Studies on the Kinetics and Mechanism of the Complex Formation Between Hexa-aquachromium(III) and Phthalic Acid

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Kinetic studies of the interaction of $[Cr(OH_2)_6]^{3+}$ with phthalic acid have been carried out at 30, 35, and 40 °C, the hydrogen-ion concentration ranging from 0.25×10^{-3} to 3.16×10^{-3} mol dm^{-3}. The variation of the pseudo-first-order rate constant ($k_{obs.}$) with [H$^+$] and ligand concentration indicates a mechanism based on ion-pair formation. The reaction is believed to be of the associative-interchange (I_a) type. Activation parameters calculated by the Eyring equation are $\Delta H^\ddagger = 93$ kJ mol^{-1} and $\Delta S^\ddagger = -5 \pm 2$ J K^{-1} mol^{-1} for the formation of $[Cr(OH_2)_5(O_2CC_6H_4CO_2)]^+$, and $\Delta H^\ddagger = 94$ kJ mol^{-1} and $\Delta S^\ddagger = -2 \pm 1$ J K^{-1} mol^{-1} for the formation of $[Cr(OH_2)(O_2CC_6H_4CO_2H)]^{2+}$.

HAMM and his co-workers[1-3] studied the kinetics of complex formation of $[Cr(OH_2)_6]^{3+}$ with phthalic acid using a polarographic technique and put forward a dissociative mechanism. A similar mechanism was given by Kelm and Harris[4] and also by Benerjea and Chaudhuri[5] for the oxalato-complexes. In contrast, evidence for an associative mechanism has been presented for the substitution reactions of anionopenta-aquachromium(III) complexes[6] and for the effect of pressure on the kinetics of exchange of $H_2{}^{18}O$ between $[Cr(OH_2)_6]^{3+}$ and solvent water.[7] Swaddle[8] has also reviewed the activation parameters and mechanism of octahedral substitution reactions and has shown that the reaction of $[Cr(OH_2)_6]^{3+}$ with various anions is of the associative-interchange (I_a) type.

In continuation[9,10] of our studies on the composition and kinetics of complex formation by $[Cr(OH_2)_6]^{3+}$ with (N,N)-, (N,O)-, and (O,O)-containing ligands, we report studies of the anation reaction of $[Cr(OH_2)_6]^{3+}$ with phthalic acid.

EXPERIMENTAL

Stock solutions of chromium(III) nitrate, sodium nitrate, sodium hydroxide, and nitric acid were prepared from AnalaR grade reagents in double distilled water. Phthalic acid (B.D.H.) was used after double crystallization. The solution of chromium(III) nitrate was standardized by an ion-exchange method.[11] The pH measurements were made with type AT-2 Titrierautomat, which was calibrated with buffer solutions of pH 4.0 and 9.2.

The kinetic measurements for the reaction of phthalic acid with Cr^{III} were made by mixing solutions in a two-necked flask fitted with a double-walled condenser to check evaporation. The reaction flask was kept in a thermostat controlled at the desired temperature within ±0.1 °C. The concentration of Cr^{III} in the reaction vessel was 4.0×10^{-3} mol dm^{-3} and that of phthalic acid was varied from 0.033 to 0.250 mol dm^{-3}. Nitrogen gas was bubbled through the reaction mixture for stirring as well as to maintain an inert atmosphere. The ionic strength of the reaction mixture was adjusted to the desired value by addition of the required amount of sodium nitrate solution. Aliquot portions (5 cm^3) of the reaction mixture were pipetted from the reaction vessel at definite time intervals and cooled in ice-bath to quench the reaction. The optical density of this solution was measured at 600 nm using a Bausch and Lomb Spectronic-20. The concentration of the complex was calculated as described by Gibbs.[12]

RESULTS AND DISCUSSION

The composition of the chromium(III)–phthalic acid complex in aqueous solution was determined by Job's method of continuous variations. It was found that 1 mol of Cr^{III} reacts with 1 mol of phthalic acid. The kinetic measurements were made at 30, 35, and 40 °C. The hydrogen-ion concentration of the reaction medium was varied from 0.25×10^{-3} to 3.16×10^{-3} mol dm^{-3}. The results are given in Figures 1 and 2. The variations of the pseudo-first-order rate constants ($k_{obs.}$) with hydrogen-ion and phthalic acid concentrations indicate an ion-pair mechanism.

On the basis of these results and previous observations[9, 10] the mechanism may be represented by the following scheme:

$$HO_2CC_6H_4CO_2H \overset{K_1}{\rightleftharpoons} HO_2CC_6H_4CO_2{}^- + H^+ \quad (1)$$

$$HO_2CC_6H_4CO_2{}^- \overset{K_2}{\rightleftharpoons} {}^-O_2CC_6H_4CO_2{}^- + H^+ \quad (2)$$

$$[Cr(OH_2)_6]^{3+} + {}^-O_2CC_6H_4CO_2{}^- \overset{K_I}{\rightleftharpoons} [Cr(OH_2)_6]^{3+},{}^-O_2CC_6H_4CO_2{}^- \quad (3)$$

$$[Cr(OH_2)_6]^{3+} + {}^-O_2CC_6H_4CO_2H \overset{K_I'}{\rightleftharpoons} [Cr(OH_2)_6]^{3+},{}^-O_2CC_6H_4CO_2H \quad (4)$$

$$[Cr(OH_2)_6]^{3+},{}^-O_2CC_6H_4CO_2{}^- \overset{k_{an}}{\rightleftharpoons} [Cr(OH_2)_5(O_2CC_6H_4CO_2)]^+ + H_2O \quad (5)$$

$$[Cr(OH_2)_6]^{3+},{}^-O_2CC_6H_4CO_2H \overset{k_{an}'}{\rightleftharpoons} [Cr(OH_2)_5(O_2CC_6H_4CO_2H)]^{2+} + H_2O \quad (6)$$

$$[Cr(OH_2)_5(O_2CC_6H_4CO_2)]^+ \overset{\text{fast}}{\rightleftharpoons} [Cr(OH_2)_4(O_2CC_6H_4CO_2)]^+ + H_2O$$

$$[Cr(OH_2)_5(O_2CC_6H_4CO_2H)]^{2+} \overset{\text{fast}}{\rightleftharpoons} [Cr(H_2O)_4(O_2CC_6H_4CO_2)]^+ + [H_3O]^+$$

The rate equation consistent with the above mechanism is (7) where [Phthalic acid]$_T$ is the total concentration

$$k_{obs.} = \frac{(k_{an}K_IK_2 + k_{an}'K_I'[H]^+)\,[\text{Phthalic acid}]_T}{([H^+]^2/K_1) + [H^+] + K_2 + (K_IK_2 + K_I'[H^+])[\text{Phthalic acid}]_T} \quad (7)$$

$$\frac{1}{k_{obs.}} = B_1 + \frac{B_2}{[\text{Phthalic acid}]_T} \quad (8)$$

$$\text{where } B_1 = \frac{K_IK_2 + K_I'[H^+]}{k_{an}K_IK_2 + k_{an}'K_I'[H^+]}$$

$$B_2 = \frac{([H^+]^2/K_1) + [H^+] + K_2}{k_{an}K_IK_2 + k_{an}'K_I'[H^+]}$$

of phthalic acid added. The values of the different rate parameters in equation (7) were determined by Newton's method[13] of iteration with a program developed for an IBM-1130 computer, and are given in Table 1.

TABLE 1

Values of the rate parameters[a] based on equation (7), at different temperatures, $[H^+] = 0.25 \times 10^{-3}$ mol dm^{-3}, and $I = 1.0$ mol dm^{-3}

θ_c/°C	10^4k_{an}/s^{-1}	K_I/dm^3 mol^{-1}	$10^4k_{an}'$/s^{-1}	K_I'/dm^3 mol^{-1}	10^3K_1/mol dm^{-3}	10^4K_2/mol dm^{-3}	10^5 R.m.s. deviation[b]
30	4.29 ± 0.78	5.12	3.00 ± 0.55	2.35	1.60	2.64	2.29
35	7.71 ± 0.66	4.75	5.39 ± 0.46	2.22	2.01	5.82	2.24
40	14.42 ± 2.12	4.64	10.11 ± 1.48	2.12	3.14	9.74	7.13

[a] Values within ±10%. [b] Root-mean-square deviation between the observed and calculated values of the pseudo-first-order rate constants.

TABLE 2

Values of the parameters B_1 and B_2 used in equation (8), at different temperatures and $[H^+]$; $I = 1.0$ mol dm^{-3}

θ_c/°C	10^{-3} B_1/s			10^{-2} B_2/s mol dm^{-3}		
10^3 [H$^+$]/mol dm^{-3}	0.25	0.99	3.16	0.25	0.99	3.16
30	5.99 ± 0.12	7.18 ± 0.15	8.12 ± 0.10	4.54 ± 0.07	4.49 ± 0.09	4.52 ± 0.06
35	2.12 ± 0.06	2.56 ± 0.08	2.76 ± 0.11	2.41 ± 0.04	3.22 ± 0.05	4.13 ± 0.07
40	1.37 ± 0.09	1.63 ± 0.05	1.80 ± 0.05	1.23 ± 0.05	1.31 ± 0.03	1.41 ± 0.03

Equation (7) on rearrangement gives (8) which shows a linear dependence of $1/k_{obs.}$ on $1/[\text{Phthalic acid}]_T$ at a given pH (Figure 2). B_1 and B_2, which are the intercepts and gradients of the plots in Figure 2, were calculated and are given in Table 2. The values of $\Delta H^‡$ and $\Delta S^‡$ were calculated using the Eyring equation and are given in Table 3.

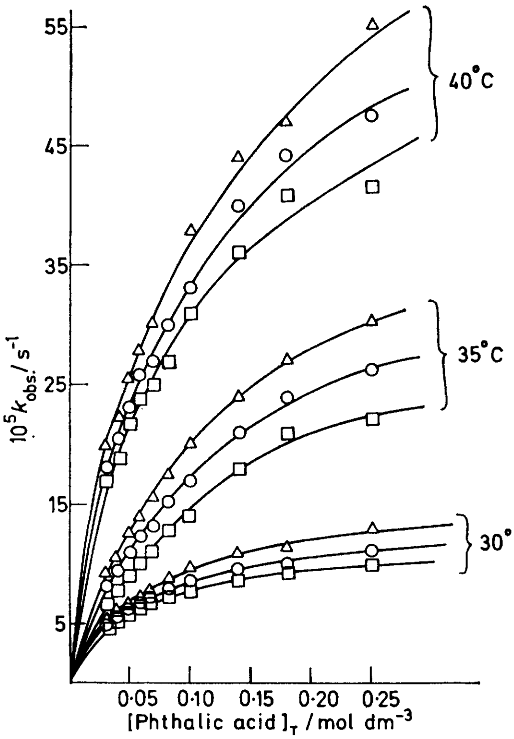

FIGURE 1 Dependence of k_{obs} on $[\text{Phthalic acid}]_T$ at $[Cr^{III}] = 4.0 \times 10^{-3}$ mol dm^{-3} and $I = 1.0$ mol dm^{-3}, $[H^+] = 0.25 \times 10^{-3}$ (△), 0.99×10^{-3} (○), and 3.16×10^{-3} mol dm^{-3} (□)

The reaction of $[Cr(OH_2)_6]^{3+}$ with different ligands was studied by Espenson[14] who pointed out the possibility of the interaction of $[Cr(OH_2)_6]^{3+}$ with ionized ligands and of $[Cr(OH_2)_5(OH)]^{2+}$ with un-ionized ligands to give the same product. It was also pointed out that kinetic studies could not differentiate the two paths, since the two transition states have the same composition, and there is a ' proton ambiguity ' in the mechanism of monosubstituted chromium(III) complexes in aqueous solutions. Similar conclusions were made for the formation of monosubstituted chromium(III) complexes.[15] The

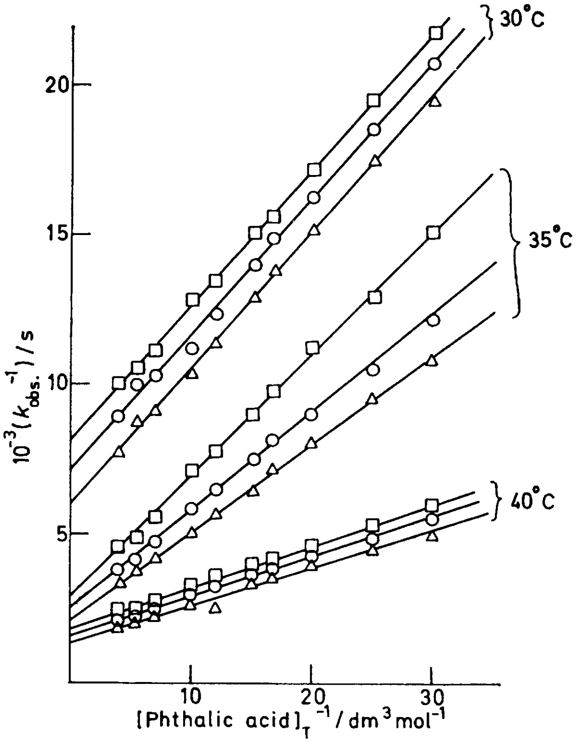

FIGURE 2 Linear dependence of $k_{obs.}^{-1}$ against $[\text{phthalic acid}]_T^{-1}$ under the conditions in Figure 1. Lines show calculated values and points observed values

value of k_{ex} (first-order rate constant for water exchange) was found to be greater than k_{an} (first-order rate constant for anation). However, in our case, $k_{an} > k_{ex}$ in both steps and leads us to conclude that the process is of the associative-interchange (I_a) type and the reaction should take place between $[Cr(OH_2)_6]^{3+}$ and ionized species, not between $[Cr(OH_2)_5(OH)]^{2+}$ and un-ionized species. The I_a process has also been proposed by Stranks and Swaddle[7] from the effect of pressure on the rate of exchange of $H_2{}^{18}O$. The values of the thermodynamic parameters summarized in Table 3 also support the I_a process as discussed by Swaddle[8] and Sasaki and Sykes.[16]

TABLE 3

Activation parameters, calculated from the values of the rate constants recorded in Table 1 using the Eyring equation, at $[H^+] = 0.25 \times 10^{-3}$ mol dm^{-3} and $I = 1.0$ mol dm^{-3}

Rate parameter	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
k_{an}	93	-5 ± 2
k_{an}'	94	-2 ± 1
k_{ex} *	109	
	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
K_I	-8 ± 3	-11 ± 8
K_I'	-8 ± 1	-19 ± 2

* From R. A. Plane and H. Taube, *J. Phys. Chem.*, 1952, **56**, 33.

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