Kinetics of Acid, Iron(III) & Aluminium(III) Catalysed Aquation of trans-Bis(Hmalonato)bis(ethylenediamine)cobalt(III) Ion

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The H^+, Fe^{3+} and Al^{3+} catalysed aquation of *trans*-bis(Hmalonato)-bis(ethylenediamine)cobalt(III) yields *cis*-(aquo)(Hmalonato)bis(ethylenediamine)cobalt(III) as the major cobalt(III) product. The binuclear complexes, *trans*-$[(en)_2Co(malH)malM]^{(n+1)+}$ ($M = Fe^{3+}$, Al^{3+}) are the reactive species. The equilibrium constant for formation of binuclear species and the rate constant of its aquation are reported. For the acid catalysed aquation in the range of $[H^+] = 0.1-0.8$ mol dm^{-3} ($I = 1.0$ mol dm^{-3}), k_{obs} versus $[H^+]$ plot is linear indicating that the complex does not undergo significant protonation under the condition of acidity employed. The activation parameters ($\Delta H^\dagger$ and $\Delta S^\dagger$) for the metal ion and H^+ catalysed paths are comparable to those for the *trans* → *cis* isomerisation of *trans*-$[Co(en)_2(OH_2)malH]^{2+}$. This is consistent with the fact that *trans* → *cis* isomerisation in the present situation actually occurs during substitution reaction.

In an earlier paper[1] it was shown that Cu(II) catalysed aquation of *cis*-(diformato)bis(ethylenediamine)cobalt(III) yields *cis*-(aquo)(formato)bis(ethylenediamine)cobalt(III). Copper(II) catalysis of aquation of aquo-formato complex to diaquo species was, however, not observable. The *trans*-bis(Hmalonato)bis(ethylenediamine)cobalt(III) is another suitable substrate to examine metal ion catalysis. Both the malonato groups of this substrates can act as bridging ligands separately to the catalyst metal ions (M^{n+}) leading to the formation of various catalytically active species, such as *trans*-$(en)_2CoL_2HM^{n+}$ $[L^{2-} = CH_2(COO^-)_2]$. The results of metal ion catalysed aquation of malonatopentaaminecobalt(III) reported earlier[2] also provides ample evidence that half-bonded malonate in $[(NH_3)_3CoOOCCH_2COO]$ can also act as a bridging ligands for the catalyst metal ion. The present work was undertaken (i) to examine the catalytic effect of H^+, Al^{3+} and Fe^{3+} on the aquation of *trans*-bis(malonato)bis(ethylenediamine)cobalt(III) and (ii) to unravel the mechanistic details of the aquation reaction of the title complex in the presence of metal ions and H^+.

Materials and Methods

The *trans*-bis(malonato)bis(ethylenediamine)cobalt (III) perchlorate was prepared by the method of Chatterjee *et al.*[3] (Calcd for $[(en)_2Co(O_2CCH_2CO_2H)_2]ClO_4 \cdot H_2O$:Co, 11.7. Found: Co, 11.79%); λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1}): 540 (60.6), 450 (31.06), 355 (73.4) Reported[3]: 542.6 (62.1), 448 (31.5), 357.4 (75.0). The IR spectrum of the complex in KBr displayed $\nu N - H$ modes at 3125, 3190, 3230 and 3340 cm^{-1}. The multiplicity of these bands indicated that the site symmetries of all the $N - H$ groups in the complex were not same and this might presumably be due to the intramolecular hydrogen bonding effect of the dangling carboxyl groups with the NH protons. This was further corroborated by the appearance of multiple δNH modes at 1600, 1610, 1650, 1700 and 1740 cm^{-1} for the free and the cobalt(III) bound carboxyl group. Potentiometric titration yielded $pK_1 = 3.3 \pm 0.01$ and $pK_2 = 4.0 \pm 0.02$ ($I = 0.1$ mol dm^{-3}; 30°C) for the free carboxyl groups, in reasonable agreement with those reported by Chatterjee *et al.*[3] ($pK_1 = 3.0 \pm 0.1$, $pK_2 = 4.10 \pm 0.1$ at $I = 1.0$ mol dm^{-3}; 25°C).

All the chemicals used were of A R grade. Solutions were prepared in freshly prepared doubly distilled water. UV-vis spectra were run ona Shimandzu recording spectrophotometer model-240; for kinetic measurements, however, a visible Elico spectrophotometer model CL-24 (Hyderabad) was used. *p*H measurements were made using an Elico digital *p*H meter model ŁI-120 with combination electrode model CL-51. The *p*H meter was standardised against NBS buffers of *p*H 4.01, 6.86 and 9.2. Iron(III) perchlorate and Al(III) perchlorate were prepared and estimated for metal ions and free acid contents as reported earlier[4]. Dowex 50W-X8 resin (20-50 mesh) (H^+-form) was used for ion exchange experiments.

Kinetics

The H^+ and M^{n+} ($M^{n+} = Al^{3+}$ and Fe^{3+}) catalysed malonate elimination from the title complex was studied spectrophotometrically at 480 nm at which large absorbance change occurred during

the reaction. The details of experimental procedure adopted were the same as reported in our earlier work[1]. In order to minimise error due to evaporation, for kinetic runs carried at higher temperatures, reaction flasks with standard ground glass joints were used. The $\log(A_\infty - A_t)$ versus time plots were linear, the slopes of which yielded the observed rate constant for runs which were made under pseudo-first order conditions with respect to $[M^{3+}]_T$ and $[H^+]_T$. The rate constants reported are average of atleast duplicate runs and errors quoted are average deviation of the mean from atleast duplicate runs.

Results and Discussion

Preliminary observation

The absorption spectra of the H^+, Fe^{3+} and Al^{3+} catalysed reactions of the *trans*-dimalonato complex exhibit isosbestic points around 430 and 530 nm. Neither freshly prepared *cis*- $[(en)_2Co(OH_2)_2]^{3+}$ nor *cis*-$[(en)_2Co(mal)]^+$ (mal = malonato dianion) display isosbestic points if used as substrates. Spectral comparison shows that in each case, the absorption spectrum of the reaction mixture at infinite time is intermediate between those of *cis*-$[(en)_2Co(OH_2)_2]^{3+}$ and *cis*-$[(en)_2Co(mal)]^+$. These facts are indicative of the formation of the aquomalonate complex, $[Co(en)_2(OH_2)malH]^{2+}$ as an intermediate. Since the spectrum of the intermediate is very similar to that of a *cis*-complex, we believe that the aquomalonate complex exist in the *cis*-configuration. Since the pseudo-first order kinetics was strictly adhered upto 85% completion of the reaction it is reasonable to believe that *trans* → *cis* isomerisation in the product must have taken place in the transition state. Formation of the chelated malonato complex in the reaction as a minor product cannot be completely ruled out. But, the formation of this species does not complicate the overall kinetics. The stoichiometry of the reaction was established by estimating the liberated malonic acid using Ce(IV) as the oxidant[5]. For this a known volume of the reaction mixture after $10t_{1/2}$ was subjected to cation exchange in $1M$ $HClO_4$ medium using Dowex 50W-X8(20-50 mesh) resin (H^+-form) to remove the Co(III) and other metal ions. The malonic acid content in the filtrate and resin washings taken together was estimated and the value is in accord with Eq. (1)

$$CH_2(CO_2H)_2 + 6Ce(IV) \xrightarrow{H_2O} 6\,Ce(III) + 6H^+ + 2CO_2 + HCO_2H \quad \ldots (1)$$
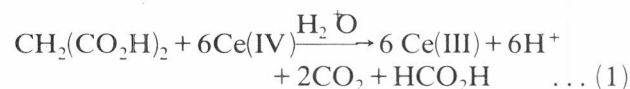
established by Mc Auley *et al.*[5] Analogous standard experiment was also run under identical condition using malonic acid. Our results agree with stoichiometry of the reaction as represented by Eq. (2)

$$[(en)_2Co(malH)_2]^+ \xrightarrow[H_2O]{H^+/M^{n+}} Co(III)\ product + H_2mal \quad \ldots (2)$$
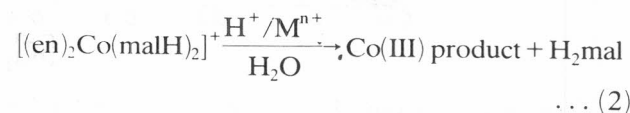
where the cobalt(III) product as evident from the absorption spectra, is predominantly the aquo malonate species.

Rate data for aquation reaction

Table 1 presents the pseudo-first order rate constants for the acid-catalysed aquation reaction.

Table 1 — Pseudo-first Order Rate Constants and Activation Parameters for Acid-catalysed Aquation of *trans*-$[(en)_2Co(malH)_2]^+$ at Different Temperatures

($[complex]_i = 5 \times 10^{-3}$ mol dm^{-3}, $\lambda = 480$ nm, $I = 1.0$ mol dm^{-3})

$[H^+]$ (mol dm^{-3})	$10^4\,k_{obs}$ (s^{-1}) at							
	60.0 ± 0.1°C		65.0 ± 0.1°C		70.0 ± 0.1°C		75.0 ± 0.1°C	
	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc
0.1	0.315(±0.01)	0.288	0.60(±0.02)	0.57	1.16(±0.04)	1.25	2.25(±0.11)	2.34
0.2	0.56(±0.01)	0.56	1.11(±0.05)	1.08	2.13(±0.01)	2.20	4.18(±0.23)	4.11
0.3	0.77(±0.01)	0.83	1.57(±0.05)	1.59	3.21(±0.06)	3.16	5.79(±0.10)	5.88
0.4	1.21(±0.05)	1.10	2.02(±0.01)	2.10	4.35(±0.10)	4.11	8.00(±0.10)	7.56
0.6	1.70(±0.05)	1.65	3.11(±0.11)	3.11	5.92(±0.09)	6.01	11.11(±0.16)	11.20
0.7	1.93(±0.04)	1.92	3.60(±0.07)	3.62	7.00(±0.11)	6.97	12.56(±0.28)	12.97
0.8	2.16(±0.06)	2.20	4.19(±0.21)	4.13	7.85(±0.03)	7.92	15.05(±0.54)	14.74
	$10^4\,k_H$ (dm^3 mol^{-1} s^{-1})							
	2.72(±0.06)	—	5.09(±0.08)	—	9.53(±0.20)	—	17.72(±0.44)	—

$\Delta H^\neq = 117.6 \pm 0.9$ kJ mol^{-1}; $\Delta S^\neq = +38 \pm 2.7$ JK^{-1} mol^{-1}.
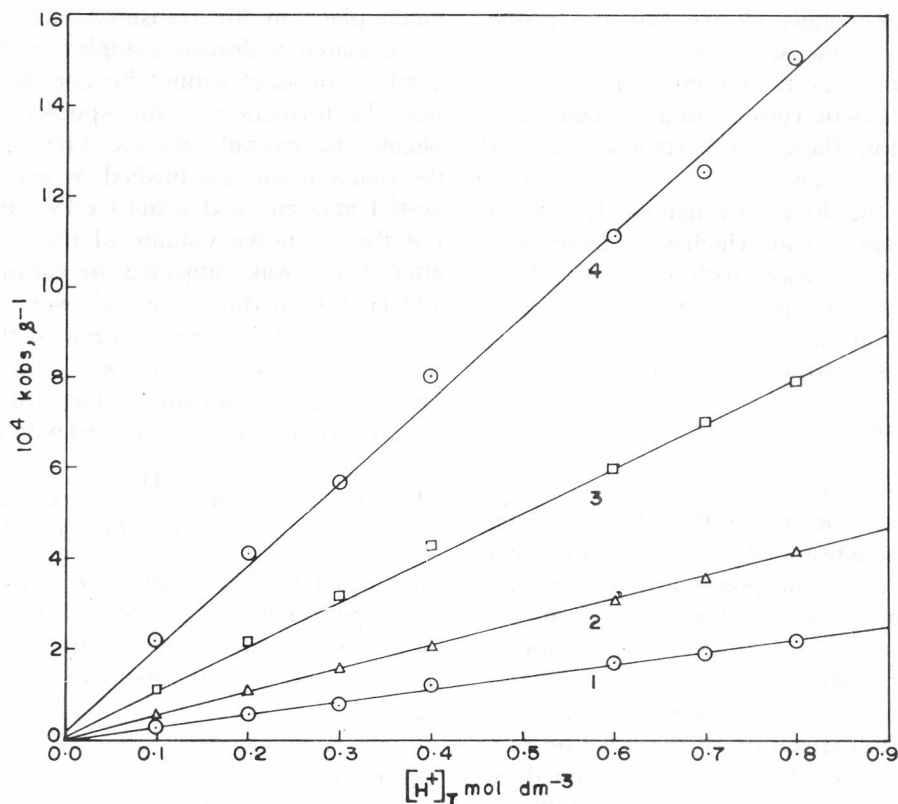
Fig. 1—$10^4 k_{obs}$, s^{-1} versus [H$^+$]$_T$ plot for the acid catalysed aquation of *trans*-[(en)$_2$Co(malH)$_2$]$^+$ at (1) 60°C (2) 65°C (3) 70°C (4) 75°C

The observed rate constants fit the relationship (3) (see Fig. 1).
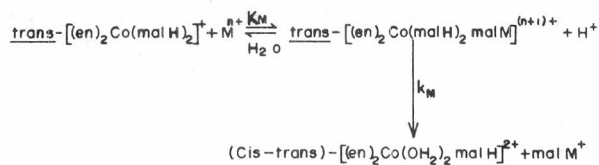
$$k_{obs} = k_0 + k_H[\text{H}^+] \qquad \ldots (3)$$

where k_0 and k_H are the rate constants for spontaneous and acid catalysed aquation respectively.

The spontaneous aquation of the dimalonate complex is hardly significant and the acid-catalysed aquation is the most important path. Only one malonate is released in the process as evident from the determination of stoichiometry of the reaction. The spectral scan of the reaction mixture is very similar to the time variation absorption spectrum of the *trans* → *cis* isomerisation of *trans*-[(en)$_2$Co(OH$_2$)malH]$^{2+}$ (pH = 2.5, 30°C) reported by Carunchio *et al.*[6] These workers also reported that at equilibrium, *trans* to *cis* ratio for the aquomalonato-bis(ethylenediamine)cobalt(III) was 0.25. Our results also indicate that the product of acid-catalysed aquation of the *trans*-[(en)$_2$Co(malH)$_2$]$^+$ is predominantly the *cis*-[(en)$_2$Co(OH)$_2$malH]$^{2+}$. The value of k_H and associated activation parameters are given in Table 1.

The aquation of the dimalonato complex is strongly catalysed by Fe(III) and Al(III). Rate data collected in Tables 2 and 3 and also the k_{obs} versus [M^{n+}]$_T$ plots in Fig. 2 point to rate saturation

at high [M^{n+}]$_T$ at a given [H$^+$]$_T$. Variation of k_{obs} with [H$^+$]$_T$ in the absence of metal ions is in keeping with the fact that protonation of the dimalonato complex is not very significant at $0.1 \leqslant [\text{H}^+]_T \leqslant 0.8$ mol dm^{-3}. The mechanism consistent with our observations is shown in Scheme 1.

trans-[(en)$_2$Co(mal H)$_2$]$^+$ + M^{n+} $\underset{\text{H}_2\text{O}}{\overset{K_M}{\rightleftharpoons}}$ trans-[(en)$_2$Co(malH)$_2$ malM]$^{(n+1)+}$ + H$^+$

$\downarrow k_M$

(Cis−trans)-[(en)$_2$Co(OH$_2$) mal H]$^{2+}$ + mal M$^+$

Scheme 1

The product is predominantly *cis*-(aquo)(malonato) complex consistent with Scheme 1. The pseudo-first order rate constant is given by Eq. (4).

$$k_{obs} = \frac{k'_{obs} + k_M K_M[\text{M}^{3+}]/[\text{H}^+]}{1 + K_M[\text{M}^{3+}]/[\text{H}^+]} \qquad \ldots (4)$$

where $k'_{obs} = k_{obs}$ at [M^{3+}] = 0, K_M is the equilibrium constant of formation and k_M is the rate constant of aquation of binuclear species (Scheme 1).

Table 2—Pseudo-first Order Rate Constant for Al(III) Catalysed Aquation of *trans*-$[en)_2Co(malH)_2]^+$ at Different Temperatures

$([complex] = 5 \times 10^{-3}, [HClO_4]_T = 5 \times 10^{-3}, I = 1.0 \text{ mol dm}^{-3}, \lambda = 480 \text{ nm})$

$[M^{3+}]_T$ (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1}) at							
	60.0 ± 0.1°C		65.0 ± 0.1°C		70.0 ± 0.1°C		75.0 ± 0.1°C	
	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc
0.00	0.115	—	0.209	—	0.465	—	0.816	—
0.01	0.38(±0.02)	0.382	0.75(±0.01)	0.756	1.46(±0.04)	1.47	2.45(±0.07)	2.29
0.02	0.60(±0.02)	0.586	1.20(±0.03)	1.15	2.25(±0.02)	2.21	3.54(±0.02)	3.32
0.03	0.75(±0.01)	0.746	1.46(±0.03)	1.45	2.83(±0.09)	2.77	4.29(±0.07)	4.07
0.04	0.88	0.875	1.68(±0.03)	1.69	3.30(±0.07)	3.21	5.04(±0.07)	4.65
0.05	0.98(±0.04)	0.98	1.86(±0.05)	1.88	3.49(±0.04)	3.58	5.61(±0.05)	5.10
0.06	1.02(±0.06)	1.07	1.96(±0.02)	2.03	3.67(±0.09)	3.87	6.02(±0.11)	5.47
0.07	1.01(±0.03)	1.14	1.98(±0.02)	2.16	3.65(±0.05)	4.12	6.01(±0.04)	5.77
0.08	1.01(±0.06)	1.21	1.96(±0.03)	2.28	3.65(±0.03)	4.34	5.99(±0.04)	6.03
0.09	1.02(±0.02)	1.27	1.95(±0.05)	2.37	3.66(±0.04)	4.52	6.07(±0.05)	6.25
0.10	1.01(±0.01)	1.32	1.96(±0.02)	2.46	3.64(±0.02)	4.68	6.01(±0.10)	6.44
$10^4 k_M$ (s^{-1})								
	2.08(±0.13)	—	3.64(±0.25)	—	7.03(±0.47)	—	9.79(±0.30)	—
K_M								
	0.078(±0.005)	—	0.095(±0.007)	—	0.090(±0.006)	—	0.11(±0.004)	—

$\Delta H^{\ddagger} = 99.5 \pm 8.3 \text{ kJ mol}^{-1}$; $\Delta S^{\ddagger} = -17.4 \pm 24.6 \text{ JK}^{-1}\text{mol}^{-1}$.

Table 3—Pseudo-first Order Rate Constant for Fe(III) Catalysed Aquation of *trans*-$[(en)_2Co (malH)_2]^+$ at Different Temperatures

$([complex] = 5 \times 10^{-3} \text{ mol dm}^{-3}, [HClO_4] = 0.25 \text{ mol dm}^{-3}, I = 1.0 \text{ mol dm}^{-3}, \lambda = 480 \text{ nm})$

$[M^{3+}]$ (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1}) at							
	60.0 ± 0.1°C		65.0 ± 0.1°C		70.0 ± 0.1°C		75.0 ± 0.1°C	
	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc
0.00	0.61(±0.03)	—	1.32(±0.05)	—	2.65(±0.07)	—	4.50(±0.05)	—
0.02	0.92(±0.03)	0.92	1.90(±0.15)	1.90	3.65(±0.10)	3.63	5.71(±0.07)	5.70
0.03	1.02(±0.04)	1.02	2.09(±0.12)	2.09	3.98(±0.26)	4.02	6.16(±0.08)	6.19
0.04	1.10(±0.05)	1.11	2.29(±0.14)	2.25	4.30(±0.28)	4.36	6.58(±0.12)	6.62
0.05	1.19(±0.02)	1.19	2.35(±0.13)	2.38	4.76(±0.22)	4.67	7.01(±0.10)	7.00
0.06	1.28(±0.02)	1.25	2.48(±0.09)	2.48	5.00(±0.30)	4.94	7.45(±0.02)	7.35
0.07	1.29(±0.02)	1.30	2.48(±0.07)	2.57	5.09(±0.20)	5.17	7.60(±0.37)	7.66
0.08	1.28(±0.01)	1.35	2.51(±0.05)	2.65	5.08(±0.13)	5.39	7.57(±0.31)	7.94
0.09	1.28(±0.02)	1.40	2.52(±0.06)	2.72	5.03(±0.18)	5.58	—	—
0.10	1.29(±0.01)	1.43	2.53(±0.07)	2.78	5.03(±0.08)	5.80	7.53(±0.26)	8.43
$10^4 k_M$ (s^{-1})								
	2.03(±0.14)	—	3.66(±0.19)	—	9.43(±1.14)	—	13.66(±1.11)	—
K_M								
	3.44(±0.33)	—	4.13(±0.34)	—	2.12(±0.12)	—	1.88(±0.23)	—

$\Delta H^{\ddagger} = 125.7 \pm 13.9 \text{ kJ mol}^{-1}$; $\Delta S^{\ddagger} = +61 \pm 40 \text{ JK}^{-1}\text{mol}^{-1}$.

Equation (4) can be linearised to Eq. (5)

$$\frac{1}{(k_{obs} - k'_{obs})} = \frac{1}{(k_M - k'_{obs})} + \frac{1}{(k_M - k'_{obs})K_M} \frac{[H^+]}{[M^{n+}]} \quad (5)$$

Taking $[H^+]_T = [HClO_4]_T$ and $[M^{n+}] = [M^{n+}]_T$ the rate data upto $[M^{n+}]_T < 0.06$ mol dm^{-3} for Al^{3+} and Fe^{3+} fitted to Eq. (4) satisfactorily. Typical plots consistent with Eqs (4) and (5) are presented
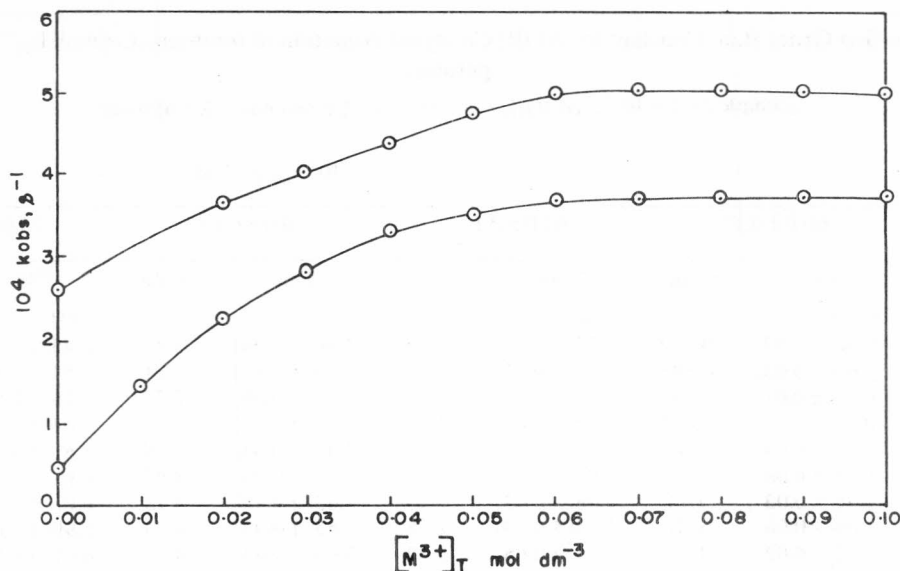
Fig. 2—$10^4 \, k_{obs}$, s^{-1} versus $[M^{n+}]_T$ plot at 70°C, (1) For$[Al^{3+}]_T$, $[H^+]_T = 5 \times 10^{-3}$ mol dm^{-3}; (2) for Fe^{3+}, $[H^+]_T = 0.25$ mol dm^{-3})
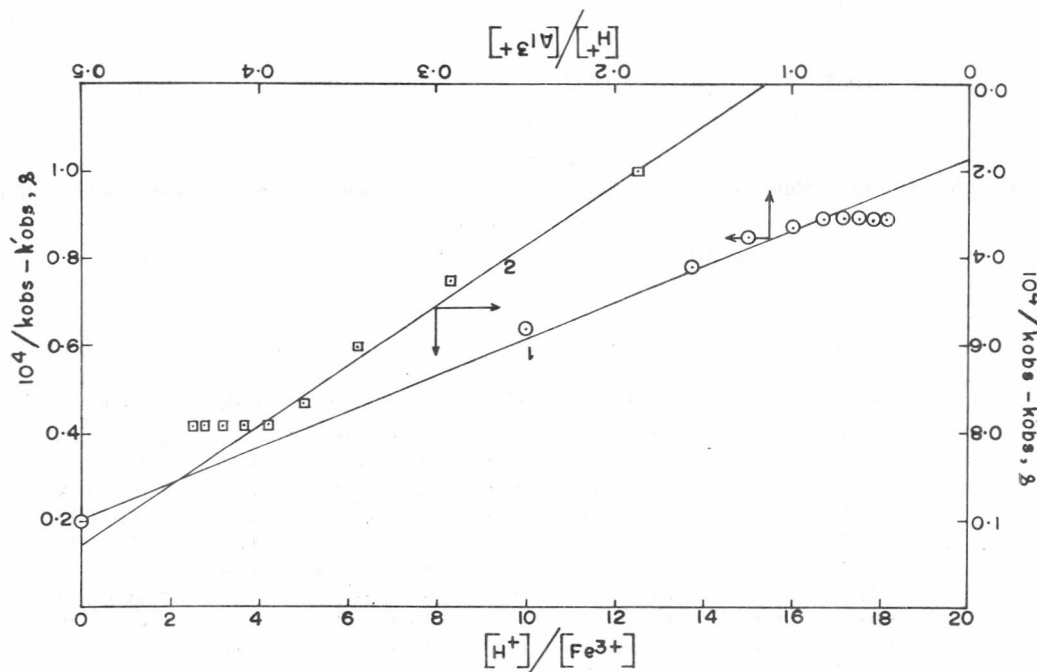

Fig. 3—$10^4/(k_{obs} - k'_{obs})$, versus $[H^+]/[M^{n+}]_T$ plot at 70°C (1) for Al^{3+} (2) for Fe^{3+}

in Figs 2 and 3. The values of k_M and K_M calculated from the slopes and intercepts of such plots are presented in Tables 2 and 3. The values of k_M at any temperature is higher than the limiting value of k_{obs} at that temperature obtained at $0.06 < [M^{n+}] < 0.1$ mol dm^{-3}. It appears that at high $[M^{n+}]$ (= 0.06-0.1 mol dm^{-3}) the metal ion catalysed aquation is retarded. This could be a medium effect. However, we have no definite answer to this observation at the moment. We attempted to in-

terpret this observation in Fe(III)-catalysed aquation via formation of non-reactive hydroxo-bridged Fe(III) dimers. But it was found that depletion of $[Fe^{3+}]$ by this path did not cause significant rate retardation.

The values of K_M are comparable to those of Fe(III)-(NH$_3$)$_5$Co(malH)$^{2+}$ equilibrium reaction reported earlier[7]. The values of k_M for the dimalonato complex are significantly higher than those for [(NH$_3$)$_5$ComalH]$^{2+}$, both for Fe(III) and Al(III) catalysed reactions reported earlier. Furthermore it is

also worth noting that catalyst metal ions do not efficiently promote the aquation of $[(en)_2Co(OH_2)malH]^{2+}$ to the corresponding diaquo species.

The activation parameters for the metal ion catalysed path (k_M path), viz. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are little sensitive to the nature of the metal ions (i.e Al^{3+} and Fe^{3+}; see Tables 2 and 3). Further more, these parameters are also comparable to those for *trans* → *cis* isomerisation[6] of *trans*-$[(en)_2Co(OH_2)malH]^{2+}$ ($E_a = 115.5$ kJ mol^{-1}, $\Delta S^{\ddagger} = 39.75$ JK^{-1} mol^{-1}). This leads us to believe that the *trans* → *cis* isomerisation in the product occurs during substitution of $malM^{(n-2)+}$ by H_2O at the cobalt(III) centre.

Acknowledgement

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