	−0.2	+1.2	−0.6	−0.6	[−0.7]	[−0.6]
	$\log \beta_2$	+1.0	−0.5	−0.5	[−0.4]	[−0.2]	+1.8	[−1.0]	[−1.0]	[−1.0]	[−0.9]

Ionic Strength		M^{3+}					M^{4+}				
		0.0	0.5	1.0	2.0	3.0	0.0	0.5	1.0	2.0	3.0
L^-	$\log K_1$	+0.6	−0.3	−0.3	−0.3	−0.2	[+0.8]	[−0.4]	[−0.4]	[−0.5]	[−0.4]
	$\log \beta_2$	+1.0	−0.5	−0.5	[−0.4]	[−0.2]	[+1.6]	[−0.6]	[−0.6]	[−0.6]	[−0.5]
L^{2-}	$\log K_1$	+1.2	−0.6	−0.6	[−0.7]	[−0.6]	[+1.6]	[−0.8]	[−0.8]	[−1.0]	[−0.9]
	$\log \beta_2$	+1.8	[−1.0]	[−1.0]	[−1.0]	[−0.9]	[+2.4]	[−1.4]	[−1.4]	[−1.5]	[−1.4]
L^{3-}	$\log K_1$	[+1.8]	[−0.9]	−0.9	[−1.1]	[−1.0]	[+0.4]	[−1.2]	[−1.2]	[−1.5]	[−1.4]
	$\log \beta_2$	[+2.6]	[−1.5]	[−1.5]	[−1.6]	[−1.5]	[+3.4]	[−2.0]	[−2.0]	[−2.2]	[−2.1]

plexes. Critical constants measured at other ionic strengths were corrected to 0.10 M by the use of variations of stability constants observed as a function of ionic strength for the same ionic types.

The methods of estimation of constants not measured are dependent on the initial observations of the measured constants, and the apparent trends observable from these constants. Therefore the precise comparisons made and their use in making estimates, are best explained below under Results and Discussion

Results and Discussion

The magnitudes of the logarithms of the stability constants of representative type A metal carboxylates are given in Table I. The values cited without brackets were taken from the critical stability constant compilations [5, 6], and references therein. The metal ions selected for presentation in Table I are the reference metals for a group or series of related metal ions, plus metal ions that are not part of a related series, because of their unique nature (Be^{2+}, Sc^{3+}, Y^{3+}, NpO_2^+), or because data on other members of the series are lacking (Th^{4+}).

The trends of stability constants with ionic strength observable from the Critical Stability Constant tables were found to be reasonably uniform when separated into carboxylate to metal ratios (1:1, 2:1) and charge of the metal ion (+1, +2, +3, and +4). The results obtained are summarized in Table II, and were employed in the determination of many of the estimated constants in Table I. The bracketed numbers in Table II are estimates of values expected from the trend observed as charges of metal ion or ligand are increased.

Estimation Methods for Various Types of Metal Ions

Estimates for missing log K_1 values based on measured values of those of Na^+, Mg^{2+}, La^{3+}, and UO_2^{2+} were made by considering the trends of measured values among similar ligands. Estimates for log K_1 of Be^{2+} were made from the more numerous Mg^{2+} values by using the observed ratio of log constants for Mg^{2+}/Be^{2+} of about 0.38 except for oxalic (0.68) and tricarballylic (0.49) acids which are perhaps able to chelate the larger Mg^{2+} more effectively. Log K_1 values for Sc^{3+} were estimated from La^{3+} values and the observed ratio of log constants La^{3+}/Sc^{3+} of about 0.60. The ions Y^{3+}, Am^{3+} and Th^{4+} were also estimated from the La^{3+} values for most of the carboxylates but in these cases the oxalate, malonate, and tricarballylic complexes appear to be more favorable to La^{3+}, relative to the other metal ions, than to the La^{3+} complexes of the other ligands. The observed ratios of the log values of La^{3+}/M^{n+} constants for oxalate, malonate, and tricarballylate are about 0.85 for Y^{3+}, 0.89 for Am^{3+}, and 0.52 for Th^{4+}. For monocarboxylates, succinates, and higher homologs the ratio is about 0.83 for Am^{3+} and 0.41 for Th^{4+}. With Y^{3+}, monocarboxylates appear to have a ratio of about 1.03 and for succinates and higher homologs a ratio of about 0.94.

TABLE III. Alkali Metal Carboxylate Internal Trends for Log K_1 Relative to those of Na^+.

	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
$RCO_2^{-\,a}$	+0.44	0.00				
$^-O_2CR'CO_2^{-\,b,\,c}$	[+0.1]	0.00	−0.10	[−0.2]	[−0.3]	+0.12

[a] R = short chain alkyl. [b] R′ = alkylene group containing a small number of carbon atoms. [c] Estimated values may also fit tri- and polycarboxylates.

Log K_1 values of NpO_2^+ were estimated from the UO_2^{2+} values using an observed ratio of log values of NpO_2^+/UO_2^{2+} of about 0.56 for oxalate, malonate, and tricarballylate complexes and about 0.40 for monocarboxylates, succinates, and higher homologs.

Log β_2 values were estimated from the corresponding log K_1 values. Almost all of the measured values have a log K_1/log β_2 ratio of 0.6 ± 0.1 and seem to be relatively independent of the metal ion and ligand involved.

Log K_1 values for monoprotonated oxalate, cyclopropane-1,1-dicarboxylate, and di-substituted malonates were not estimated because of the lack of reference values. The affinity for adding a second proton to these ligands is very small (log K_2^H = 1.1 ± 0.1 for oxalate, 1.6 ± 0.0 for cyclopropane-1,1-dicarboxylate, 1.9 ± 0.1 for di-substituted malonates), an indication that the stability constants with metal ions should also be very small and this interpretation is apparently confirmed by the general lack of data.

Protonation Trends

The affinities of alkylcarboxylic acids for protons indicated in Table I are relatively independent of the alkyl group and greater than that of formic acid because of the electron-releasing effect of the alkyl group [7]. The presence of a second carboxylate in the molecule increases its affinity for protons. As the separation in the ligand molecule of the second protonated carboxylate from the first one increases, the effect is reduced and then levels off when they are separated by three carbons (glutaric acid). The slightly higher affinity of glutaric acid and higher homologs compared to alkyl monocarboxylic acids is due to the statistical effect because of the presence of two associating groups rather than one.

The second carboxylate can apparently also exert a chelate effect involving the proton to give a bifurcated [8] hydrogen bond. The effect appears to be at a maximum with malonic acid. With substituted malonic acids the two carboxylates show increased affinity for the chelated proton, perhaps because of a change in the angle between the two carboxylates to give a more optimal distance for forming a bifurcated hydrogen bond [9]. A third carboxylate in the molecule gives a further increase in affinity of the chelated proton, perhaps indicating the presence of a tri-furcated hydrogen bond when the positioning is favorable, as in tricarballylic acid.

A protonated carboxylate exerts an electron withdrawing effect arising from the associated dipole which provides electrostatic stabilization of the negative charge of an intramolecular carboxylate anion thus resulting in the lowering of the affinity for a second proton. This effect is greater than that of a second unprotonated carboxylate.

Alkali Metal Trends

The few values available indicate that the affinity of sodium ion for carboxylates is relatively weak. In general, the values of log K_1 for monocarboxylates are very small, for oxalate and malonate somewhat larger, and for succinate in between these two levels. On this basis the formation of chelates involving the two carboxylate groups is suggested.

Trends among the alkali metal carboxylates are given in Table III. Only with monocarboxylate ligands is a value for Li^+ relative to Na^+ available. The other alkali metal ions would be expected to form weaker complexes than that of Na^+ because of their smaller charge/radius ratio. For the di- and poly-carboxylate ligands, only values for K^+ and NH_4^+ are available. The estimated values for the other alkali metal polycarboxylates in Table III are based on the trends observed for malic acid and citric acid.

Beryllium and Alkaline Earth Trends

Carboxylates of Be^{2+} have stability constants that are considerably larger than those of the alkaline earth ions because of the large charge/radius ratio. Carboxylate complexes of Be^{2+} and the alkaline earth ions show evidence of a contribution from a chelate effect in their stability constants, and of a further chelate effect when a third carboxylate group is present. With Be^{2+}, malonate shows a greater stability constant than oxalate but all larger alkaline earth ions show the reverse order.

Internal trends among the alkaline earth carboxylates, shown in Table IV appear to fall within five subgroups. Formate complexes show the least varia-

TABLE IV. Alkaline Earth Internal Trends. Log K_1 Relative to Mg^{2+}.

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Ra^{2+}
HCO_2^-	0.00	−0.03 ± 0.04	−0.07 ± 0.03	−0.08 ± 0.03	[−0.09]
$RCO_2^{-\,a}$	0.00	−0.03 ± 0.06	−0.11 ± 0.07	−0.20 ± 0.04	[−0.26]
$^-O_2CCO_2^-$	0.00	−0.36 ± 0.07	−0.79 ± 0.10	−1.02 ± 0.10	[−1.20]
$^-O_2CCH_2CO_2^{-\,b}$	0.00	−0.52 ± 0.08	−0.73 ± 0.08	−0.78 ± 0.10	[−0.81]
$^-O_2CCHRCO_2^{-\,c}$	0.00	−0.04 ± 0.04	−0.25 ± 0.06	−0.27 ± 0.04	[−0.29]

[a] Similar trends were observed with succinic acid and glutaric acid. [b] Similar trends were observed with cyclobutane-1,1-dicarboxylic acid. [c] Similar trends were observed with dimethylmalonic acid, monoprotonated oxalic acid, and monoprotonated malonic acid.

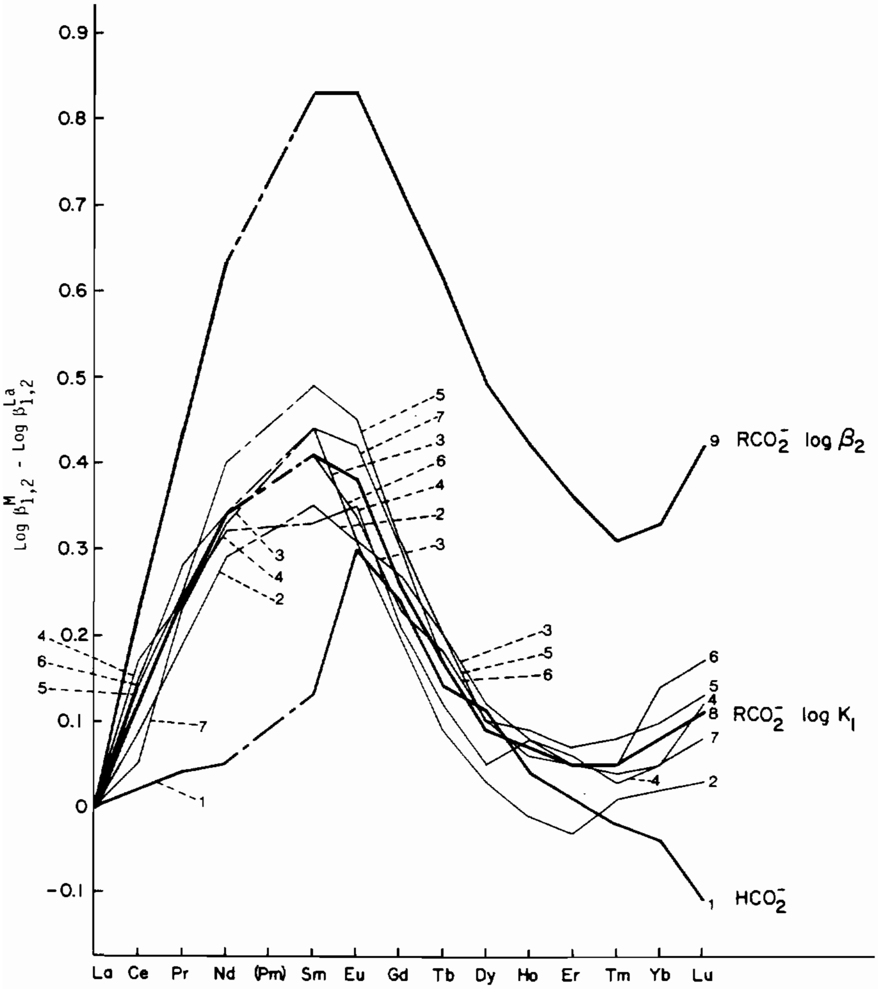


Fig. 1. Lanthanide mono-carboxylate trends. Log K_1 and log β_2 values relative to those of La^{3+} at the following temperatures and ionic strengths: 1, formic acid log K_1, 25.0 °C, 0.10 M; 2, acetic acid log K_1, 25.0 °C, 0.10 M; 3, acetic acid log K_1, 25.0 °C, 2.0 M; 4, propanoic acid log K_1, 20.0 °C, 0.10 M; 5, propanoic acid log K_1, 25.0 °C, 2.0 M; 6, isobutyric acid log K_1, 25.0 °C, 0.50 M; 7, isobutyric acid log K_1, 25.0 °C, 2.0 M; 8, average of 2–7; 9, average log β_2 for 2–7.

tion with the size of the metal ion. Oxalate chelates show the greatest variation with metal ion size while malonate chelates show the greatest relative preference for Mg^{2+} compared to the larger metal ions. This is not true, however, for alkyl substituted malonates, as indicated in the Table. Carboxylate binding constants of Ra^{2+} were estimated on the basis of trends observed for the other alkaline earths.

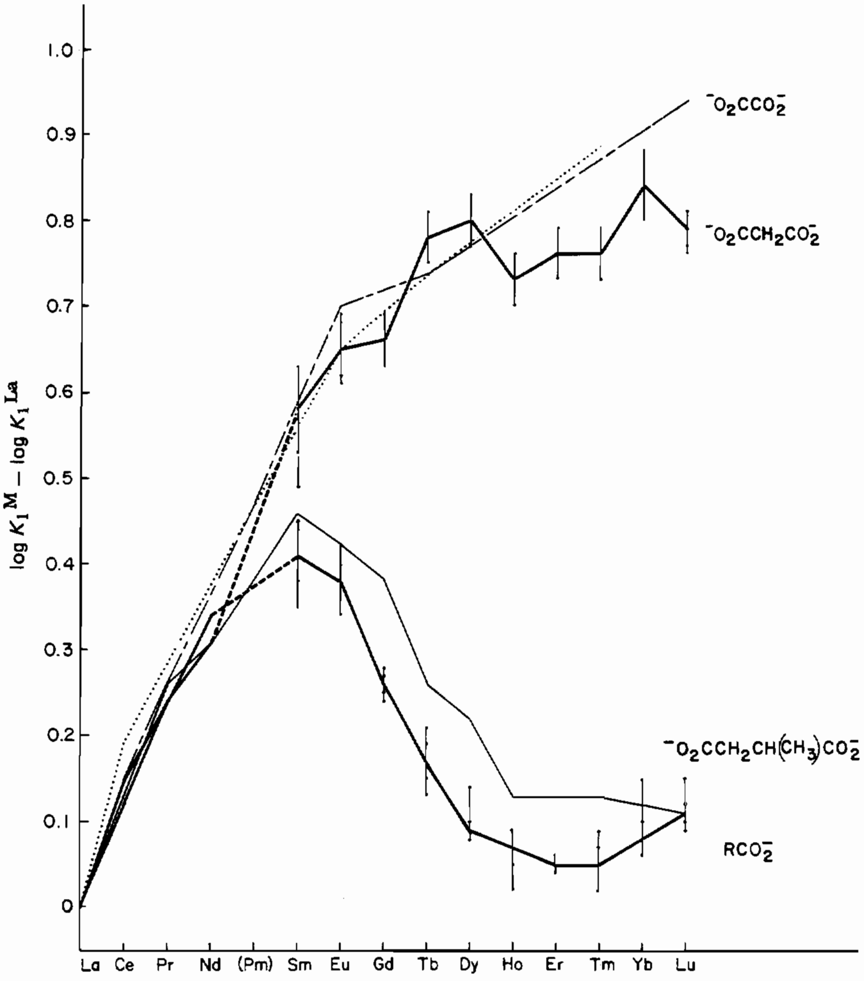


Fig. 2. Lanthanide di-carboxylate trends. Values of log K_1 relative to those of La^{3+} with average and maximum deviations of individual differences between that lanthanide and the preceeding lanthanide; ·····, – – –, two partial sets of oxalate data; ——, average of malonate and substituted malonate constants; ——, methyl succinate constants; ——, average of mono-carboxylates for comparison.

Scandium, Yttrium, and Lanthanide Trends

Stability constants for Sc^{3+}, Y^{3+}, and La^{3+} carboxylates show a decrease in magnitude as the ionic radius of the metal ion increases. The internal trends of the lanthanide carboxylates relative to those of La^{3+} are shown in Table V. In general, the magnitudes increase to about Eu^{3+} and Gd^{3+} and then change with variable increments through the heavier lanthanides. When the stability constants relative to that of La^{3+} are plotted *vs.* atomic number, the resulting line connecting the mono-carboxylates and the succinates of the heavier lanthanides have a negative slope. The oxalates, malonates, and substituted malonates have a positive but decreased slope through the heavier lanthanides. The change in slope near Gd^{3+} is a reflection of the so-called 'gadolinium break' which is well known [10, 11].

With formic acid the internal trend of lanthanide complexes is based on only one set of data and may be modified somewhat when the stabilities of these complexes are measured by another research group. Log β_2 values were also reported but the trend is highly irregular and completely different from that observed with other lanthanide carboxylates. They probably contain relatively large errors and are not considered reliable enough. The log K_1 values of the formates, shown in Fig. 1, increase slowly with increase in atomic number to samarium(III) and then rapidly to a maximum at europium(III). Then, beginning with Gd(III), there is a steady decrease through the rest of the series.

Lanthanide internal trends with alkyl mono-carboxylic acids are based on six sets of data with acetic acid, propanoic acid, and 2-methylpropanoic acid but should apply to any alkyl mono-carboxylic acid, to mono-protonated dicarboxylic acids, to di-protonated tricarboxylic acids, and to glutaric acid and longer chain dicarboxylic acids. The indi-

TABLE V. Lanthanide Internal Trends Relative to La^{3+}.

		La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}
HCO_2^-	Log K_1	0.00	+0.02	+0.04	+0.05	[+0.07]	+0.13
RCO_2^{-} [a]	Log K_1	0.00	+0.12 ± 0.04	+0.25 ± 0.03	+0.33 ± 0.04	[+0.40]	+0.45 ± 0.04
	Log β_2	0.00	+0.24 ± 0.03	+0.39 ± 0.06	+0.60 ± 0.07	[+0.72]	+0.79 ± 0.03
	Log β_3	0.00	+0.15 ± 0.00	+0.29	+0.52	[+0.75]	+0.86
$^-O_2CCO_2^-$	Log K_1	0.00	[+0.15]^c + 0.04	[+0,24]	[+0.31]	+0.47	[+0.58]
	Log β_2	0.00	+0.43	[+0.57]	[+0.71]	+0.95	[+1.08]
	Log β_3*		0.00*				
	Log β_4		0.00*				
$^-O_2CCH_2CO_2^-$	Log K_1	0.00	+0.16 ± 0.03	+0.24 ± 0.03	+0.29 ± 0.03	[+0.45]	+0.55 ± 0.05
	Log β_2	0.00	+0.27	+0.40	+0.51	[+0.79]	+0.94 ± 0.01
$^-O_2CCHRCO_2^-$	Log K_1	0.00	+0.12 – 0.01	+0.25 ± 0.04	+0.30 ± 0.04	[+0.45]	+0.56 ± 0.02
	Log β_2	0.00	+0.26 ± 0.02	+0.46 ± 0.05	+0.52 ± 0.04	[+0.76]	+0.88
$^-O_2CC(CH_3)_2CO_2^{-}$ [b]	Log K_1	0.00	+0.12 ± 0.03	+0.27 ± 0.04	+0.34 ± 0.03	[+0.43]	+0.52 ± 0.03
	Log β_2	0.00	+0.23	+0.44 ± 0.02	+0.47 – 0.01	[+0.58]	+0.66 ± 0.06
$^-O_2CCR_2CO_2^-$	Log K_1	0.00	+0.17	+0.33 ± 0.03	+0.40 ± 0.00	[+0.57]	+0.74 ± 0.02
	Log β_2	0.00	+0.5 ± 0.1	+0.7 ± 0.2	+0.9 ± 0.2	[+1.0]	+1.1 ± 0.2
$^-O_2CCH_2CHRCO_2^-$	Log K_1	0.00	[+0.13]	[+0.24]^c + 0.02	[+0.33]^c – 0.02	[+0.40]	[+0.45]^c + 0.01
	Log β_2	0.00	[+0.16]	+0.30	+0.42	[+0.46]	+0.46

*Relative to Ce^{3+}. [a] Probably includes mono-protonated dicarboxylic acids and glutaric acid and higher homologs. [b] Also measured values.

vidual log K_1 values relative to those of lanthanum(III) are shown in Fig. 1 along with the average values. There is a steady increase in value with atomic number to samarium, then a steady decrease to thulium(III), followed by a small increase to lutetium(III). For log β_2 values, the average values, also shown in Fig. 1, show a similar trend, except that the maximum is between samarium(III) and europium(III). Log K_2 (log β_2 – log K_1) have a similar trend except that there is a broad maximum from promethium(III) to terbium(III), centered at europium(III). Log β_3 values increase with atomic number to a maximum at europium(III) and then decrease. Log K_3 values (log β_3 – log β_2) appear to decrease to praseodymium(III) and then increase to a broad maximum from dysprosium(III) to ytterbium(III), which is centered at europium(III). Log β_4 values were also reported but these show trends that are 0.1 higher but parallel to those observed for log β_3 within experimental error and are not included.

Lanthanide oxalate values are available in two partial sets of data which show only overall trends. Log K_1 values show a steady increase to europium(III) and then a lesser increase through the rest of the series. The trend in log β_2 appears to be similar to that of log K_1. The very few log β_3 values seem to show a steady increase throughout the series, while log β_4 values seem to show a maximum, which is near gadolinium(III).

The lanthanide malonate values are based on three sets of data and the average relative log K_1 values are shown in Fig. 2. The trend relative to lanthanum(III) is similar to that of the oxalates. The malonate and substituted-malonate trends appear to be composed of two segments with decreased slope for the heavier lanthanides. It is interesting to note the small discontinuity at Tb(III) and Dy(III) which is similar to the 'tetrad' effect reported by others [11–13]. With the data presently available the effect seems to be greater than experimental error.

The substituted malonates show trends similar to those of the parent malonate anion, but with lesser or greater increases in magnitude as the atomic number increases. Complexes of dimethylmalonate, cyclobutane-1,1-dicarboxylate, and cyclopentane-1,1-dicarboxylate are very similar in their trends relative to lanthanum and show the smallest increments through the series. The increases become larger with the unsubstituted malonates, increases somewhat more with the mono-substituted malonates, and then still larger increases are observed for the dialkyl-substituted malonates. These trends probably apply to all alkyl-substituted ligands in which two carboxylates are bound to the same carbon atom.

The lanthanide succinate trend is based on only one set of data for methyl succinate and may be somewhat modified when other substituted succinate data become available. This trend should

Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
+0.30	+0.24	+0.14	+0.11	+0.04	+0.01	−0.02	−0.04	−0.11
+0.43 ± 0.02	+0.29 ± 0.02	+0.20 ± 0.04	+0.10 ± 0.02	+0.07 ± 0.02	+0.05 ± 0.02	+0.04 ± 0.04	+0.07 ± 0.03	+0.11 ± 0.03
+0.84 ± 0.02	+0.69 ± 0.06	+0.65 ± 0.03	+0.52 ± 0.03	+0.40 ± 0.03	+0.30 ± 0.07	+0.22 ± 0.02	+0.33 ± 0.05	+0.33 ± 0.03
[+0.89]	+0.73 – 0.01	+0.84 ± 0.02	+0.79 ± 0.02	+0.76 ± 0.02	+0.68 – 0.01	+0.64	+0.60 ± 0.02	+0.49
+0.68 ± 0.03	[+0.71]	+0.74 ± 0.00	[+0.77]	[+0.81]	[+0.84]	[+0.88][c] + 0.01	[+0.91]	+0.95
+1.21 + 0.01	[+1.31]	+1.40 ± 0.03	[+1.48]	[+1.56]	[+1.63]	+1.67	[+1.67]	+1.60
+1.15*		+1.55*						+2.44*
+1.34*		+2.66*						+0.99*
+0.65 ± 0.04	+0.66 ± 0.03	+0.78 ± 0.03	+0.80 ± 0.03	+0.73 ± 0.03	+0.76 ± 0.03	+0.76 ± 0.03	+0.84 ± 0.04	+0.79 ± 0.03
+1.10 – 0.01	+1.11 ± 0.05	+1.24 ± 0.01	+1.25 ± 0.05	+1.15 ± 0.08	+1.20 ± 0.07	+1.25 ± 0.03	+1.33 ± 0.04	+1.26 ± 0.03
+0.67 + 0.01	+0.69 ± 0.01	+0.81 ± 0.02	+0.86 ± 0.02	+0.83 ± 0.02	+0.82 ± 0.02	+0.83 ± 0.02	+0.85 ± 0.03	+0.80 ± 0.02
+0.97 ± 0.00	+0.94 ± 0.06	+1.12 ± 0.04	+1.18 ± 0.08	+1.10 ± 0.08	+1.10 ± 0.04	+1.12 ± 0.03	+1.20 ± 0.06	+1.15 ± 0.08
+0.60 ± 0.02	+0.61 ± 0.01	+0.70 ± 0.02	+0.72 ± 0.02	+0.68 ± 0.01	+0.67 ± 0.02	+0.68 ± 0.02	+0.70 ± 0.02	+0.66 ± 0.03
+0.68 ± 0.04	+0.65 ± 0.06	+0.81 ± 0.04	+0.83 ± 0.03	+0.76 ± 0.03	+0.79 ± 0.04	+0.84 ± 0.03	+0.90 ± 0.04	+0.86 ± 0.07
+0.87 ± 0.03	+0.89 ± 0.03	+1.04 ± 0.03	+1.10 ± 0.02	+1.04 ± 0.02	+1.06 ± 0.01	+1.08 ± 0.02	+1.14 ± 0.01	+1.10 ± 0.02
+1.2 ± 0.2	+1.18 ± 0.09	+1.37 ± 0.08	+1.39 ± 0.05	+1.25 ± 0.04	+1.38 ± 0.07	+1.36 ± 0.00	+1.51 ± 0.03	+1.48 ± 0.03
+0.42	+0.38	+0.26	+0.22	+0.13	+0.13	+0.13	+0.12	+0.11
+0.43	+0.53	+0.46	+0.54	+0.50	+0.56	+0.55	+0.57	+0.53

including cyclobutane-1,1-dicarboxylic and cyclopentane-1,1-dicarboxylic acid. [c]Estimated constants considered better than

TABLE VI. Trivalent Actinide Internal Trends Relative to Am^{3+}.

		Ac^{3+}	Pu^{3+}	Am^{3+}	Cm^{3+}	Bk^{3+}	Cf^{3+}
HCO_2^-	$\log K_1$		+0.4	0.00			
RCO_2^-	$\log K_1$		+0.4 ± 0.2	0.00	+0.07 ± 0.00	+0.10	+0.15
	$\log \beta_2$			0.00	−0.19		
$^-O_2CCO_2^-$	$\log K_1$	−1.0 ± 0.1		0.00	0.00	+0.20	+0.25
	$\log \beta_2$	−2.0 ± 0.2		0.00	0.00	+0.29	+0.52

approximate that of all alkyl-substituted dicarboxylate ligands with carboxylic acids bonded to two adjacent carbon atoms. Log K_1 values show a trend similar to that of alkyl mono-carboxylic acids but with greater stability for gadolinium(III) through thulium(III) relative to lanthanum(III). The expected 'gadolinium(III)break' is anticipated here by europium(III), but the largest drop in stability does seem to begin with gadolinium(III). Log β_2 values increase to samarium(III) and then remain approximately constant as atomic number is increased. Log K_2 values (log β_2 − log K_1) remain approximately constant up to europium(III) and then increase to a maximum between erbium(III) and thulium(III).

Trivalent Actinide Trends

The magnitudes of the logarithms of the stability constants of the carboxylate complexes of Am(III) show evidence for chelation when a second or third carboxylate group is present in the ligand (Table I).

Internal trends for the log stability constants of trivalent actinide carboxylates relative to those of Am(III) are shown in Table VI. Stability constants increase from Am^{3+} to the heavier metal ions and also increase to Pu^{3+} and decrease to Ac^{3+}.

Hexavalent Dioxo Actinide Trends

Carboxylate constants of UO_2^{2+} show a trend similar to those of the carboxylates of La^{3+}, except for the existence of a stronger chelate effect with the oxalate and malonate complexes. The internal trends for the hexavalent actinide carboxylates are shown in Table VII. The stability constants decrease from UO_2^{2+} through the heavier metal ion complexes.

TABLE VII. Hexavalent Dioxoactinide Internal Trends of Carboxylate Stability Constants Relative to those of UO_2^{2+}.

		UO_2^{2+}	NpO_2^{2+}	PuO_2^{2+}
RCO_2^-	log K_1	0.00	−0.10 ± 0.03	−0.30 + 0.01
	log β_2	0.00	−0.20 ± 0.02	−1.0 ± 0.1
	log β_3	0.00	−0.4	−1.4
$^-O_2CCO_2^-$	log β_2	0.00	[−0.4]	−1.2
$^-O_2CCH_2CH_2CO_2^-$	log K_1	0.00	[−0.1]	−0.26

Conclusions

In addition to providing an expanded data base for the calculation of metal carboxylate concentrations in aqueous solution, this study shows that stability constants for unmeasured complexes may be estimated systematically from measured values to about a tenth of a log unit. Such estimated values should have sufficient accuracy for most studies involving the modeling of environmental or physiological systems. If greater accuracy is necessary, it would be possible to effect improvement of the treatment given above by making special limited estimates based on correlations within groups of similar complexes, provided the required values of a sufficient number of reference complexes are available.

Acknowledgement

This research was supported by grant No. ES02971 from The National Institute of Environmental Health Sciences, U.S. Public Health Service.

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