

Kinetic and mechanistic studies on substitution reactions of oxalato ligands from tris(oxalato)chromate (III) with bis-(2-aminoethyl)-amin-N,N,N',N'',N'''-pentaacetic acid (DTPA)

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The kinetics of substitution of oxalato from tris(oxalato)chromate(III) with bis-(2-aminoethyl)-amin-N,N,N',N'',N'''-pentaacetic acid (DTPA) has been studied spectrophotometrically in alkaline medium. From the observed dependence of the rate on pH and DTPA concentration a probable mechanism has been suggested for the overall change involving two concurrent paths; corresponding ΔH^\ddagger and ΔS^\ddagger values have also been determined. The rates are found to be dependent on ionic strength and independent of nature of different electrolytes.

The kinetics of substitution reactions in octahedral chromium(III) and cobalt(III) are still of interest due to their importance in biological and physical sciences. In the last two decades ligand substitution reactions of octahedral complexes of chromium(III) and cobalt(III) have been investigated extensively¹⁻¹². In spite of that work on chromium(III) complexes, many questions are still unsolved and no single mechanism is sufficient to explain the variety of observations and as such controversy among different authors persists related to mechanisms. A fairly large volume of work has been reported on the reactions of aquated-metal ions with multidentate ligands^{1,6,7-10} but so far little work on the mechanistic aspects of metal complexes involving the replacement of chelating ligand by a multidentate ligand has been carried out. It was, therefore, thought worthwhile to study the kinetics of the title reaction which involved the substitution of a chelating agent by a multidentate ligand.

Experimental

Potassium tris(oxalato)chromate(III) [$K_3[Cr(ox)_3]$] (complex-I) was prepared by literature method

and characterised by elemental analysis. Absorption spectrum of complex-I solution (3×10^{-3} mol dm^{-3}) in water recorded by a CECIL ultraviolet double beam spectrophotometer exhibits λ_{max} at 590 nm which is similar to that reported in literature⁴. The composition of the product complex (complex-II) was determined by recording the spectra of three different solutions thermally equilibrated at 338.15K for 24 h in which the concentration of the complex-I and DTPA were maintained at 1:1, 1:2 and 1:3 ratios. All the three compositions exhibited identical spectra having maximum absorption at 582 nm. The 1:1 metal ligand composition of the product (complex-II) was verified by Job's method of continuous variation. Spectral changes with time associated with the product complex showed a clear isobestic point at 450 nm throughout the period in which the data were recorded. The spectra of complex-II obtained from $[Cr(ox)_3]^{3-} + DTPA$ system matches the spectra obtained from $[Cr(en)_3]^{3+} + DTPA$ system, isolated $[Cr(DTPA)]^{2-}$ complex and the $[Cr(DTPA)]^{2-}$ obtained from Aldrich. The λ_{max} in all the cases have been observed at 582 nm. This confirms the formation of $[Cr(DTPA)]^{2-}$ complex ion in the present study.

AR grade chemicals and doubly distilled water was used throughout the experiment. Potassium nitrate was used to adjust the ionic strength of the reaction medium and the pH of the medium was adjusted (Systronic Digital pH meter, 335) with the addition of $HNO_3/NaOH$. Freshly prepared solutions of the complex-I and the ligand were employed throughout the experiment. All kinetic experimentals were carried out spectrophotometrically at 490 nm where a substantial difference existed between the absorption of complex-I and complex-II as a function of time. The ligand concentration was always high so that the pseudo-first order rate law could be applied. The pseudo-first order rate constants (k_{obs}) were evaluated graphically from the slope of the linear plot of $\log(A_\infty - A_t)/(A_\infty - A_0)$ versus time (t), where A_∞ , A_t and A_0 were the absorbance at infinite time, at an arbitrary time ' t ' and the beginning of the reaction, respectively. The temperature was controlled within $\pm 0.1^\circ C$. The reported k_{obs} values represent an average of three replicate runs and all values were reproducible within $\pm 3\%$ error limits.

Table 1—Variation of rate constant with pH
 $[\text{Cr}(\text{ox})_3]^{3-} = 0.003 \text{ mol dm}^{-3}$, $[\text{DTPA}] = 0.02 \text{ mol dm}^{-3}$,
 $\mu = 0.25 \text{ mol dm}^{-3}$ and temp. = 338.15 K

pH	$k_{\text{obs}} \times 10^5 (\text{s}^{-1})$	pH	$k_{\text{obs}} \times 10^5 (\text{s}^{-1})$
9.30	4.90	10.30	58.10
9.60	16.80	10.60	73.10
10.00	46.00	11.00	162.40

Results and discussion

Effect of varying [complex-I] on rate constant

At fixed $[\text{DTPA}] = 0.02 \text{ mol dm}^{-3}$, pH 9.60, ionic strength (μ) = 0.25 mol dm^{-3} , temp. = 338.15K and at six different $[\text{complex-I}]$ (0.001, 0.002, 0.003, 0.004, 0.005 and 0.006 mol dm^{-3}) the $10^4 \times k_{\text{obs}}$ values were 1.69, 1.68, 1.68, 1.68, 1.80 and 1.71 s^{-1} , respectively. The data indicate that the reaction is first order in $[\text{complex-I}]$.

Effect of varying pH on rate constant

The k_{obs} values at fixed $[\text{complex-I}]$ (0.003 mol dm^{-3}), ionic strength (0.25 mol dm^{-3}), $[\text{DTPA}]$ (0.02 mol dm^{-3}) and temperature 338.15K and at pH values ranging from 9.30 to 11.00 are given in Table 1. The rate constant values have been found to increase with increase in pH. The increase in reaction rate with increase in pH can be explained by considering the addition of OH⁻ group to the carbonyl group^{13,14}. Moreover DTPA species (HL^{4-}) predominantly exists in the zwitter ion form similar to EDTA¹⁵ and it is quite possible for the zwitter ion to orient with its positive end pointing towards the anionic complex-I and thus causing specific electrostatic interactions as in an ion pair⁴.

Effect of varying [DTPA] on rate constant

At fixed $[\text{complex-I}]$ (0.003 mol dm^{-3} , ionic strength (0.25 mol dm^{-3}) and pH (9.60), the $[\text{DTPA}]$ was varied in the range 0.01 to 0.045 mol dm^{-3} at 313.15, 318.15, 323.15, 328.15 and 338.15K. In each case the k_{obs} versus $[\text{DTPA}]$ plot is linear at all the temperatures with an intercept (Fig. 1).

Effect of varying ionic strength

In these experiments $[\text{complex-I}]$ and $[\text{DTPA}]$ were kept constant at 0.003 and 0.02 mol dm^{-3} , respectively. The $10^4 \times k_{\text{obs}}$ values were 1.68, 3.11, 3.84, 5.87 and 6.72 s^{-1} at 0.25, 0.50, 0.75, 1.00 and 2.00 mol dm^{-3} ionic strength at 338.15K.

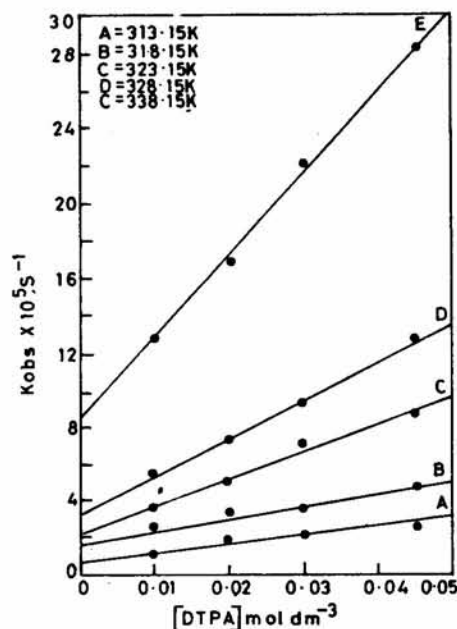
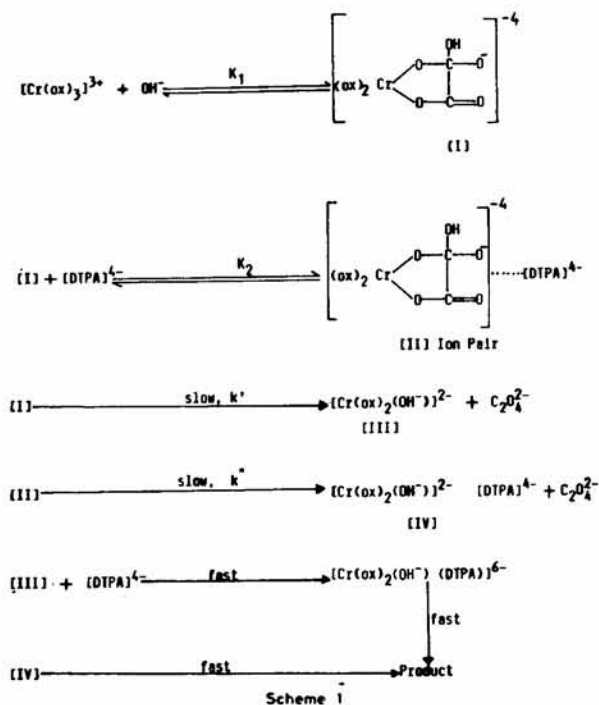


Fig. 1—Effect of DTPA concentration on rate constant at various temperatures. $[\text{Cr}(\text{ox})_3]^{3-} = 3 \times 10^{-3} \text{ mol dm}^{-3}$; $\mu = 0.25 \text{ mol dm}^{-3}$; pH = 9.6



The increase in the rate constant values with the ionic strength is in agreement for a reaction between ions having similar charges⁴. The value of $Z_A \cdot Z_B$ was 1.04, which is smaller than the expected value if only the reactants were $[\text{Cr}(\text{ox})_3]^{3-}$ and DTPA^{5-} . The factor which appears to affect the value is the possible formation of ion pairs of

Table 2—Rate constants k_1 and k_2 at different temperatures

Temp. (K)	$k_1 \times 10^5 (s^{-1})$	$k_2 \times 10^5 (mol s^{-1})$
313.15	0.6	5.2
318.15	1.6	6.8
323.15	2.2	15.0
328.15	3.2	20.0
338.15	8.4	43.0

$[Cr(ox)_3]^{3-}$ and $DTPA^{5-}$ with the K^+ ions present in sufficient concentration in the reaction medium¹⁶. A series of runs at pH 9.60 to study the effect of different inert electrolytes ($NaNO_3$, KNO_3 , KCl , $NaCl$ and $NaClO_4$) on the rate constant indicated that the k_{obs} values increased on changing Na^+ to K^+ ion.

Based on the results the reaction steps in Scheme I may be proposed to explain the variation in rate with $[DTPA]$ and pH .

On the basis of Scheme I the following rate expression can be deduced:

$$k_{obs} = [k' \cdot K_1 [OH^-] + k'' \cdot K_1 \cdot K_2 [OH^-] [DTPA]^{4-}]$$

but

$$[OH^-] = K_w / [H^+]$$

then

$$k_{obs} = \left[\frac{k' \cdot K_1 \cdot K_w}{[H^+]} \right] + \left[\frac{k'' \cdot K_1 \cdot K_2 \cdot K_w}{[H^+]} \times [DTPA]^{4-} \right]$$

and

$$\frac{k' \cdot K_1 \cdot K_w}{[H^+]} = k_1; \quad \frac{k'' \cdot K_1 \cdot K_2 \cdot K_w}{[H^+]} = k_2$$

so

$$k_{obs} = [k_1 + k_2 [DTPA]^{4-}]$$

where k_1 and k_2 are the gross rate constants evaluated from the intercept and slope, respectively, of the linear plot of k_{obs} versus $[DTPA]$ (Fig. 1). The values of k_1 and k_2 are given in Table 2.

The activation parameters corresponding to the two independent concurrent reaction paths have also been calculated by using Eyring equation and found to be:

$$\text{Path I—}(\Delta H_1^\ddagger = 32.18 \text{ kJ mol}^{-1};$$

$$\Delta S_1^\ddagger = -47.15 \text{ JK}^{-1} \text{ mol}^{-1})$$

$$\text{Path II—}(\Delta H_2^\ddagger = 37.79 \text{ kJ mol}^{-1};$$

$$\Delta S_2^\ddagger = -13.14 \text{ JK}^{-1} \text{ mol}^{-1})$$

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