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A High Performance Liquid Chromatography Investigation of the Nucleophilic Substitution of *trans*-bis(thiosulphato)bis(ethylenediamine)cobaltate(III) in Water

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The use of high pressure liquid chromatography, HPLC, as a quantitative analytical technique in kinetic studies of ionic complexes has lagged considerably behind the advances achieved in the organic field, although some work has now begun to appear [1]. In this paper we present a preliminary account of a study which would be impossible using the older analytical techniques since it depends on the analysis of mixtures of complexes having very similar physical and spectral properties.

We have established by kinetic and competition studies that the nucleophilic substitution of *trans*-$Coen_2(S_2O_3)_2^-$, (en = ethylenediamine), takes place via a simple dissociative D-type mechanism [2] probably *via* a square pyramidal and highly reactive intermediate $Coen_2(S_2O_3)^+$.

Experimental

The thiosulphatobis(ethylenediamine)cobalt(III) complexes used were prepared using methods described in the literature [3, 4]. Other chemicals were used without further purification.

HPLC analysis [5] was performed using a Perkin-Elmer Series 3B Chromatograph, LC-75 photometric detector and Hewlett-Packard 3380S integrator. The separations were produced using a 25 × 0.5 cm Spherisorb-5 ODS column and an aqueous eluent containing 0.3% tributylmethylammonium bromide adjusted to a pH between 4 and 5 with perchloric acid.

The kinetic experiments were carried out at 25 °C and unit ionic strength maintained with sodium perchlorate. The procedure was the same for every run. A solution containing all the reagents except $Coen_2(S_2O_3)_2^-$ was equilibrated in a thermostat at 25 °C for 15 min. The necessary amount of solid complex to produce a final concentration of 0.01 *M* was then dissolved by vigourously shaking the flask for about 20 sec. Subsequently 1 ml aliquots of the solution were diluted to 10 ml at 0 °C and 20 µl of the product were analysed by HPLC.

Results and Discussion

The stoicheiometric reaction:

$$trans\text{-}Coen_2(S_2O_3)_2^- + X^- \longrightarrow trans\text{-}Coen_2(S_2O_3)X + S_2O_3^{2-} \qquad (1)$$

occurs apparently with complete retention of stereochemistry, at least during the first 100 minutes of reaction.

Generally the conventional plot [6] for two opposed pseudo-first order reactions, reactions (1) and (−1), is linear and its slop is denoted by k_{obs}. The forward rate constant k is calculated from equation (2),

$$k = k_{obs}/(1 + R_\infty) \qquad (2)$$

where R_∞ is the ratio of the concentrations of the reactant and product at equilibrium and is made after at least 10 half-lives. Reactions between equal concentrations of complex and nucleophile, (0.01 *M*), were not pseudo-first order and in those cases a simple log plot of reactant concentration and time was used. The gradients of this curve were corrected individually for the back-reaction using the corresponding reactant and product concentrations and the equilibrium constant K_{1X}. At this nucleophile concentration the rate of the first 10% of the reaction can be up to a factor of 3 slower than that expected on the basis of the remaining reaction. The same acceleractory period occurs in the hydrolysis reaction and seems to be suppressed by the addition or the formation of the thiosulphate anion. The kinetic analysis was based on data taken after the acceleratory period.

The hydrolysis reaction, $X^- = H_2O$, was not studied in detail but the rate constant for the formation of *trans*-$Coen_2(S_2O_3)(H_2O)^+$ observed at 0.01 *M* total complex concentration, ($6 < pH < 7$), was 3.5×10^{-5} s^{-1}. The value extrapolated from studies [7] of the base catalysed hydrolysis of 0.005 *M* complex is 2.3×10^{-4} s^{-1}. In the latter case the ionic strength was 0.5 rather than 1 and several corrections were needed to allow for the base catalysed path, isomerisation and hydrolysis to $Coen_2(OH_2)_2^{3+}$ but the discrepancy remains surprising and a further study is in progress. Under our conditions, $6 < pH < 7$, hydrolysis is of minor importance since at equilibrium only 6% of a 0.01 *M* solution hydrolyses and

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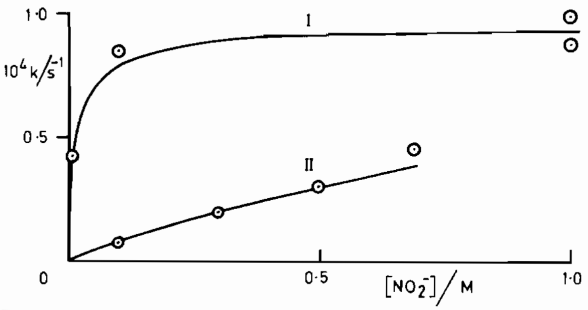

Fig. 1. Variation of k with nitrite ion concentration. Temperature = 25 °C, ionic strength = 1 ($NaClO_4$); Curve I: $[S_2O_3^{2-}] = 10^{-3}$ *M*, Curve II; $[S_2O_3^{2-}] = 0.1$ *M*.

there is no evidence of the formation of $Coen_2(OH_2)_2^{3+}$.

The rate constant for the substitution of thiosulphate by X^- tends to a limiting value at high nucleophile concentrations although in the presence of 0.1 *M* thiosulphate this limiting behaviour disappears. All cases closely resemble the example shown in the figure for X = NO_2^-. Such kinetic behaviour is consistent with a dissociative mechanism similar to that proposed for the related substitution reactions of other cobalt complexes containing *trans*-sulphur bonded ligands [8]:

$$trans\text{-}Coen_2(S_2O_3)_2^- \longrightarrow Coen_2(S_2O_3)^+ + S_2O_3^{2-} \quad (3)$$

$$Coen_2(S_2O_3)^+ + S_2O_3^{2-} \longrightarrow trans\text{-}Coen_2(S_2O_3)_2^- \quad (4)$$

$$Coen_2(S_2O_3)^+ + X^- \longrightarrow trans\text{-}Coen_2(S_2O_3)X \quad (5)$$

Assuming a steady state concentration for $Coen_2(S_2O_3)^+$:

$$k = \frac{k_3 k_{5,X}[X^-]}{k_{5,H_2O}[H_2O] + k_{5,X}[X^-] + k_4[S_2O_3^{2-}]} \quad (6)$$

The data for X = N_3^-, NCS^-, NO_2^- and $CH_3CO_2^-$ fit an equation of this form although in all cases k_{5,H_2O} is too small to allow it to be calculated from the rate measurements. The solid lines in Fig. 1 correspond to the equation:

$$k = \frac{[NO_2^-]}{A[NO_2^-] + B[S_2O_3^{2-}]} \quad (7)$$

where $A = 1.04 \times 10^4\ s^{-1}$ and $B = 1.08 \times 10^5\ s^{-1}$.

The constants A and B do not vary markedly with the nature of X^- suggesting that the rate constant for reaction (5) is the same for all nucleophiles used. Competition studies confirmed this result directly using nucleophile mixtures N_3^-–NCS^-, NO_2^-–NCS^- and NO_2^-–$CH_3CO_2^-$.

The possibility exists that the labile aquo-complex *trans*-$Coen_2(S_2O_3)(H_2O)^+$ acts as the intermediate in the formation of $Coen_2(S_2O_3)X$ but it seems unlikely in view of the three following lines of argument:

1. The initial rate of formation of $Coen_2(S_2O_3)X$ is not zero.

2. The inhibitory effect of the thiosulphate ion is not correctly predicted by the alternative mechanism:

$$Coen_2(S_2O_3)_2^- \rightleftharpoons Coen_2(S_2O_3)(H_2O)^+ + S_2O_3^{2-} \quad (8)$$

$$Coen_2(S_2O_3)(H_2O)^+ + NO_2^- \longrightarrow Coen_2(S_2O_3)(NO_2) + H_2O \quad (9)$$

The term B in eqn. (7) deduced from this model is $1/k_9K_8$ where K_8 is the equilibrium constant for the hydrolysis reaction (8). Since we have found $K_8 = 4 \times 10^{-5}$ mol l^{-1} and $k_9 = 0.043$ l mol^{-1} s^{-1} [3] the value of B should be 5.8×10^5 in gross disagreement with the value observed, 1.08×10^5.

3. The concentration of $Coen_2(S_2O_3)(H_2O)^+$ required to give the observed values of k for X = NCS^- and NO_2^- may be calculated from the known anation rate constants [3]. The observed concentrations are all at least a factor of ten less than those calculated.

In short, we have concluded that the evidence supports the hypothesis that the nucleophilic substitution of $Coen_2(S_2O_3)_2^-$ takes place via a simple D-type mechanism involving the highly reactive intermediate $Coen_2(S_2O_3)^+$ and that this intermediate is probably square pyramidal in view of the retention of configuration during substitution.

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