AN ATOMIC ABSORPTION/ION-EXCHANGE TECHNIQUE FOR THE ANALYSIS OF CHROMIUM COMPLEX MULTISTAGE REACTIONS

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SUMMARY

Chromium (III) complex ions at low concentrations (p.p.m.) can be separated rapidly on small ion-exchange columns and the chromium content of the eluted fractions measured directly by atomic absorption spectroscopy. The $Cren_2ox^+$ ion undergoes four successive displacement reactions in its hydrolysis. Using the atomic absorption/ion-exchange technique four product ions are characterized and rate constants found for the four displacement steps.

INTRODUCTION

Although many substitutionally inert complexes of chromium (III) are known, the study of the kinetics and mechanisms of their reactions is much less well developed than for cobalt(III)[1]. Two major difficulties have hindered the systematic study of chromium complexes, firstly the difficulty of preparing a suitable range of complexes for study and secondly the complexity of the reactions. Whereas cobalt(III) amine complexes of the type $Co(N)_4X_2^+$ (where (N) is any amine ligand) almost invariably hydrolyse with the loss of the non-amine ligands, X, and have a single rate determining step, the chromium complex *trans*-$Cren_2Cl_2^+$ hydrolyses with Cr–N bond fission competing with Cr–Cl bond fission[2]. We have also found a complex pattern of hydrolysis for the $Cren_2ox^+$ ion (en = ethylenediamine; ox = oxalate $C_2O_4^{2-}$) and this is reported in the present work.

Ion-exchange chromatography has proved an invaluable aid in the preparation of pure chromium complexes and in reaction product analysis[2-4]. In theory the reaction products for most reactions can be separated chromatographically and hence the progress of a reaction can be followed and the rate constants obtained directly. In practice the technique has seldom been used. Reactions are usually followed spectrophotometrically but the spectral changes involved are open to misinterpretation.

Direct chromatographic separation of chromium complexes is usually carried out either with relatively high (0.01 M) complex ion concentrations so that band

separation can be followed visually and the spectra of the eluted product solutions obtained directly, or with lower complex ion concentrations when the chromium content of the eluate fractions is obtained spectrophotometrically after oxidation to chromate(VI)[5]. Both of the above techniques are slow, impracticable for reactions with half-lives less than 1 h, and inconvenient for the collection of large amounts of kinetic data.

In our studies of the hydrolysis of the $Cren_2ox^+$ ion, we found that the spectral changes were complex and four major reaction products occur in significant concentration. In order to follow directly the changes in reactant and product ion concentrations we have devised a technique in which rapid chromatographic separation of the chromium complexes at low concentrations (p.p.m.) is coupled to direct chromium analysis by means of atomic absorption spectroscopy. We believe that this technique will be of great value in the general study of the reactions of chromium and other metal complex ions in solution.

EXPERIMENTAL

Reagents

$Cren_2oxBr \cdot H_2O$ was prepared via $Cren_2oxCrenox_2 \cdot 2H_2O$ according to SCHLESSINGER's[6] method, recrystallized from water (333K) and used directly to give solutions of the $Cren_2ox^+$ ion. Elemental analysis agreed with the suggested formula, $Cren_2oxBr \cdot H_2O$. Calculated: C, 20.1%; H, 5.04%; N, 15.6%. Found: C, 19.8%; H, 5.00%; N, 15.5%. $Crenox(H_2O)_2Br \cdot H_2O$ was prepared from $Cren_2oxCrenox_2 \cdot 2H_2O$ as described by WERNER[7], the complex was recrystallized from dilute hydrobromic acid (2 M, 323K) and then used to give solutions of the $Crenox(H_2O)_2^+$ ion. Elemental analysis was in agreement with WERNER's formula, $Crenox(H_2O)_2Br \cdot H_2O$. Calculated: C, 14.3%; H, 4.2%; N, 8.4%. Found: C, 14.5%; H, 4.3%; N, 8.6%.

Ion-exchange resins and chromatographic columns

Zeocarb 225, 8% DVB, 100–200 mesh, H^+ form, was used for the separation of cationic complexes. Deacidite FF-IP, 100–200 mesh, OH^- form, was used for the separation of anionic complexes.

5 mm diameter × 30 mm columns were used for the complete separation of the complex ions. 10 mm diameter × 30 mm columns were used for the preparation of solutions of selected ions for separate study. The columns were eluted under slight positive pressure giving flow rates of 5–10 cm^3 min^{-1}.

Atomic absorption analysis

The Unicam SP 90 and Techtron Atomic Absorption Spectrometers were used with chromium lamps under standard conditions. Chromium standards were prepared from AR potassium dichromate with chromium concentrations in the range of 0 to 10 p.p.m. Separate experiments were used to show that the chromium signal was independent of the chemical state of the chromium in solution[8]. The signal was dependent on the total ion content of the solutions (e.g., 1 M HNO_3 and 1 M $NaNO_3$ depressed the signal by 6% and 8%, respectively) and sets of standards were prepared with acid and salt concentrations matching those of the

column eluents. Chromium concentrations in the range of interest, 0–4 p.p.m., were obtained with an accuracy of ± 0.02 p.p.m. Cr.

Procedure for kinetics

Solutions of the complex ions were prepared either directly by dissolving the appropriate salts (Cren$_2$oxBr, Crenox(H$_2$O)$_2$Br) in solutions of the required acid and ionic strength at the working temperature, or by adjusting the ion content of solutions obtained by column separation (Cren(enH)ox^{2+}, Cr(enH)ox(H$_2$O)$_2$$^{2+}$). and then allowing the solutions to come to temperature equilibrium before taking the first aliquot. All reaction flasks were shielded against light to prevent photochemical decomposition.
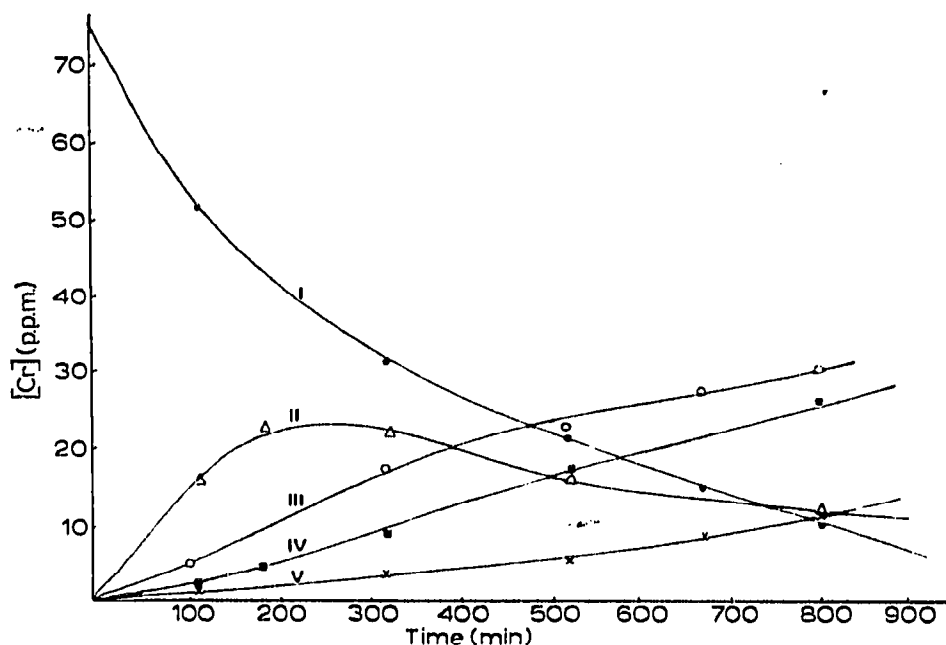

Fig. 1. The growth and decay of product ions during the hydrolysis of Cren$_2$ox$^+$ in 0.1 M HCl at 308K. Eluting acid strength: (I) 0.2 mole/l; (II) 5.0 moles/l, (III) 0.05 mole/l; (IV) 0.5 mole/l; (V) 0.01 mole/l.

The thermostat bath was controlled to ± 0.01K. Aliquots of the reactant solutions (1–10 cm^3) containing about 5 mg of total chromium were run onto the columns at appropriate times and the component ions selectively eluted according to the predetermined pattern (using increasing concentrations of HNO$_3$ or HCl for cations, NaCl for anions). The chromium content of the eluted fractions was determined directly by atomic absorption. The chromium content of eluate fractions with volumes down to 1 cm^3 could readily be determined.

RESULTS AND DISCUSSION

The characterization of reaction products.

In earlier work on the hydrolysis of the Cren$_2$ox$^+$ ion, other workers have identified one[9] or two[10] reaction products. We have isolated and characterized four products which can be separated by selective elution from the cation-exchange

TABLE I

MAIN IONS SEPARATED DURING THE ACID HYDROLYSIS OF $Cren_2ox^+$

Ion	Eluting acid (HCl) concentration (M)	Volume (cm³)	$\lambda_{max.}$ (nm)	E	$\lambda_{max.}$ (nm)	E
$Cren_2ox^+$(I)	0.2	20	372	85	496	91
$Cren(enH)ox^{2+}$(II)	5.0	120	392	65	524	52
$Crenox(H_2O)_2^+$(III)	0.05	150	394	63	524	60
$Cr(enH)ox(H_2O)_2^{2+}$(IV)	0.5	80	409	45	549	36
$Crox(H_2O)_4^+$(V)	0.01	40	420	47	563	38

columns as shown in Table I. The spectra of the ions (I) and (V) are in good agreement with published values[11,12]. The ions (II) and (IV), which are here characterized for the first time, are considered to be formed by protonation of ions (I) and (III), respectively, probably with ring opening and incorporation of an additional water molecule in the inner coordination sphere. The hydrolysis was also followed by addition of acid to maintain a constant pH and this work confirmed the uptake of one proton to give (II) and of a further proton to give (III) and the fully protonated free ethylenediamine. The formation of (IV) from (III) is expected to be a very similar reaction.

BROOMHEAD et al.[10] reported a similar spectrum to that of (II) for one of two products found at 343K, but its early elution from their column and the high coefficient of absorption at the longer wavelength suggests that the product may be (III) since the spectra are very similar. The close similarity of the spectra of (II) and (III) has the effect of allowing approximate but not sharp isosbestic points to be observed during the initial stages of the hydrolysis of (I), but conventional plots of the change of absorbance with time do not correspond to first-order kinetics. The spectrum of (III) is identical with that of a solution of $Crenox(H_2O)_2^+$ prepared as the bromide by WERNER's method[7]. VALENTIN reported this ion as the only product of the photolytic decomposition of (I)[9], but we find that the photolytic reaction is also a multi-step process.

In addition to the above, certain other products can form. More concentrated solutions of (I), 0.1 M, slowly give a deposit of the insoluble red double complex salt, $Cren_2oxCrenox_2 \cdot 2H_2O$. A very small proportion of the chromium in aged 0.008 M solutions (1 %) could not be retained on a cation-exchange column. These observations suggest that the ion $Crenox_2^+$ may be formed in a side reaction possibly involving intermolecular rearrangement since at no time have we been able to detect free oxalate in these solutions. An insoluble purple compound, noticed by a number of workers[13,14], forms as ethylenediamine is liberated from unbuffered solutions of (I) or (III) and when the pH of the solutions becomes greater than 6. We have identified this compound by elemental analysis and infrared spectrum as $Crenox(OH)H_2O$, and it was identical with the compound first prepared by WERNER[7] from solutions of (III).

Reaction kinetics

The major aquation path for the $Cren_2ox^+$ ion involves the successive dis-

placement of the two ethylenediamine groups, each being lost in a two-step process. There is thus a sequence of four first-order or pseudo-first-order reactions.

$$\text{I} — k_1 \rightarrow \text{II} — k_2 \rightarrow \text{III} — k_3 \rightarrow \text{IV} — k_4 \rightarrow \text{V}$$

Typical growth and decay curves for the various species at 308.1K, obtained from the chromatographic/atomic absorption analysis, are shown in Fig. 1. We have followed the aquation of the ions (I), (II) and (III) by separating the ions from their aquation products and following the decrease in their concentration by atomic absorption; in all cases good first-order plots were obtained. After isolating ion (IV), its decomposition to the stable ion (V) has been studied spectrophotometrically since the absorption changes for this single-stage reaction can be interpreted unequivocally. Values obtained for the rate constants of the successive steps under standard conditions are given in Table II.

TABLE II .

RATE CONSTANTS FOR THE SUCCESSIVE HYDROLYSIS STEPS OF $Cren_2ox^+$, IN 0.1 M ACID (HCl, $HClO_4$, HNO_3) AT UNIT IONIC STRENGTH

Ion	Initial ion concentration (mM)	Temperature (K)	$10^5 k\ sec^{-1}$
I, $Cren_2ox$ (k_1)	8.0	308.1	4.01
I[a]		308	4.0
II, $Cren(enH)ox^{2+}$ (k_2)	0.3	308.1	5.68
II	8.0[b]	308.1	4.9
III $Crenox(H_2O)_2^+$, (k_3)	8.6	313.0	3.21
III	6.1	323.0	7.14
III	6.1	338.0	35.8
IV, $Cr(enH)ox(H_2O)_2^{2+}$, (k_4)	4.0	338.0	14.0

[a] Calculated from the results of BROOMHEAD et al.[10].

[b] Calculated from k_1 and the ratio k_1/k_2 derived from the maximum concentration of (II) formed during the decomposition of (I)[15].

A comparison of our rate constants with recently published values for the racemization of cis-$Cren_2ox^+$ (ref. 10), as shown in Table II, suggests that in this latter work loss of optical activity is almost entirely due to aquation not racemization.

CONCLUSION

Kinetic studies on the $Cren_2ox^+$ ion were first carried out more than thirty years ago[14] but the system is still incompletely understood. The present study emphasizes the need for careful analysis of reaction products before interpreting kinetic data in any system. The reactions we have investigated so far by the ion-exchange/atomic absorption technique have had half-lives of 1 h or more at room temperature. The method can be used for any reaction for which the complex ions involved are sufficiently stable to be separated effectively, that is having half-lives of 10 min or more at the temperature of the exchange column. Reactions such as the above can be followed at higher temperatures by freezing aliquots of the reaction and subsequently separating the reactant and products in the cooled solutions. We therefore believe that this technique will help considerably in the

study of complex ion reactions, particularly of chromium, as we have shown for the $Cren_2ox^+$ ion.

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