

Stability Constants of the Complexes of Al(III), Ga(III), In(III), Fe(III) & Cr(III) with Malonic & Substituted Malonic Acids

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The formation constants of Al(III), Ga(III), In(III), Fe(III) and Cr(III) complexes with malonic, methylmalonic, *n*-butylmalonic, phenylmalonic and bromomalonic acids have been determined. The stability constants of ($\log \beta_3$) group IIIA metal complexes with most of the dicarboxylic acids follow the order Ga(III) > Al(III) > In(III), which is also followed by Z_{eff}/r^2 values of these metal ions. Among the Fe(III) and Cr(III) complexes, the stability constants of the former have been found to be greater. For a particular metal ion, the gradation in the stability constants of its complexes derived from the acids is methyl > *n*-butyl > phenyl > malonic > bromo, which is also the decreasing order of first dissociation constants (pK_1) of the acids.

THE sustained interest in the study of the oxalato complexes of metal ions in solutions is consequence of their being used as model systems in the investigation on structure, stability, liability and other aspects of coordination compounds¹. As a result, stability constants of various oxalato complexes have been determined². Compared to the oxalato complexes, however, much less informations are available regarding stability constants of malonato complexes. The dissociation constants of Al(III) and Ga(III) malonates were determined by Dutt and Bose³ by acid hydrolysis of the corresponding tris malonates and that of Fe(III) malonato complex was determined polarographically by Schaap *et al.*⁴. However, these authors failed to determine the stepwise formation constants. In malonic acid, since the methylene hydrogen atoms can be suitably substituted by electron donating or electron withdrawing groups, it was thought of interest to undertake a systematic study on the solution chemistry of their metal complexes. In this paper we wish to report the formation constants of Al(III), Ga(III), In(III), Fe(III) and Cr(III) complexes with malonic, methylmalonic, *n*-butylmalonic, phenylmalonic and bromomalonic acids.

Materials and Methods

Sodium perchlorate, perchloric acid, sodium hydroxide and other chemicals used were of reagent grade. Malonic acid (BDH grade) was recrystallized twice from water and dried at 105°, m.p. 135° (lit. m.p. 136°). The perchlorates of aluminium, gallium, iron and chromium were prepared by digestion of the corresponding freshly prepared hydroxides with dil. perchloric acid. These were filtered and the filtrates appropriately diluted with doubly distilled water. The concentrations of Al(III), Ga(III) and In(III) were determined gravimetrically as their oxinates and those of Cr(III) and Fe(III) were deter-

mined by standard volumetric procedures. Excess perchloric acid in the stock solutions was determined by passing an aliquot of the solution through Amberlite IR-120 (H⁺) and titrating the total acid liberated. The results were checked by comparing with the pH of the stock solutions.

Ethyl methylmalonate (b.p. 196-98°/750 mm) was prepared⁵ by heating (at 130-150°) oxalopropionic ester which in turn was obtained by refluxing a mixture of ethyl propionate, diethyl oxalate and sodium ethoxide.

Ethyl-*n*-butylmalonate was prepared by refluxing sodium ethoxide with *n*-butylbromide and diethyl malonate. The fraction boiling between 130-35°/20 mm was collected.

Ethyl phenylmalonate (b.p. 158-62°/10 mm) was obtained⁷ by heating (at 175°/15 mm) phenyl oxaloacetic ester.

Ethyl bromomalonate was prepared⁸ by the photochemical reaction of bromine with diethyl malonate in carbon tetrachloride. The product boiling in the range 120-25°/15 mm was used.

Sodium salts of the acids were obtained by alkaline hydrolysis of the above esters. An ethanolic solution of the ester was refluxed with calculated amount of sodium hydroxide in ethanol. The sodium salt separated was filtered and made free from alkali by repeated washing with ethanol. It was then dissolved in a minimum amount of water and reprecipitated by adding a large excess of ethanol. The purity of sodium salts was checked by chemical analyses.

Titration — The pH titrations were carried out at 30° ± 0.2° and $\mu = 0.1M$ (NaClO₄) on a Cambridge (Bench type) pH-meter having glass-calomel electrode assembly. The dissociation constants of malonic acid were determined by titrating its aq. solution against standard carbonate-free NaOH. In the case of substituted malonic acids which were in the form of their sodium salts, the titrations were performed against a standard solution of perchloric

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acid. For determining the formation constants of metal complexes, the general procedure consisted in titrating a 50 ml aq. solution having [metal ion] = $\sim 1 \times 10^{-3}M$, known volume of added perchloric acid and excess of ligand against standard NaOH solution. In several cases it was not possible to obtain sufficient number of \bar{n} values to determine each successive formation constants through a single titration. In such cases, experiments were performed using different metal-ligand ratios (1:2 to 1:10) and varying the added [perchloric acid] from 10^{-2} to $10^{-3}M$. In the case of Cr(III) systems, due to slow reaction kinetics, a series of similarly prepared solutions with gradually increased amount of NaOH were kept overnight, and pH of the solutions measured the following day. Preliminary experiments revealed that equilibria were established in less than 16 hr.

Computation of the formation constants—The formation constants were determined by Schröder's method⁹ using the sets of \bar{n} and $[A]$ values where $[A]$ refers to free [ligand] in the anionic form. In the case where ligand was used in the acid form (*viz.* malonic acid) expressions (1) and (2) were used for \bar{n} and $[A]$ respectively.

$$\bar{n} = \frac{1}{C_M} \left[C_A - (2C_A + E - C_B - [H^+]) \times \frac{[H^+]^2 + K_1^a[H^+] + K_1^a K_2^a}{2[H^+]^2 + K_1^a[H^+]} \right] \quad \dots(1)$$

$$[A] = (2C_A + E - C_B - [H^+]) \times \frac{K_1^a K_2^a}{2[H^+]^2 + K_1^a[H^+]} \quad \dots(2)$$

When the sodium salts of substituted malonic acids were used, it was borne in mind that two equivalents of perchloric acid were required to liberate the corresponding dicarboxylic acid.

Thus expressions (1) and (2) were modified to give Eqs. (3) and (4) respectively.

$$\bar{n} = \frac{1}{C_M} \left[C_A - (E - C_B - [H^+]) \times \frac{[H^+]^2 + K_1^a[H^+] + K_1^a K_2^a}{2[H^+]^2 + K_1^a[H^+]} \right] \quad \dots(3)$$

$$[A] = (E - C_B - [H^+]) \times \frac{K_1^a K_2^a}{2[H^+]^2 + K_1^a[H^+]} \quad \dots(4)$$

where C_A stands for total [ligand], E is the concentration of perchloric acid present in the solution, C_B is the concentration of alkali added and K_1^a and K_2^a are the first and second acid dissociation constants of the ligand.

In Eqs. (1-4), the contribution due to $[OH^-]$ was neglected, since formation of the complexes is completed at $pH < 7$. Preliminary experiments established that equilibria involving polynuclear complex formation can be neglected.

The generalized expression (5) for the formation function may be utilized to obtain determinants⁹ which may be alternatively expressed by the linear forms (Eqs. 6-9 for systems where $N = 3$).

$$\sum_{n=0}^N (\bar{n} - n)[A]^n \beta_n = 0 \quad \dots(5)$$

$$D_0 = A_1 A_2^2 A_3^3 + 3A_1 A_2^2 A_3^2 - 27A_1^2 A_3^2 A_3 + 3A_1^2 A_2 A_3^3 + 5A_1^3 A_2 A_3^2 + 15A_1^3 A_2^2 A_3 \quad \dots(6)$$

$$D_1 = A_2^2 A_3^3 + 3A_2^2 A_3^2 + 45A_1^2 A_3^3 - 15A_1^3 A_3^2 - 25A_1^3 A_2^2 \quad \dots(7)$$

$$D_2 = 3A_1 A_3^3 - 15A_1 A_2^3 - 9A_2^3 A_3 + A_2 A_3^3 + 45A_1^3 A_3 - 25A_1^3 A_2 \quad \dots(8)$$

$$D_3 = 5A_1 A_2^2 + 3A_1 A_3^2 - 27A_1^2 A_3 + 15A_1^2 A_2 + A_2 A_3^2 + 3A_2^2 A_3 \quad \dots(9)$$

where $A_1 = [A]_{n=1/2}^-$; $A_2 = [A]_{n=3/2}^-$; and $A_3 = [A]_{n=5/2}^-$.

The stepwise stability constants were determined from relation (10).

$$K_i = D_i / D_{i-1} \quad \dots(10)$$

Results and Discussion

The acid dissociation constants (K_1^a and K_2^a) of the dicarboxylic acids, *viz.* malonic(I), methylmalonic(II), *n*-butylmalonic(III), phenylmalonic(IV) and bromomalonic(V) acids, are given in Table 1. The acids distinctly fall into two categories: (a) containing electron-donating substituents such as II and III, and (b) containing electron-withdrawing substituents such as IV and V. The acids (II) and (III) are weaker than malonic acid and II is a weaker acid as compared to III. The alkyl groups affect primarily the first dissociation constant (K_1^a), while the second dissociation constant (K_2^a) is controlled mainly by the electrostatic field of the carboxylate ion. As expected, bromomalonic acid is a stronger acid than malonic acid. Phenylmalonic acid also due to the electron-withdrawing effect of the phenyl group should have been expected to be stronger acid than malonic acid. Contrary to this, its dissociation constant ($pK_1^a = 2.96$) is somewhat less than malonic acid ($pK_1^a = 2.80$). A possible explanation for this anomaly may be traced to the hydrogen bonding of carboxyl hydrogen with the phenyl ring.

The formation constants of the complexes of I-IV with Al(III), Ga(III), In(III), Fe(III) and Cr(III) are given in Table 2. Obviously, the metal ions fall into two categories. The first three metal ions have the inert gas configuration, while Fe(III) and Cr(III) have incompletely filled *d*-orbitals. The dicarboxylic acids under consideration have O_2^- -chromophoric groups and are hard bases. The metal ions of the first category would form electrostatic bond with the ligand ions and the bond strength should have relation with the effective nuclear charge and ionic radii of the metal ions. On the basis of electrostatic model, considering the anions as point charges, the bond strength is proportional to Z_{eff}/r^2 , where Z_{eff} is the effective

TABLE 1 — ACID DISSOCIATION CONSTANTS OF MALONIC AND SUBSTITUTED MALONIC ACIDS

Acid	pK_1^a	pK_2^a
Malonic	2.80	5.45
Methylmalonic	3.26	5.61
<i>n</i> -Butylmalonic	3.19	5.76
Phenylmalonic	2.96	5.73
Bromomalonic	2.53	3.76

TABLE 2 — STABILITY CONSTANTS OF THE COMPLEXES OF Al(III), Ga(III), In(III), Fe(III) AND Cr(III) WITH MALONIC AND SUBSTITUTED MALONIC ACIDS

Al ³⁺			Ga ³⁺			In ³⁺			Fe ³⁺			Cr ³⁺		
log K ₁	log K ₂	log K ₃	log K ₁	log K ₂	log K ₃	log K ₁	log K ₂	log K ₃	log K ₁	log K ₂	log K ₃	log K ₁	log K ₂	log K ₃
MALONIC ACID														
6.15	3.95	—	6.81	4.81	—	5.55	3.77	3.08	6.39	5.97	5.70	5.81	4.04	3.47
						(log β ₃ = 12.40)			(log β ₃ = 18.06)			(log β ₃ = 13.32)		
METHYLMALONIC ACID														
6.75	6.71	3.51	7.64	6.47	6.16	6.19	5.09	3.71	7.15	6.98	5.96	7.25	6.36	4.74
(log β ₃ = 16.97)			(log β ₃ = 20.27)			(log β ₃ = 14.99)			(log β ₃ = 20.09)			(log β ₃ = 18.35)		
n-BUTYLMALONIC ACID														
6.71	5.69	2.80	7.31	6.97	5.76	5.86	4.38	3.14	7.07	5.81	3.54	6.92	5.54	3.87
(log β ₃ = 15.20)			(log β ₃ = 20.04)			(log β ₃ = 13.38)			(log β ₃ = 16.42)			(log β ₃ = 16.33)		
PHENYLMALONIC ACID														
6.66	6.54	5.01	6.63	5.53	3.35	6.09	5.33	—	6.65	5.70	3.28	—	—	—
(log β ₃ = 18.21)			(log β ₃ = 15.51)						(log β ₃ = 15.63)					
BROMOMALONIC ACID														
4.47	4.22	4.16	5.51	4.89	4.71	5.08	3.81	3.39	6.35	5.48	4.50	—	—	—
(log β ₃ = 12.85)			(log β ₃ = 15.11)			(log β ₃ = 12.28)			(log β ₃ = 16.33)					

nuclear charge and r the radius of the metal ion. Though, this would be a naive picture, still this seems to be a useful model for a comparative study. Thus, the values of Z_{eff}/r^2 for Al(III), Ga(III) and In(III) were calculated to be 34.0, 41.3 and 26.5 respectively. It may be pointed out, as against the usual practice, the effective atomic numbers of the metal ions have been used instead of simple Z values because the attractive power of the nucleus for the electrons would be different for the metal as compared with its ion. Apparently on the basis of Z_{eff}/r^2 values, the stability constants of Al(III), Ga(III) and In(III) with a particular ligand should follow the trend Ga(III) > Al(III) > In(III).

It would be appropriate at this stage to compare the stability constants of the complexes of Al(III), Ga(III) and In(III) with malonic acid and its derivatives. The comparison may be made either on the basis of $\log K_1$ or $\log \beta_3$ values. In few cases, e.g., the formation of tris-complex species of Al(III) and Ga(III) with malonic acid and that of In(III) with phenylmalonic acid could not be determined. Moreover, accumulation of error in each successive formation constants would render the overall stability constant values more unreliable. In any case, it may be seen from Table 2 that, in general, similar trend is followed by $\log K_1$ as well as $\log \beta_3$ values, wherever available. The general trend as expected on the basis of Z_{eff}/r^3 values, i.e. Ga(III) > Al(III) > In(III), was followed in the complexes with methylmalonic and *n*-butylmalonic acids. In the case of phenylmalonic acid the order is Ga(III) \sim Al(III) > In(III) on the basis of $\log K_1$, though on the basis of $\log \beta_3$ values it is Al(III) > Ga(III). This anomaly is probably due to the steric effect of the phenyl ring. In the case of bromomalonic acid the order is Ga(III) >

In(III) > Al(III) on the basis of $\log K_1$ values. However, on the basis of $\log \beta_3$ values the expected trend, i.e. Ga(III) > Al(III) > In(III), is obvious.

In literature, one encounters very few systems in which the stability constants of the above three metal ion complexes have been compared. Izatt *et al.*¹⁰ determined the formation constants of acetylacetonato complexes and observed a trend similar to that obtained by us. Stary¹¹ also reported the same order of the overall stability constants of oxalato complexes. In several polyaminocarboxylic acid complexes, however, the following order of stability constants In(III) > Ga(III) > Al(III) has been reported¹²⁻¹⁴.

It appears, therefore, that there exist two trends in the formation constants of Al(III), Ga(III) and In(III) complexes. While with ligands having oxygen donors, viz. oxalic acid, malonic and substituted malonic acids, acetylacetonato, etc., the order of stability constants is Ga(III) > Al(III) > In(III). On the other hand, with ligands having both nitrogen and oxygen donors the stability constants follow the sequence In(III) > Ga(III) > Al(III). It seems that nitrogen atom acts as a better donor for In(III) and has least affinity for Al(III).

It may be noted from Table 2 that the formation constants of Cr(III) complexes with phenyl and bromomalonic acids could not be determined. Table 2 also shows that the stability constants of Fe(III) complexes are greater than those of Cr(III) complexes. Further, in literature though the stability constants for a large number of Fe(III) complexes are available, those of Cr(III) are meagre. The oxalato complexes have been studied for both the metal ions by different workers² using various techniques. Broadly, $\log \beta_3$ of the ferrioxalato complex is greater than that of chromioxalato complex. With

malonic acid only, the overall stability constant of Fe(III) complex has been determined polarographically⁴. This value ($\log \beta = 15.7$) is somewhat lower than our value ($\log \beta = 18.0$). Muro *et al.*¹⁵ reported for Cr(III)-malonato complexes: $\log K_1 = 7.06$, $\log K_2 = 5.79$ and $\log K_3 = 3.30$, these values are somewhat higher than those obtained by us. With EDTA, the stability constants of both Fe(III) and Cr(III) complexes have been determined^{12,16-18}, and in this case also Fe(III) complex has been found to be stabler than Cr(III) complex.

It may be mentioned that although the electronic configurations of Fe(III) and Cr(III) have no similarity with those of Al(III), Ga(III) and In(III), except that all are in their trivalent state, the stability constants of these two categories of metal ions are not widely different. Particularly, one can rather find analogy in the overall stability constants of Fe(III) and Ga(III) complexes; the Fe(III) complexes in most cases are slightly more stable than Ga(III) complexes. Such trend in the stability constants has also been observed in literature² for aminopolycarboxylates.

It is well known that the increases in basicity of a ligand increases the stability of its metal complexes. The trend in basicity of the substituted malonic acids in terms of pK_1^a is: methyl > *n*-butyl > phenyl > malonic > bromo. Inspection of the results in Table 2 reveals the following orders in $\log K_1$ values of the substituted malonato complexes of each metal ion: Al(III): methyl \sim *n*-butyl > phenyl > malonic > bromo; Ga(III): methyl > *n*-butyl > malonic > phenyl > bromo; In(III): methyl > *n*-butyl > phenyl > malonic > bromo; Fe(III): methyl > *n*-butyl > phenyl > malonic > bromo; and Cr(III): methyl > *n*-butyl > malonic.

From the above comparison it is apparent that for each metal ion the sequence of $\log K_1$ values is based on the basicity of the ligands. In a case or two, methyl and *n*-butylmalonates have similar

$\log K_1$ values, this is not unexpected as one can see in Table 1 that though pK_1^a of methylmalonic acid is slightly higher than that of *n*-butylmalonic acid. On the other hand, pK ($pK_1^a + pK_2^a$) of *n*-butylmalonic acid is slightly higher than that of methylmalonic acid.

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