

Kinetics & Mechanism of Formation of Chromium(III) Phosphate Complexes from Tetraaquomonomalatochromium(III) Cation & Orthophosphoric Acid

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The kinetics of the formation of chromium(III)-phosphate complexes from tetraaquomono(malonato)-chromium(III) and orthophosphoric acid have been investigated. A mechanism involving the formation of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is suggested for the substitution process.

THE substitution of tris(oxalato)chromate(III)¹, tetraaquomono(oxalato)chromium(III)² and tris(malonato)chromate(III)³ by orthophosphoric acid has recently been reported from our laboratory. It was found that the rate of substitution was faster in the case of mono(oxalato) complex than for tris(oxalato) complex. This was attributed to the presence of water molecules in the monocomplex. In the light of the above conclusion it seemed of interest to investigate the substitution of tetraaquomono(malonato)chromium(III) so as to see the trends in the analogous malonate systems. In surprising contrast to the oxalate case, the substitution reactions show a reverse trend, the rate of substitution in the mono(malonato) complex being less than that of the tris(malonato) complex.

Tetraaquomono(malonato)chromium(III) cation was prepared by the method of Olson and Behnke⁴ with some modifications.

A solution (200 ml) containing 0.75M malonic acid, 0.25M perchloric acid and 0.25M hexaaquochromium(III) was thermostated at 60° for 60 hr, diluted to 500 ml and then passed through a column of Dowex 50W-X8 (100-200 mesh) cation-exchange resin. The column was rinsed with 0.05M perchloric acid to remove free malonic acid and anionic complexes. The cationic complex was eluted with 0.5M perchloric acid. The stock solution was stored at 0°. The malonate/chromium ratio in the complex was found to be 1.03.

All other chemicals used were of reagent grade. The distilled water passed through a mixed bed ion-exchange resin column was used.

Absorbance measurements are made with a Unicam SP 600 spectrophotometer fitted with 1 cm glass cells. Temperature control in the rate studies was achieved using a thermostat with circulating pump attachment controlling the cell temperature fluctuation to within $\pm 0.05^\circ$.

Procedure—To follow the rate of reaction a solution containing requisite quantities of phosphoric acid and sodium nitrate (for maintaining ionic strength) was thermostated at the experimental temperature, the requisite quantity of mono(malonato) complex was added, the solution was shaken quickly and diluted to a definite volume with water thermostated at the experimental temperature. A portion of the reaction mixture was then trans-

ferred to the cell which is placed in the cell compartment of the spectrophotometer. The absorbance at 560 nm, where the reactant, the mono(malonato) complex showed an absorption maximum, was measured at regular time intervals.

The pseudo first order rate constant is evaluated graphically by plotting $\log(A_t - A_\infty)$ vs time where A_t and A_∞ represent the absorbance at time t and infinite time respectively. The plots are found to be linear and the rate constants are evaluated from slopes. The rate of the reaction is followed as a function of concentration of metal complex, phosphoric acid, added malonate and nitric acid. The rate of the reaction is also followed at different ionic strengths. The results are presented in Tables 1 and 2.

The rate of substitution increased with increase in the molarity of orthophosphoric acid. A plot of k_{obs} vs $[\text{H}_3\text{PO}_4]$ is linear passing through the origin indicating the dependence of the reaction rate on the molarity of H_3PO_4 . The order of reaction with respect to the [metal complex] is found to be unity. The k_{obs} increases with an increase in $[\text{H}^+]$, the source for H^+ being nitric acid. Under the experimental conditions the contribution of H_3PO_4 to $[\text{H}^+]$ is not significant and can hence be ignored. The plot of k_{obs} vs $[\text{H}^+]$ is linear with a positive intercept on the rate axis and with a slope equal to unity. From this it can be concluded that there are two reaction paths, viz. acid dependent and acid independent. The rate of substitution decreases with added [malonate] suggesting the release of the malonate from the metal complex. A plot of k_{obs} vs $1/[\text{H}_2\text{mal}]$ is linear with a positive intercept on the rate axis. An increase in the ionic

TABLE 1 — VARIATION OF RATE CONSTANT WITH PHOSPHORIC ACID MOLARITY

{[Cr(mal⁺) = 0.004M; ionic strength, $\mu = 1.0$ }

[H ₃ PO ₄] M	$k_{\text{obs}} \times 10^3 \text{ min}^{-1}$	
	30°	46.5°
1.0	0.28	3.0
2.0	0.51	5.6
2.5	0.66	7.0
3.0	0.77	8.1
3.5	0.95	10.1
4.0	1.07	11.2
4.5	1.0	12.8
5.0	1.29	14.0

TABLE 2 — VARIATION OF RATE CONSTANT WITH HYDROGEN ION*

{[Cr(mal⁺) = 0.004M; [H₃PO₄] = 5.0M; $\mu = 2.0$
temp. = 30°}

[H ⁺] M	$k_{\text{obs}} \times 10^3$ min ⁻¹	[H ⁺] M	$k_{\text{obs}} \times 10^3$ min ⁻¹
0.00	2.20	1.00	3.30
0.25	2.50	1.50	3.73
0.50	2.70	2.00	4.36
0.75	3.10		

*Source of hydrogen ion is nitric acid.

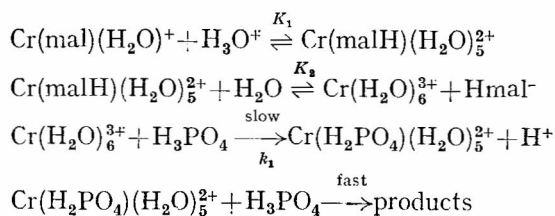
strength increases the rate constant indicating that the reaction is between ions of the same charge type.

The reaction is followed at two temperatures, viz. 30° and 46.5°. The energy of activation for the substitution process is found to be 27.0 kcal/mole.

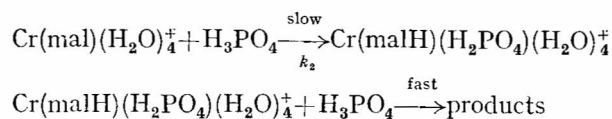
The absorption spectrum of the product in these studies is identical with that obtained in the substitution studies of tris(malonato) chromate(III) complex by H₃PO₄, with two peaks at 440 (ε = 19.0) and 630 nm (ε = 19.0). Ion exchange studies on the product species failed to show the presence of either cationic or anionic phosphate complexes. Hence the product species may be neutral possibly of the type Cr(HPO₄)(H₂PO₄).

The following mechanism is suggested to explain the experimental observations.

Acid dependent path:



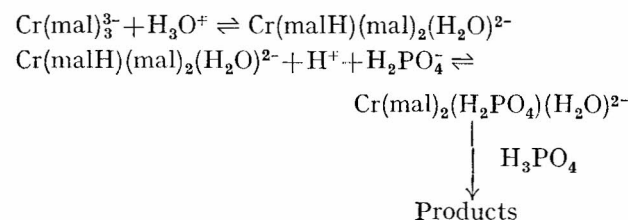
Acid independent path:



This leads to the rate law

$$\begin{aligned} \text{Rate} &= \frac{k_1 K_1 K_2 [\text{complex}][\text{H}_3\text{PO}_4][\text{H}_3\text{O}^+]}{[\text{Hmal}^-]} + k_2 [\text{complex}][\text{H}_3\text{PO}_4] \\ &= \left\{ \frac{[k_1 K_1 K_2 [\text{H}_3\text{O}^+]}{[\text{Hmal}^-]} + k_2 \right\} [\text{complex}][\text{H}_3\text{PO}_4] \end{aligned}$$

In the substitution of tris(malonato)chromate(III) by H₃PO₄, the first step is observed to be the attack of H₃O⁺ on Cr(mal)₃³⁻ to give a monodentate malonato complex, Cr(malH)(mal)₂(H₂O)²⁻. This monodentate complex enters into reaction with H₃PO₄ to give the products.



In the present case the monodentate malonato complex in the equilibrium step yields hexaaquochromium(III) which is attacked by H₃PO₄. This may be the cause for the relative slowness of substitution of the monocomplex.

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2-Methylbenzothiazole Complexes of Hg(II) Halides & Pseudohalides

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Hg(II) chloride, bromide, cyanide and thiocyanate form 1:1 complexes with 2-methylbenzothiazole. The complexes have been characterized by molar conductance, IR and far-IR spectral data. The Hg(II) chloride, bromide and thiocyanate complexes are tentatively suggested to have halogen/pseudohalogen-bridged dimeric tetrahedral structures in the solid state. The Hg(II) cyanide complex possesses a cyano-bridged polymeric structure.

THE ligand, 2-methylbenzothiazole having two bonding sites — sulphur and nitrogen in the thiazole ring — possesses strong anti-bacterial, anti-tubercular and anti-viral activities. Metal complexes of biologically important ligands are sometimes more effective than the free ligands. Although complexes of 2-methylbenzothiazole with some metal(II) salts are known¹ its complexes with Hg(II) salts which are likely to have significant biological effects have not been reported. In this note we report the preparation and characterization of the solid complexes of 2-methylbenzothiazole (L) with Hg(II) halides and pseudohalides.

Hg(II) chloride, bromide and cyanide complexes with 2-methylbenzothiazole were obtained by adding an excess of the ligand to a hot solution of the respective Hg(II) salt in ethanol. Hg(II) thiocyanate complex was prepared by boiling a suspension of the metal thiocyanate with an excess of the ligand, in ethanol. The solution was filtered hot and the complex which crystallized out on cooling was suction-filtered, washed with ethanol and dried. Stoichiometry of the complexes isolated was established by standard analytical methods. Hg(L)Cl₂, m.p. 220° (Found: Hg, 48.0; Cl, 17.0. Calc.: Hg, 47.6; Cl, 16.9%); Hg(L)Br₂, m.p. 202° (Found: Hg, 39.1; Br, 31.5. Calc.: Hg, 39.3; Br, 31.4%); Hg(L)(CN)₂, m.p. 145° (Found: Hg, 50.0. Calc.: Hg, 49.9%); and Hg(L)(SCN)₂, m.p. 113° (Found: Hg, 43.1; SCN, 25.1. Calc.: Hg, 43.0; SCN, 24.9%).

The 1:1 complexes are quite stable and soluble in methanol and dimethylformamide. Molar conductance of ~10⁻³M solutions in purified dimethylformamide (Philips conductivity bridge) indicate