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The oxidation of cis-dioxalatodioquochromate (III)ion by cerium (IV)

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THE OXIDATION OF CIS-DIOXALATODIAQUOCHROMATE(III) ION BY CERIUM(IV).

by

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INTRODUCTION

An investigation of the oxidation of cis-dioxalatodiaquochromate(III) ion by cerium(IV) in aqueous acidic solution is herein reported. The purposes of this work were:

1) To establish the stoichiometry of the reaction.

2) To determine the rate law for the reaction by investigating the effect on the rate of the reaction of varying the concentrations of cis-dioxalatodiaquochromate(III) ion, cerium(IV), sulphate ion, and hydrogen ion.

3) To determine the effect of varying the ionic strength on the rate of the reaction.

4) To interpret the information obtained in parts 1 through 3 , together with other relevant data, in terms of a plausible reaction mechanism.

This investigation forms the initial part of a more general plan to study the influence of the environment of oxalate within oxalatochromate(III) complexes on the rates and mechanisms by which the oxalate is oxidised by various reagents.

The solutions employed contained sulphuric acid. Values of the second dissociation constant of sulphuric acid, that apply to the concentration range used at 25 ^{o}C,

have been determined by Zebroski and co-workers.[21] Hardwick and Robertson[6] have obtained values for the stability constants of the various cerium(IV)-sulphate complexes. Applying these data to aqueous solutions obtained by mixing known amounts of ceric sulphate, sodium sulphate, sulphuric acid, perchloric acid, and sodium perchlorate, the concentrations of the following species, which were present in any particular solution, could be calculated: $SO_4^{=}$, HSO_4^{-}, ClO_4^{-}, Na^{+}, Ce^{+4}, H^{+}, $[Ce\,SO_4]^{+2}$, $[Ce(SO_4)_2]$, and $[Ce(SO_4)_3]^{-2}$.

In the majority of the experiments described in the thesis, ceric ion was present in solutions containing a large excess of sulphate and bisulphate ions. Under these conditions, Hardwick and Robertson's[6] data indicate that most of the cerium(IV) would be in the form of the $[Ce(SO_4)_3]^{-2}$ ion. This conclusion agrees with data obtained earlier, by Jones and Soper[7] and by Smith and Getz,[18] on the electrical migration of ions in ceric sulphate solutions. The migration experiments showed that in one molar sulphuric acid solutions all the cerium(IV) was present in anionic species. In one molar perchloric acid solutions, however, no anionic cerium(IV) species were detected.

The oxidation of oxalate by cerium(IV) in aqueous sulphuric acid solutions has been studied by Dodson and Black[4]. They report that the reaction is kinetically of the second order, being first order in cerium(IV) and first order in oxalate, bioxalate, or

oxalic acid. An experimental activation energy of 16.5 ± 0.4 k. cals/mole is reported for 0.5; 1.0, and 2.0 molar sulphuric acid solutions. The rate of the reaction decreased with increasing ionic strength. The authors concluded that the rate determining step was either:

$$2\left[Ce(SO_4)_3\right]^{-2} + H_2C_2O_4 \rightarrow 2Ce^{+3} + 2CO_2 + 4SO_4^{-2} + 2HSO_4^{-2}$$

or

$$2\left[Ce(SO_4)_3\right]^{-2} + HC_2O_4^{-1} \rightarrow 2Ce^{+3} + 2CO_2 + 5SO_4^{-2} + HSO_4^{-1}$$

(The step given by Dodson and Black would imply a third order reaction. Presumably they mean that the rate determining step is the reduction of a trisulphatocerium(IV) ion by an oxalate molecule.) Ross and Swain[15], who potentiometrically studied the oxidation of oxalate ion by cerium(IV) in acidic solution, also found the reaction to be kinetically of the second order.

King and Pandour[9] studied the oxidation of bromide ion by cerium(IV) in sulphuric acid solutions, and obtained the following expression for the rate of the reaction,

$$\frac{-d(Ce(IV))}{dT} = \frac{(Ce(IV))}{(SO_4^{-2})}\left[k_{12}(Br^-)^2 + k_{11}(Br^-)\right]$$

where k_{12} and k_{11} are constants.

From this expression they concluded that the reaction proceeds through parallel paths involving the two activated complexes $\left[Ce(SO_4)_2Br_2\right]^{-2}$ and $\left[Ce(SO_4)_2Br\right]^{-1}$.

In solution, cis-dioxalatodiaquochromate(III) ion is in equilibrium with its trans isomer. This equilibrium has been studied by Hamm[5], who found the equilibrium mixture to be composed almost entirely of the cis isomer. A solution of the trans-dioxalatodiaquochromate(III) ion

rapidly equilibrates, with a half-life of approximately 20 minutes at 25.0°C. The equilibration is first order with respect to the cis ion concentration, and is practically independent of the hydrogen ion concentration and the ionic strength. Cunningham[3] recommends that solutions of the various salts containing the cis-dioxalatodiaquochromate(III) anion be prepared by heating solutions of the corresponding trans salts. The trans anion is readily obtainable in a pure form as its potassium salt, because potassium trans-dioxalatodiaquochromate(III) is fairly insoluble in water.

Assuming that the oxalate to chromium bonds in cis-dioxalatodiaquochromate(III) ion and trioxalatochromate(III) ion are similar, an indication of the nature of the cis-dioxalato ion in solution may be obtained from a consideration of the properties of the trioxalato ion in solution. Trioxalatochromate(III) ion may be resolved into a pair of enantiomorphs. These enantiomorphs racemise in solution. (Cis-dioxalatodiaquochromate(III) ion is also theoretically capable of resolution). It was originally suggested by Werner[20] that racemisation of the trioxalato ion in solution might involve the breaking of only one of the bonds between the chromium and a given oxalate addendum. Reattachment of the freed end of the oxalate, at a different coordination position, could involve inversion of the optical form of that ion.

Much later, exchange experiments were conducted by Long[10] using oxalate ions labelled with carbon 11. They showed that in the time required for a solution of a potassium trioxalatochromate enantiomorph to racemise, no appreciable exchange took place between bound oxalate and oxalate in solution. It was therefore concluded that an internal racemisation mechanism was involved.

In 1922, Rideal and Thomas[14] separated the enantiomorphs of trioxalatochromate(III)ion, utilizing the differing solubilities of the potassium d-strychnine salts. Later, Bushra and Johnson[2] resolved the following ions by similar methods: $\left[Cr(C_2O_4)_3\right]^{-3}$, $\left[Co(C_2O_4)_3\right]^{-3}$, and $\left[Cr(\text{ethylenediamine})(C_2O_4)_2\right]^{-1}$. They then studied the kinetics of racemisation of solutions of these ions. The results of this work indicated that the racemisation took place by some form of internal mechanism not involving dissociation of the ligands. Investigations by Johnson[8] revealed that a wide variety of metal ions catalysed racemisation reactions of chromium and cobalt complexes.

The above experiments suggest that bonds between the central metal ion and the oxalate addenda are continually breaking and then reforming; not necessarily at the coordination position where the original breaking took place. It is not unreasonable to assume that in potassium cis-dioxalatodiaquochromate(III) solutions, bonds between the chromium and the oxalate addenda are continually breaking in a similar manner.

Parker and Hatchard[13] have obtained evidence which could possibly supplement the above conclusions. They exposed solutions of potassium trioxalatoferrate(III) and potassium trioxalatocobaltate(III) to intense flashes of visible radiation. Immediately after this flash photolysis, the spectra of the reaction mixtures indicated the presence of intermediates, which existed for several seconds. They postulate that these intermediates could consist of oxalate addenda attached to the metal atom by single bonds.

Very recently, Saffir and Taube[16] have studied the oxidation of monooxalatopentamminecobalt(III) ion by cerium(IV). They found that the reaction proceeded with almost perfect stoichiometry, one equivalent of the cerium(IV) being consumed by one mole of the cobalt(III) complex, with the production of one equivalent of cobalt(II).

They conclude that probably the cerium(IV) first attached an oxalate addendum to form a $C_2O_4^-$ radical. This radical is then a powerful enough reducing agent to reduce cobalt(III) to cobalt(II). They did not establish whether the reduction took place in the activated complex, or whether an intermediate, of finite life, is formed.

EXPERIMENTAL

I. REAGENTS EMPLOYED

The sulphuric acid, perchloric acid, sodium sulphate decahydrate, and sodium perchlorate, used in this work, were Baker's "Analyzed Reagent" materials, obtained from the J. T. Baker Chemical Company, Philipsburg, N.J. Standardized ceric sulphate in sulphuric acid solution was purchased from the G. Frederick Smith Chemical Company, Columbus, Ohio.

II. PREPARATION, PURIFICATION, AND ANALYSIS OF REAGENTS

Potassium trans-dioxalatodiaquochromate(III) was prepared from oxalic acid and potassium dichromate.[12a] The trans salt was readily obtained by crystallization from the reaction mixture, because its solubility in water is much less than that of the reagents from which it is prepared. (Potassium cis-dioxalatodiaquochromate-(III) is much more soluble.) Then it was recrystallized from water.

The potassium trans-dioxalatodiaquochromate(III) obtained was dissolved in water and passed through Dowex 50W-X8 cationic exchange resin; the resin being in its potassium form. This treatment was undertaken to replace chromium containing cationic species by potassium ions. The effluent solution was then passed

through Dowex 1-X8 anionic exchange resin, in the perchlorate form, in an attempt to separate the potassium dioxalatodiaquochromate(III) from anionic impurities. In the time required for these operations, the dioxalatodiaquochromate(III) ion equilibrated between its cis and trans forms,[5] it was assumed.

The resultant solution was analyzed for chromium[19b] and oxalate[19c] by standard analytical procedures. The chromium analysis involved oxidation of chromium with potassium persulphate to give a potassium dichromate solution. The dichromate ion was then titrated with a standard ferrous ammonium sulphate solution. The oxalate analysis involved decomposing the complex by heating with concentrated sodium hydroxide solution. The chromic hydroxide, which was formed, was removed by filtration. The filtrate contained sodium oxalate, which was titrated with a standard ceric sulphate solution.

The analytical results obtained usually indicated a ratio of one mole of chromium to approximately 2.02 moles of oxalate in a sample of potassium dioxalatodiaquochromate(III) solution. These results could be caused by analytical errors or inefficient removal of oxalate (present in solution as $C_2O_4^{-2}$, $HC_2O_4^{-1}$, and a trace of $H_2C_2O_4$) by the anionic exchange resin.

The standardized potassium dioxalatodiaquochromate-(III) solution was allowed to stand overnight before it was used. After this period of time, approximately 99%

of the complex was in the form of its cis isomer.[5]

In the reacted solutions, which will be discussed later, it was necessary to adjust the ionic strengths, hydrogen ion concentrations, and sulphate ion concentrations to required values. This was done by adding the appropriate amounts of sulphuric acid, perchloric acid, sodium sulphate, and sodium perchlorate to the solutions (see page 1 for the source of these reagents). The two acids were standardized against a sodium hydroxide solution which had previously been standardized with potassium hydrogen phthalate.[19a]

Chromium (III) perchlorate was prepared in perchloric acid solution. The preparation consisted of heating a known weight of potassium dichromate, in a standardized perchloric acid solution, with excess hydrogen peroxide. Under these conditions the dichromate ion was reduced to chromium (III) by the hydrogen peroxide. The excess hydrogen peroxide, which remained in the reaction solution, was decomposed by boiling the solution for three hours. The solution was then kept at $0^{\circ}C$ for 24 hours to precipitate the potassium ion present, as potassium perchlorate, which was filtered from the solution. The filtrate consisted of a known amount of chromium (III) perchlorate in a known concentration of perchloric acid (contaminated by a trace of potassium ion). 100 mls. of a 0.200 molar oxalic acid solution were then added to a perchloric acid solution which contained 0.0200 moles of chromium (III) perchlorate. The resultant solution was boiled for one hour; during

which time the reactants formed monooxalatotetraaquochromium(III) perchlorate (contaminated with other chromium(III) - oxalato complexes). After cooling, the reacted solution was passed through an anionic exchange resin (Dowex 1-X8 in its perchlorate form) to remove anionic impurities, e.g. $(C_2O_4)^{-2}$, $(H\ C_2O_4)^{-1}$, $[Cr(C_2O_4)_2(H_2O)_2]^{-1}$, and $[Cr(C_2O_4)_3]^{-3}$. The effluent solution contained monooxalatotetraaquochromium(III) perchlorate and a small amount of chromium(III) perchlorate. The latter was removed by passing 250 mls. of the solution through 50 mls. of Dowex 50W-X8 cationic exchange resin in its hydrogen form. Under these conditions most of the violet-red monooxalate ion passes through the resin bed, whereas the chromic ion is retained as a blue-black band in the resin column. The resultant solution of monooxalatotetraaquochromium(III) perchlorate in perchloric acid was analyzed for chromium[19b] and oxalate.[19c] The normality of the perchloric acid was determined by adding excess standardized sodium hydroxide to 25 mls. of the solution, boiling the solution to decompose the complex, filtering off the chromium(III) hydroxide precipitated, and titrating the filtrate with a standardized sulphuric acid solution, using a phenolphthalein indicator.

III. EXPERIMENTAL PROCEDURE FOR FOLLOWING THE OXIDATION OF CIS-DIOXALATODIAQUOCHROMATE(III) ION BY CERIUM(IV).

The reaction was found to proceed as follows:

$$2H_2O + cis\ \left[Cr(H_2O)_2(C_2O_4)_2\right]^{-1} + 2Ce^{4+} \rightarrow 2Ce^{3+} + \left[Cr(H_2O)_4(C_2O_4)\right]^{+1} + 2CO_2$$

The evidence for this stoichiometry is given on page 25. As the reaction was to be followed spectrophotometrically, the spectra of the reactants and the products were taken over the visible range with a Beckman DK-1 recording spectrophotometer (see illustration 1, page 27). It was decided that 480 mμ. was the optimum wavelength for following the reaction. At this wavelength there is a large difference between the optical densities of the reaction solutions before and after reaction. Also, at 480 mμ. the sulphated ceric ions absorb light more intensly than any of the other species present. Therefore, as the reaction proceeds, most of the change in optical density of the solution is caused by the reduction of the ceric complex to a colourless cerous species. Ceric ion in excess sulphuric acid was shown to obey Beer's Law at 480 mμ. (see illustration 2, page 27.) Therefore, it was assumed that the change in optical density of the solution as the reaction proceeded was proportional to the change in concentration of the reactants.

It will be shown later that as the monooxalatotetraaquochromium(III) ion reacts much more slowly than the cis-dioxalatodiaquochromate(III) ion, only the cis ion consumes an appreciable amount of ceric ion (see page 25).

For a given experimental determination of the rate of oxidation of cis-dioxalatodiaquochromate(III) ion under specific conditions, two solutios were prepared:

1. An aqueous solution of potassium cis-dioxalatodiaquochromate(III).

2. A solution containing ceric sulphate, sulphuric acid, perchloric acid, sodium sulphate, and sodim perchlorate. The concentrations of the two solutions were such that on mixing equal volumes of 1 and 2, a solution with the required concentrations of ceric ion, cis-dioxalatodiaquochromate(III) ion, sulphate ion, hydrogen ion, and ionic strength was obtained. In calculating the concentrations of ionic species present in the solution, the equilibrium data of Zebroski[21] and co-workers on the dissociation of sulphuric acid, and the equilibrium data of Hardwick and Robertson[6] on the various ceric-sulphate complexes were utilized.

Flasks containing solutions 1 and 2 were placed in a thermostat, at a temperature of 25.0±0.1 °C, for about one hour. Ten millilitre samples of each solution were than taken, and the two aliquots were thoroughly mixed.* A portion of this solution was then placed in a one centimetre cell in a Beckman Du spectrophotometer. The cell was also thermostated at 25.0 ±0.1°C. The optical density of the mixed solution at 480 mμ. was taken at one minute intevals. The optical density at the time of mixing was obtained by extrapolation. After the reaction had proceeded for approximately one hour a white precipitate appeared in the solution. This was shown to be cerous sulphate. (see page 10).

* The heat generated by the dilution of the sulphuric acid was assumed to be negligible. Experimentally on mixing equal volumes of 1.0 molar sulphuric acid and water at 25°C, the temperature increased by 0.12 ±0.02°C.

No precipitate was obtained in reaction mixtures in which sulphate ion was absent. When the initial concentrations of the cerium(IV) ion and the cis-dioxalatodiaquochromate(III) ion were of the order of one hundredth molar, the reaction was approximately 75% completed before precipitation took place. Thus, it was possible to obtain adequate data before the solution became turbid. After one week, the cerous sulphate was filtered out of the reaction mixture. The optical density of the filtrate was taken, and considered to be the optical density of the solution when the reaction had reached completion. This value agreed within 2% with the theoretical value predicted by the stoichiometric equation on page 5. Assuming the reaction solution obeyed Beer's Law, the rate of change of the concentrations of the reactants could be determined from the variations in the optical density of the solution.

It was found that in blank reaction solutions, which did not contain cis-dioxalatodiaquochrmoate(III) ion, there was no consumption of cerium(IV).

It was convenient to standardize the spectrophotometer so that a 0.01000 M. ceric sulphate in 0.750 M. sulphuric acid solution gave an optical density of 0.245; the slit width being 0.15 mm. The reason for this is that at 480 mμ. the optical densities of $[Ce(SO_4)_3]^{2-}$ solutions increase rapidly with decreasing wavelength of the incident radiation. Therefore, it is difficult to obtain reproducible results by trying to set the spectrophotometer to

480 mμ before each determination.

IV ANALYSIS OF THE REACTION PRODUCTS

0.4060 grams of potassium cis-dioxalatodiaquo-chromate(III) were placed in a reaction vessel and 200 mls. of 1.80 molar sulphuric acid were added. A stream of nitrogen gas, which was first freed from traces of carbon dioxide by passing through a barium hydroxide solution, was passed through the solution containing the chromium complex. 51.8 mls. of a solution which was 0.124 molar in cerium(IV) sulphate and 1.0 molar in sulphuric acid were added to the complex solution. Immediately after this addition, the reaction solution was 0.0256 molar in cerium(IV), 0.0128 molar in cis-dioxalatodiaquochromate(III) ion, 1.70 molar in sulphuric acid, and the ionic strength was approximately 1.9. The nitrogen stream carried the carbon dioxide , which was produced by the reaction, from the reaction vessel into a vessel containing a standard barium hydroxide solution. After the reaction had proceeded to essential completion (5 hours at 35°C) the barium hydroxide solution was filtered, in order to remove barium carbonate, and the filtrate was titrated with standardised sulphuric acid solution, using a methyl orange indicator. From the amount of barium hydroxide consumed, the weight of carbon dioxide evolved during the oxidation was determined. (see appendix III, page 27).

It was found that if a 100 mls. of 0.005 molar chromic perchlorate in 0.75 molar sulphuric acid solution were passed through Dowex 50W-X8 cation exchange resin, the chromic ion was removed from solution and remained as a blue-black band at the top of the resin bed. (The solution was also approximately 0.05 molar with respect to perchloric acid).

The reaction mixture, which had been used to estimate the amount of carbon dioxide evolved in the reaction, consisted of a blue solution containing a white precipitate. The precipitate was removed by filtration under reduced pressure, washed with distilled water, and dried in an oven at 80° C. Two 100 mls. samples were taken from the filtrate, which had a total volume of 251 mls. One of these samples was passed through a column of Dowex 50W-X8 cation exchange resin; the column being eluted with 200 mls. of 0.5 molar sulphuric acid solution. The second sample was passed through the column under the same conditions, and this treatment repeated with the eluted solution.

The two eluted solutions were then analyzed for their total chromium content.[196] The results of these analyses are shown in appendix III, page 25 . These results show that on passing the reaction mixture through the resin the chromium content of the solution decreases. However, on passing this effluent solution through the resin again, there is no noticeable change

in the chromium content of the solution. These results could be explained by the following two processes taking place in the reaction solution. Firstly, the cis-dioxalatodiaquochromate(III) ion being oxidised by the cerium(IV) to give monooxalatotetraaquochromium(III) ion, cerium(III), and water. Secondly, some of the monooxalatotetraaquochromium(III) ion being further oxidised by cerium(IV) to give chromium(III), carbon dioxide, and cerium(III). After the reaction had reached completion, three species containing chromium would be present in the solution; namely chromium(III), monooxalatotetraaquochromium(III) ion, and dioxalatodiaquo-chromate(III) ion. Therefore, if on passing the strongly acidic reacted solution through Dowex 50W-X8 cation exchange resin only the chromium(III) were removed, the results of the ion exchange experiments, described in the preceeding paragraph, would be explained. Assuming that the above argument is correct, an estimate of the rate of oxidation of monooxalatodiaquochromium(III) ion by cerium(IV) is calculated in appendix IVI, page 25 .

As has been stated, a white precipitate had been obtained from the solution in which the cerium(IV) and the cis-dioxalatodiaquochromate(III) ion had reacted. This precipitate was boiled for an hour with one molar sodium hydroxide solution, during which time the precipitate turned yellow. This precipitate was then dissolved in one molar hydrochloric acid to give a yellow solution. On adding barium chloride solution

to a portion of the yellow solution, a white precipitate was obtained. Another portion of the solution oxidised a ferrous ammonium sulphate solution, which contained a few drops of ferroin as an indicator. On the basis of this qualitative evidence, the original white precipitate was assumed to be cerous sulphate.

In appendix III, page 25 , the actual analyses are given. They show that the reaction products agree with the predicted reaction stoichiometry within experimental error.

IV THE METHOD OF CALCULATING THE RATE CONSTANTS AND METHOD OF TABULATING THE RESULTS

The variations in the concentrations with time of cerium (IV) and cis-dioxalatodiaquochromate (III) ion, in a reaction mixture, were calculated (see page 7). From these concentrations, a second order rate constant for the reaction was obtained graphically. This procedure is described in detail in standard text-books.[11] The second order rate constants which most closely fit the results obtained during the first 30% of the various reactions are tabulated in appendix I, pages 20 to 23 .

An indication of the accuracy involved in this work is given in appendix IIb , page 24 , where the rate constants for duplicated experiments are tabulated. It can be seen that the results reported in appendix IIb are consistent with the estimate of experimental errors in appendix IIa, page 24 .

In some of the earlier determinations it was necessary to assume that a little (3-4%) of the cerium-(IV) was consumed very rapidly on mixing the reactants. Unless this allowance was made, it was impossible to obtain a consistent second order rate constant from a set of results. This initial rapid consumption of cerium(IV) was possibly caused by a trace of free oxalate in the original potassium dioxalatodiaquo-chromate(III). This would not be inconsistent with the analysis of this salt (see page 2). In the last sample of potassium dioxalatodiaquochromate(III) prepared, greater care was taken to recrystallize it. Using this material, no allowance for a rapid initial consumption of cerium(IV) was required.

In appendix I, the following details have been tabulated, the second order rate constant for a given reaction mixture, the initial equilibrium concentrations of the ionic species present, and the ionic strength of the solution. The data of Hardwick and Robertson[6] on the equilibrium constants of the various ceric-sulphate complexes, and that of Zebroski and co-workers[21] on the dissociation of sulphuric acid, were used in calculating the concentrations of the ionic species present.

The results obtained were then used to investigate the effect of hydrogen ion concentration (see illustration V, page 29) and ionic strength (see illustration III,

page 28) on the rate of the reaction. An attempt was also made to correlate the rate of the reaction with the concentrations of the various cerium(IV) species present in the solution. The best correlation was obtained by concidering $\left[Ce(SO_4)_3\right]^{-2}$ to be much more reactive than any other cerium(IV) species (see illustration IV, page 28).

DISCUSSION OF RESULTS

The oxidation of cis-dioxalatodiaquochromate(III) ion by cerium(IV) is kinetically of the first order with respect to each of the reactants; i.e. second order overall. That the reaction is not second order with respect to one of the reactants is shown by considering the results recorded in appendix I, page 20. In reactions 1 through 4 in this appendix, the initial concentrations of the reactants are varied, other conditions being kept constant. However, the second order rate constants, obtained by considering the reaction to be first order with respect to both of the reactants, are reasonably consistent. The second order rate constants at 25°C were found to be dependent on the sulphate and hydrogen ion concentrations, and on the ionic strength of the reaction solution.

Within the range of ionic strengths employed, i.e. 0.7 to 2.0, the reaction proceeded more quickly the lower the ionic strength (see illustration III, page 28).

The concentrations of the various sulphated ceric complexes were calculated from the data of Hardwick and Robertson[6] for several reaction mixtures. For these mixtures, in which the hydrogen ion concentrations and the ionic strengths are similar, there appears to be a reasonable agreement between the concentration of $[Ce(SO_4)_3]^{-2}$ ion present and the reaction rate (see illustration IV, page 28). It appears that $[Ce(SO_4)_3]^{-2}$ reacts more rapidly than any other cerium(IV) species.

An attempt was not made to estimate the error caused by cerium(IV) species other than $[Ce(SO_4)_3]^{-2}$ oxidising cis-dioxalatodiaquochromate(III) ion. In solutions in which the sulphate ion concentration was low, errors could possibly be caused by the concentrations of polynuclear cerium(IV) species becoming significant. This latter possibility would make the calculated $[Ce(SO_4)_3]^{-2}$, concentrations inaccurate. In solutions in which there was a low initial concentration of $[Ce(SO_4)_3]^{-2}$, the relative proportions of the ions containing cerium(IV) would vary significantly as the reaction proceeded.(As the optical densities of cerium(IV) in sulphuric acid solutions do not change with time, it was assumed that the various cerium(IV)-sulphate equilibria were established rapidly.) Under these conditions, there would not be a linear relationship between the change in the optical density of the solution and the amount of cis-dioxalatodiaquochromate(III) ion oxidised by cerium(IV). To allow for the above two factors would require considerably more data than has been accumulated. An extensive study of the species present in cerium(IV) solutions would be required, which could not be carried out very accurately by the oxidation technique described in this thesis.

The effect of the hydrogen ion concentration on the reaction rate is plotted in illustration V, page 29. The data were obtained for this graph by determining the effect of varying the ratios of sodium to hydrogen ions on the reaction rate; at a constant ionic strength of 2.00. Unfortunately, when cerium(IV) is used as an oxidant it is not possible to use very weakly acidic solutions, because the cerium(IV)

would be precipitated as its hydroxide. It was found that if an aqueous solution of ceric sulphate was less than 0.4 molar with respect to sulphuric acid, precipitation of a yellow solid took place on allowing the solution to stand. Also, in weakly acidic solutions species such as $CeOH^{+3}$ become very important.[1] In solutions in which the ratio of H^+ to Na^+ was varied from 1:2 to 9:1, the rate of the reaction was approximately proportional to the change in the percentage of hydrogen ion present (see illustration V, page 29). It has been shown by Hardwick and Robertson[6] that at hydrogen ion concentrations of greater than 0.6 molar the hydrogen ion concentration does not have a large effect on the proportions of the various cerium(IV) species present. Therefore, the catalytic effect of hydrogen ion must be attributed to some other factor. By extrapolation, it was found that at an ionic strength of 2.00, the reaction rate of cerium(IV) with cis-dioxalatodiaquochromate(III) would be approximately 0.9 litres equivalent $^{-1}$ minute $^{-1}$ if all the external cations were sodium, and 3.4 litres equivalent $^{-1}$ minute $^{-1}$ if all the external cations were hydrogen.

At 25.0°C and an ionic strength of 2.00, the rate law for the oxidation of cis-dioxalatodiaquochromate(III) by cerium(IV) may be expressed as follows:

$$\frac{d\ Ce(IV)}{dt} = \left[\left(0.90 \pm 0.05 + 0.025 \pm 0.002 (H^+)\right)\left(Ce(SO_4)_3^{-2}\right)\left(\text{cis-dioxalatodiaquochromate(III)}\right)^{-1}\right]$$

The units of the above constants are litres equivalent $^{-1}$ minute $^{-1}$. A normal solution of cerium(IV) would be 1 molar with respect to cerium(IV), and a normal solution of cis-

dioxalatodiaquochromate(III) ion would be 0.5 molar with respect to the latter ion.

The above rate law implies that there are two paths which lead to reaction. Path 1 could involve an activated complex of the composition ($[Ce(SO_4)_3]^{-2}[H^+]$[cis-dioxalatodiaquochromate(III)]$^{-1-2}$). A possible mechanism which could involve such an activated complex would be:

$$H^+ + \left[(H_2O)_2(C_2O_4)Cr\begin{matrix}O\text{-}C{=}O\\ |\\ O\text{-}C{=}O\end{matrix}\right]^{-1} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \left[(H_2O)_2(C_2O_4)Cr\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}H\right]^0$$

$$\left[(H_2O)_2(C_2O_4)Cr\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}H\right]^0 + \left[Ce(SO_4)_3\right]^{-2} \xrightarrow{\text{slow}} \text{reaction products (see page 8)}$$

The second path could involve an activated complex of composition ($[Ce(SO_4)_3]^{-2}$ [cis-dioxalatodiaquochromate(III)]$^{-1}$ $[Na]^{+1})^{-2}$ or ($[Ce(SO_4)_3]^{-2}$[cis-dioxalatodiaquochromate(III)]$^{-1}$)$^{-3}$. The reason for this uncertainly is that from illustration V, page 29, there is no way of ascertaining the role, if any, of sodium ion in the reaction. However, by replacing the sodium ions by other cations, it should be possible to determine whether cations other than hydrogen exert a catalytic effect on the reaction.

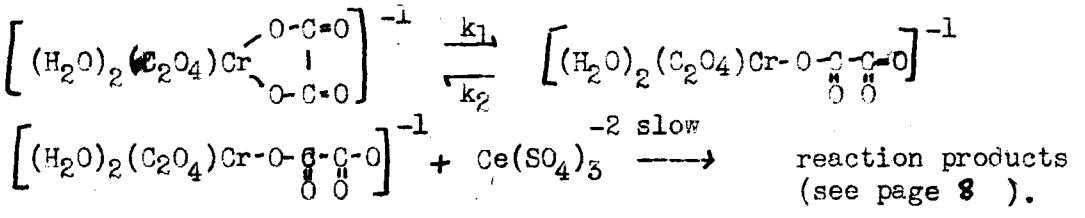
If sodium ion were involved in the reaction, a plausible mechanism for the second path could be:

$$Na^+ + \left[(H_2O)_2(C_2O_4)Cr\begin{matrix}O\text{-}C{=}O\\ |\\ O\text{-}C{=}O\end{matrix}\right]^{-1} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \left[(H_2O)_2(C_2O_4)Cr\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}Na^*\right]^0$$

$$\left[(H_2O)_2(C_2O_4)Cr\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}Na\right]^0 + \left[Ce(SO_4)_3\right]^{-2} \xrightarrow{\text{slow}} \text{reaction products}$$

* The sodium to oxygen bond is not necessarily covalent.

If sodium ion were not involved in the reaction, a plausible mechanism could be:



The concentrations of the binuclear intermediates containing both chromium and cerium must be small, if any, because they could not be detected spectrophotomerically. (On mixing equal volumes of solutions of cerium(IV) and cis-dioxalatodiaquochromate(III) ion, the optical density of the resultant solution, obtained by extrapolation (see page 7), was the mean of the optical densities of the original solutions).

The author considers it to be probable, in a solution of cis-dioxalatodiaquochromate(III) ion, that external cations electrostatically facilitate the breaking of bonds between chromium and oxalate addenda. Also, in a species in which one of the bonds between a chromium ion and an oxalate addendum has been broken, this structure could possibly be stabilized by intermediates of the type $\left[(H_2O)_2(C_2O_4)Cr\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-cation}\right]$ Both of the above effects could make the oxalate more vulnerable to attack by cerium(IV), if the oxidation proceeds by the two paths suggested in this thesis.

In the future it should be profitable to determine the temperature dependence of the oxidation of cis-dioxalatodiaquochromate(III) ion by cerium(IV), in

order to obtain the entropy and heat of activation of this system. This data should help to elucidate the nature of the activated complex(es) involved in the reaction. A study of the effects of a series of external metal cations in the reaction solution might also be profitable.

The reaction rates for the oxidation of cis-dioxalatodiaquochromate(III) ion by a variety of anionic and cationic oxidising agents should be obtained. Sodium hypochlorite, for example, should be a suitable oxidising agent for this purpose.

All of this work should then be repeated for as many chromium(III) - oxalate complexes as may be readily prepared. Preliminary work on the oxidation of monooxalatotetraaquochromium(III) ion by cerium(IV) has been undertaken by the author. However, sufficient results have not been obtained to determine accurately the rate constant for the reaction. It does appear to proceed at less than a tenth of the rate of oxidation of cis-dioxalatodiaquochromate(III) ion under similar conditions. The preparation of monooxalatotetraaquo-chromium(III) perchlorate has been included in the preparation section of this thesis (see page 3) because it may be of value to future workers.

The method, described in this thesis, could be extended to oxidisable ligands other than oxalate in transitional metal complexes.

APPENDICES

Appendix 1 Numerical Values of the Second Order Rate Constants Obtained on Oxidising cis-Dioxalatodiaquochromate(III) Ion with Cerium(IV) in Various Media at 25°C.

Composition of initial solution	Equilibrium molar concentrations of ionic species present	Ionic strength	Rate constant (litres equivalents^{-1} minutes^{-1})
1.			
H_2SO_4 -0.75M.	H^+ -0.620	1.28	1.89
Na_2SO_4-0.25M.	$SO_4^=$ -0.119		
Ce(IV)-0.01M.	HSO_4^--0.881		
* cis -0.01M.			
2.			
H_2SO_4 -0,75M.	H^+ -0.620	1.27	2.60
Na_2SO_4-0.25M.	$SO_4^=$ -0.129		
Ce(IV)-0.005M.	HSO_4^--0.881		
cis -0.01M.			
3.			
H_2SO_4 -0.75M.	H^+ -0.620	1.27	2.07
Na_2So_4-0.25M.	$SO_4^=$ -0.119		
Ce(IV)-0.01M.	HSO_4^--0.881		
cis -0.0025M.			
4.			
H_2SO_4 -0.75M.	H^+ -0.620	1.27	2.05
Na_2SO_4-0.25M.	$SO_4^=$ -0.119		
Ce(IV)-0.01174M.	HSO_4^--0.881		
cis -0.00293M.			
5.			
H_2SO_4 -0.75M.	H^+ -0.737	1.24	2.08
Na_2SO_4-0.10M.	$SO_4^=$ -0.087		
Na ClO_4-0.21M.	HSO_4^--0.763		
Ce(IV)-0.01M.	ClO_4^--0.21		
cis -0.005M.	Na^+ -0.21		
6.			
H_2SO_4 -0.75M.	H^+ -0.737	1.24	2.00
Na_2SO_4-0.10M.	$SO_4^=$ -0.087		
$NaClO_4$-0.21M.	HSO_4^--0.763		
Ce(IV)-0.01M.	ClO_4^--0.21		
cis -0.005M.	Na^+ -0.21		

* cis=cis-Dioxalatodiaquochromate(III) ion

Composition of initial solution	Equilibrium molar concentrations of ionic species present	Ionic strength	Rate constant (litres equivalent^{-1} minute^{-1})
7.			
H_2SO_4 -0.555M.	H^+ -0.624M.	2.02	1.53
$NaClO_4$ -1.30M.	$SO_4^=$ -0.066M.		
Ce(IV) -0.01M.	HSO_4^--0.490M.		
cis -0.005M.	Na^+ -1.30M.		
	ClO_4^--1.30M.		
8.			
H_2SO_4 -0.555M.	H^+ -0.624M.	2.02	1.62
$NaClO_4$ -1.30M.	$SO_4^=$ -0.066M.		
Ce(IV) -0.01M.	HSO_4^--0.490M.		
cis -0.005M.	Na^+ -1.30M.		
	ClO_4^--1.30M.		
9.			
H_2SO_4 -0.555M.	H^+ -0.624M.	1.26	2.42
$NaClO_4$ -0.54M.	$SO_4^=$ -0.066M.		
Ce(IV) -0.01M.	HSO_4^--0.490M.		
cis -0.005M.	Na^+ -1.30M.		
	ClO_4^--1.30M.		
10.			
H_2SO_4 -0.555M.	H^+ -0.624M.	1.26	2.34
$NaClO_4$ -1.30M.	$SO_4^=$ -0.066M.		
Ce(IV) -0.01M.	HSO_4^--0.490M.		
cis -0.005M.	Na^+ -1.30M.		
	ClO_4^--1.30M.		
11.			
H_2SO_4 -0.555M.	H^+ -0.624M.	0.72	3.30
Ce(IV) -0.01M.	$SO_4^=$ -0.066M.		
cis -0.005M.	HSO_4^--0.490M.		
12.			
H_2SO_4 -0.555M.	H^+ -0.624M.	0.72	3.22
Ce(IV) -0.01M.	$SO_4^=$ -0.066M.		
cis -0.005M.	HSO_4^--0.490M.		
13.			
H_2SO_4 -1.00M.	H^+ -1.072M.	1.18	3.05
Ce(IV) -0.01M.	$SO_4^=$ -0.073M.		
cis -0.005M.	HSO_4^--0.927M.		

Composition of initial solution	Equilibrium molar concentrations of ionic species present	Ionic strength	Rate constant (litres equivalent^{-1} minute^{-1})
14.			
H_2SO_4 -1.00M.	H^+ -1.002M.	1.18	3.22
Ce(IV)-0.01M.	$SO_4^=$ -0.073M.		
cis -0.005M.	HSO_4^- -0.927M.		
15.			
H_2SO_4 -1.79M.	H^+ -1.870M.	1.97	2.78
Ce(IV)-0.01M.	$SO_4^=$ -0.077M.		
cis -0.005M.	HSO_4^- -1.712M.		
16.			
H_2SO_4 -1.78M.	H^+ -1.870M.	1.97	2.63
Ce(IV)-0.01M.	$SO_4^=$ -0.077M.		
cis -0.005M.	HSO_4^- -1.712M.		
17.			
Ce(IV)-0.01M.	H^+ -2.0M.	2.01	0.024
cis -0.005M.	ClO_4^- -2.0M.		
$HClO_4$ -2.00M	$Ce(SO_4)_3$ -0.00M		
18.			
H_2SO_4 -0.05M.	H^+ -2.00M.	2.01	0.32
Ce(IV)-0.01M.	HSO_4^- -0.05M.		
cis -0.005M.	ClO_4^- -1.95M		
$HClO_4$ -1.95M.	$Ce(SO_4)_3$ -0.00184M.		
19.			
H_2SO_4 -0.20M.	H^+ -1.99M.	2.00	1.24
Ce(IV)-0.0100M.	HSO_4^- -0.20M.		
cis -0.00640M.	ClO_4^- -1.79M.		
$HClO_4$ -1.79M.	$Ce(SO)_{43}$ -0.0062M.		
20.			
H_2SO_4 -0.80M.	H^+ -0.870M.	2.00	2.14
Ce(IV) -0.01M.	HSO_4^- -0.730M.		
cis -0.0046M.	$SO_4^=$ -0.07M.		
$NaClO_4$ -1.06M.	Na^+ -1.06M.		
	ClO_4^- -1.06M.		

Composition of initial solution		Equilibrium molar concentrations of ionic species present		Ionic strength	Rate constant (litres equivalent^{-1} minute^{-1})
21.					
H_2SO_4	-1.00M.	H^+	-1.07M.	2.00	2.33
Ce(IV)	-1.01M.	HSO_4^-	-0.930M.		
cis	-0.0046M.	$SO_4^=$	-0.07M.		
$NaClO_4$	-0.86M.	Na^+	-0.86M.		
		ClO_4^-	-0.86M.		
22.					
H_2SO_4	-1.20M.	H^+	-1.27M.	2.00	2.44
Ce(IV)	-0.010M.	HSO_4^-	-1.13M.		
cis	-0.0046M.	$SO_4^=$	-0.07M.		
$NaClO_4$	-0.66M.	Na^+	-0.66M.		
		ClO_4^-	-0.66M.		
23.					
H_2SO_4	-1.40M.	H^+	-1.48M.	2.00	2.82
Ce(IV)	-0.010M.	HSO_4^-	-1.32M.		
cis	-0.0046M.	$SO_4^=$	-0.07M.		
$NaClO_4$	-0.46M.	Na^+	-0.46M.		
		ClO_4^-	-0.46M.		
24.					
H_2SO_4	-1.60M.	H^+	-1.68M.	2.00	3.10
Ce(IV)	-0.010M.	HSO_4^-	-1.52M.		
cis	-0.0046M.	$SO_4^=$	-0.08M.		
$NaClO_4$	-0.25M.	Na^+	-0.25M.		
		ClO_4^-	-0.25M.		

Appendix 11a. The Maximum Estimated Errors in Obtaining the Concentrations of the Species Present in the Reaction Solutions

Maximum error in reading the spectrophotometer	2.0%
Error caused by temperature variations of 0.10°C in the reaction vessel	1.0%
Error caused by impurities in the reactants	1.0%
Error caused by the choice of the value of the optical density for the completed reaction solutions	0.5%
	4.5%

Therefore the maximum estimated error in calculating the concentrations of both Cerium(IV) and cis-Dioxalatodiaquochromate(III) in a reaction mixture is equal to 4.5%. This means that the maximum error in determing the rate constant for the reaction is 9.0%, because it is a second order reaction.

Appendix 11b. The differences in rate constants obtained in duplicate experiments.

Solution number (as in appendix 1).	Rate constant (in equivalents minutes).	Difference.100 / Mean value
5	2.08	3.9%
6	2.00	
7	1.53	5.7%
8	1.62	
9	2.42	3.4%
10	2.34	
11	3.30	2.1%
12	3.22	
13	3.05	5.4%
14	3.22	
15	2.78	5.6%
16	2.63	
		26.1

Therefore the mean difference in rate constants determined in duplicate experiments is equal to 4.4%. This value appears to be in good agreement with the value predicted in Appendix 11a, which probably means that the equilibrium data employed were not significantly inaccurate.

APPENDIX III. ANALYSIS OF REACTION PRODUCTS (see page 8).

I) CARBON DIOXIDE EVOLVED.

0.4060 ± 0.0005 grms. of potassium cis-dioxalatodiaquo-chromate (III) were reacted with an equivalent amount of cerium (IV). (An 0.5 molar solution of cis-dioxalatodiaquo-chromate (III) ion is equivalent to a 1.0 molar cerium (IV) solution by definition of the author). The carbon dioxide evolved neutralized 43.67 mls. of 0.1040N barium hydroxide solution. Experimentally determined weight of carbon dioxide evolved = 0.1010 grms.

The theoretically predicted weight of carbon dioxide evolved, assuming the reaction to be $\left[Cr(H_2O)_2(C_2O_4)_2\right]^{-1} + 2H_2O$ + 2 cerium (IV) → $\left[Cr(H_2O)_4(C_2O_4)\right]^{+1}$ + 2 cerium (III) + $2CO_2$, = 0.1054 grms.

II) RATIO OF OXALATE TO CHROMIC ION IN THE SOLUTION AFTER THE REACTION IS COMPLETED.

251 mls. of the reacted solution contained 0.4060 grms. of potassium-dioxalatodiaquochromate (III).

100 mls. of this solution was passed through the cation exchange resin and the effluent solution was analyzed for chromium.[19] This analysis involved oxidising the chromium to dichromate ion with potassium persulphate, and reacting the dichromate solution with a standard ferrous ion solution.

Another 100 mls. of the reacted solution were passed through the resin, and this treatment was repeated with the effluent solution.

Original chromium content of the solution = 0.0248 grms/100 mls.
Chromium content after passing through the resin once = 0.0237 grms/100 ml.
Chromium content after passing through the resin twice = 0.0240 grms/100 ml.

From this data, it appears that 4-5% of the chromium in the reacted solution was in the form of $Cr(H_2O)_x^{3+}$.

If the rate of oxidation of monooxalatotetraaquochromium (III) ion by cerium (IV) were exactly 2.0% that of the dioxalatodiaquochromate (III), the chromium composition of the final solution would be expected to be; 4.8% cis-dioxalate, 90.4 % monooxalate, 4.8 % chromic ion.

(The above values were obtained arithmetically by splitting the reaction into various stages, and making self-consistent approximations until the concentrations of the various species fitted a 2 % reaction rate for the monooxalate ion compared to the cis-dioxalate ion).)

The values obtained for the three chromium analyses do not differ by more than 5%. Therefore, the significance which may be attached to the predicted rate constant for the monooxalate is uncertain, because conditions in the resin bed may have differed slightly after passing each solution through it. Also, the mechanism proposed on page 10 may not be applicable. However, the rate of oxidation of the monooxalate ion does appear to be slower than that for the cis-dioxalate ion.

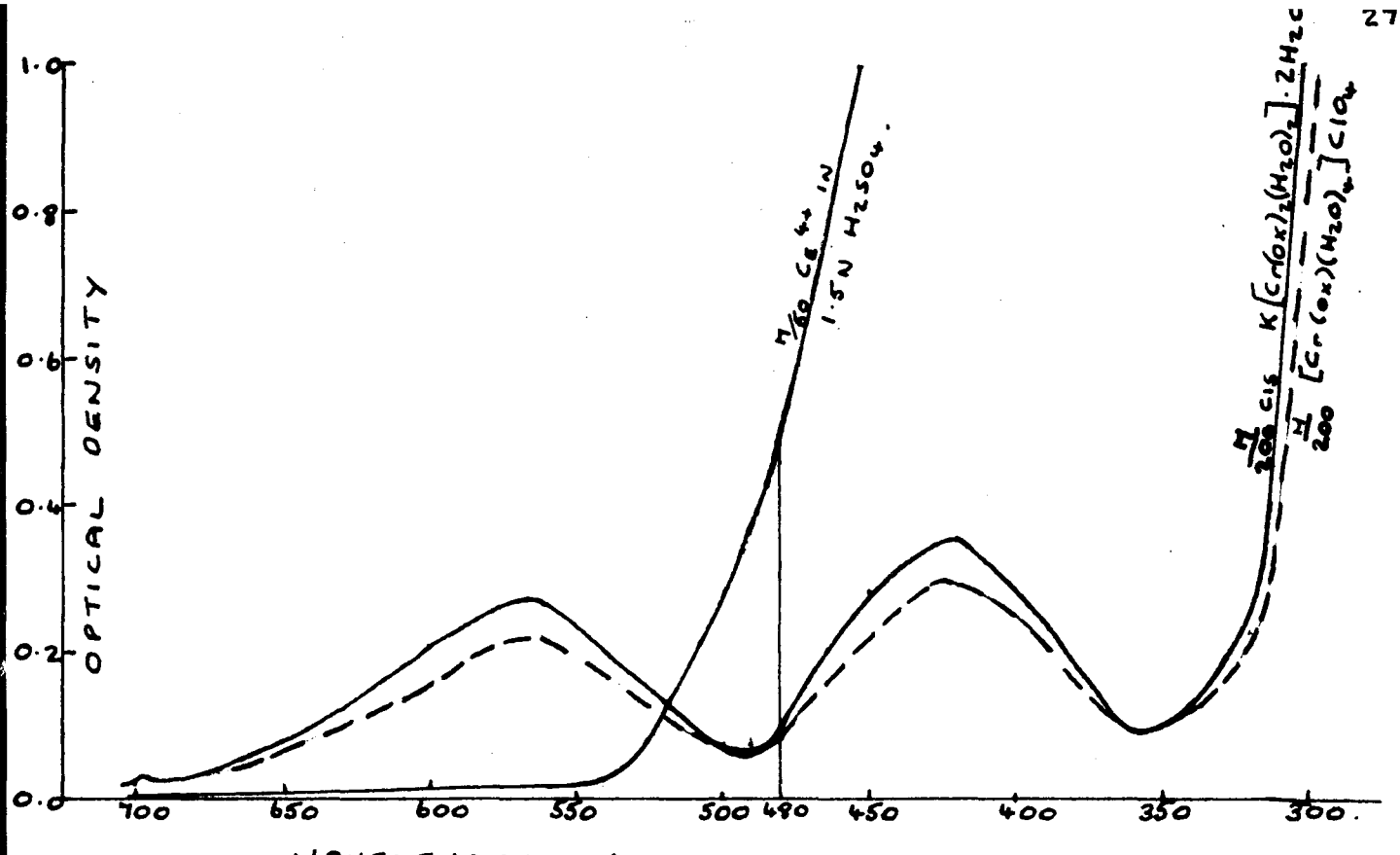
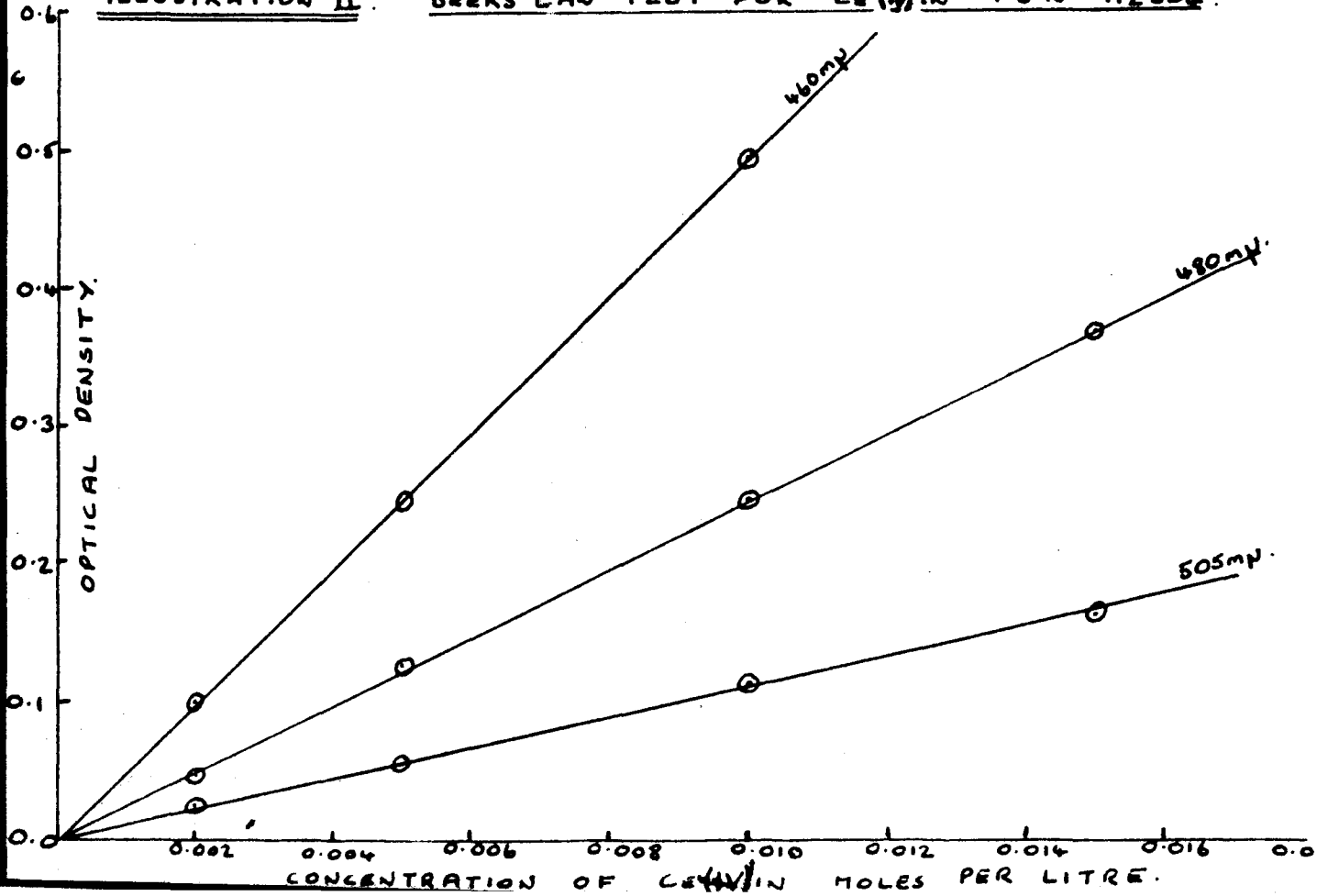


ILLUSTRATION I. OPTICAL DENSITIES OF REACTANT SPECIES IN THE VISIBLE REGION OF THE SPECTRUM.

ILLUSTRATION II. BEER'S LAW PLOT FOR Ce(IV) IN 1·5N H_2SO_4.



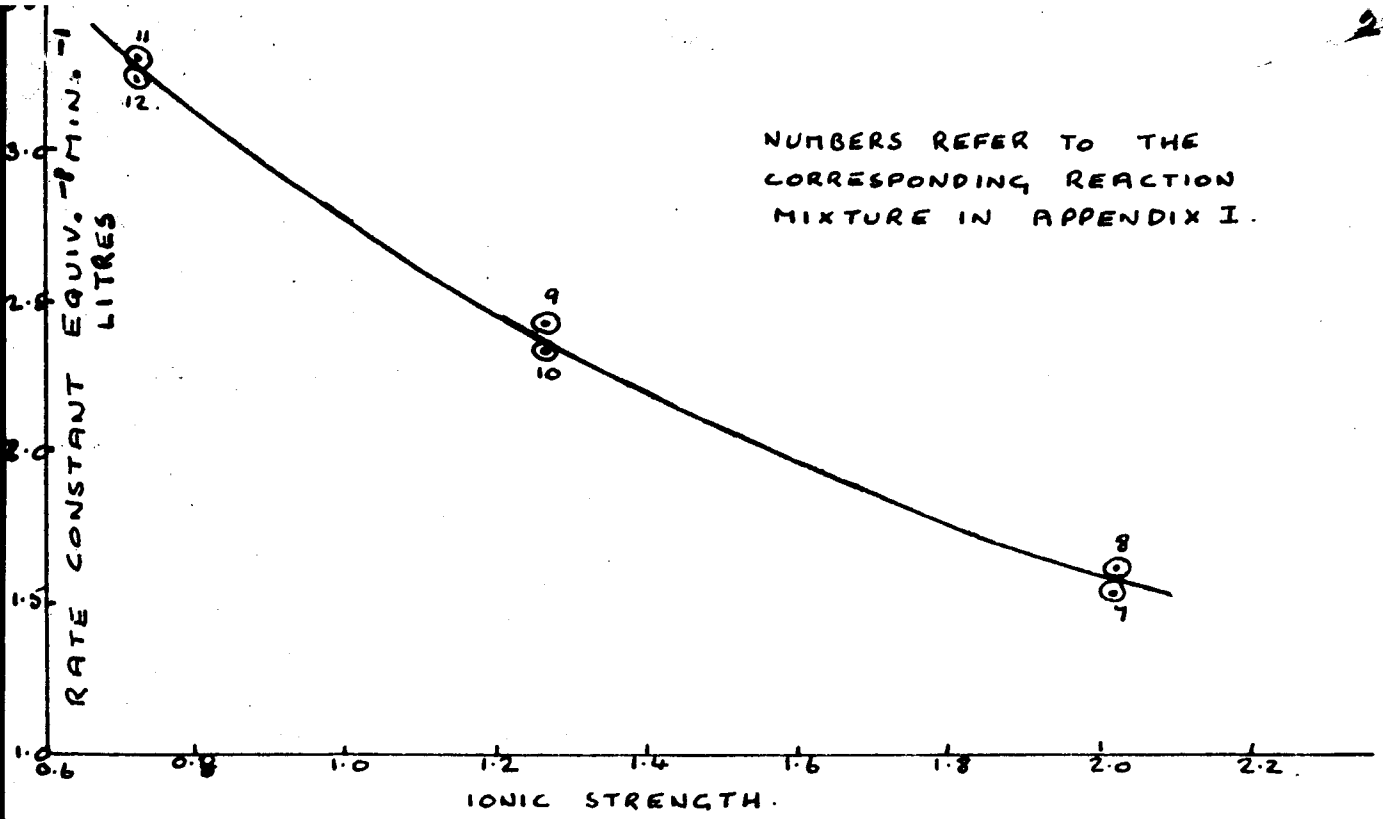


ILLUSTRATION III. EFFECT OF IONIC STRENGTH ON THE REACTION RATE AT CONSTANT H^+ CONCENTRATION.

ILLUSTRATION IV EFFECT OF $Ce(SO_4)_3^{2-}$ CONCENTRATION ON THE RATE CONSTANT AT CONSTANT IONIC STRENGTH AND H^+ CONCENTRATION.

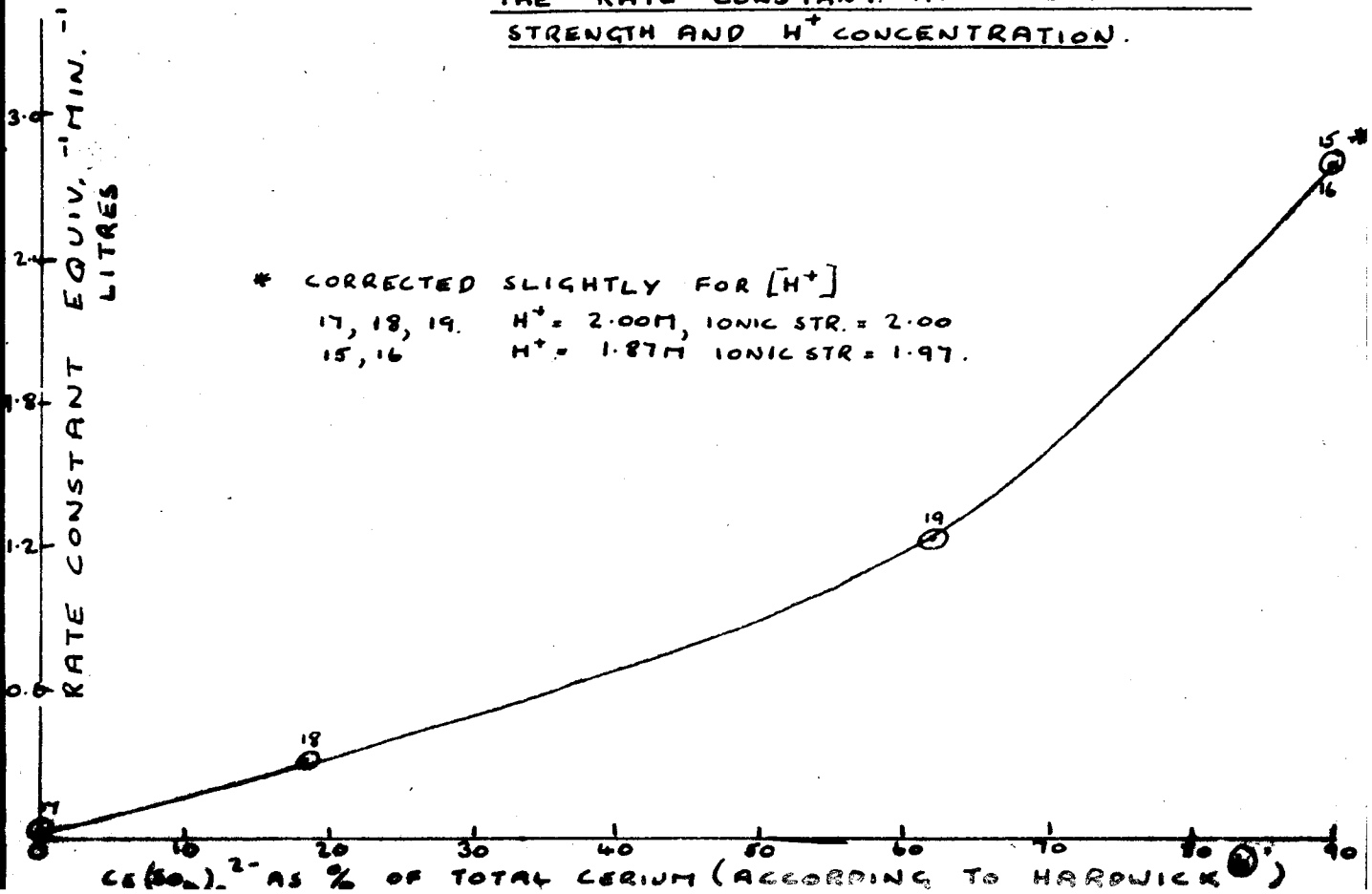
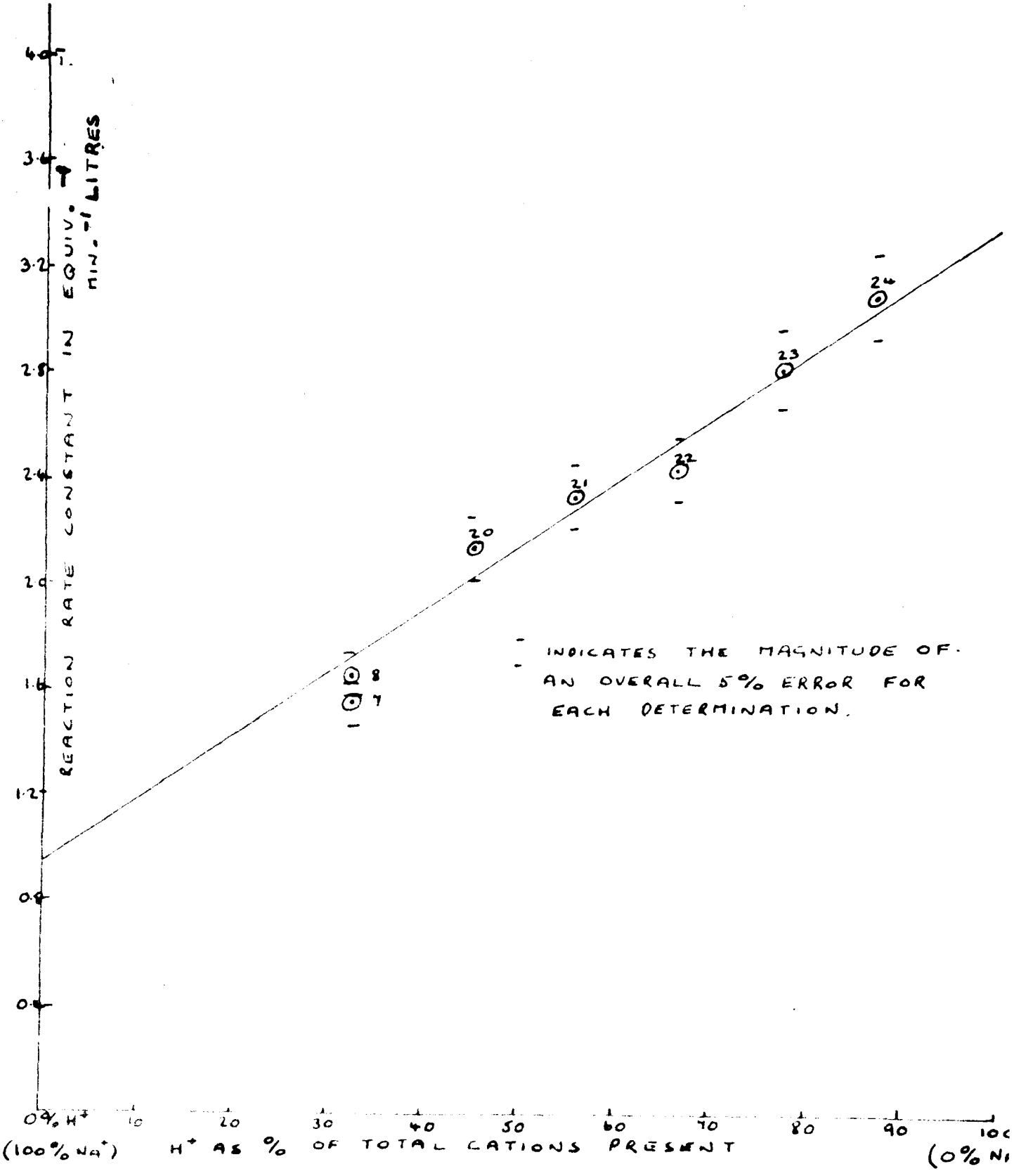


ILLUSTRATION 3. DEPENDENCE OF THE REACTION RATE CONSTANT ON HYDROGEN ION CONCENTRATION, SODIUM IONS BEING THE ONLY OTHER CATIONS PRESENT IN SIGNIFICANT CONCENTRATIONS, AT AN IONIC STRENGTH OF 2.00±0.03.



SUMMARY

Potassium trans-dioxalatodiaquochromate(III) was prepared from potassium dichromate and oxalic acid. The product was purified by recrystallization and ion exchange techniques. Potassium cis-dioxalatodiaquochromate(III) was prepared by dissolving the trans isomer in water and allowing equilibration to take place. The equilibrium mixture consists of approximately 99% of the cis isomer.

Standard solutions of potassium dioxalatodiaquochromate(III) were then oxidised by standard cerium(IV) solutions. The cerium(IV) solutions contained known amounts of sulphuric acid, perchloric acid, sodium sulphate, and sodium perchlorate, in order to obtain known concentrations of the various ionic species in the reaction solutions.

The reaction was carried out by mixing the cerium-(IV) and the complex solutions, and transferring a sample of the resultant solution to a 1 cm. cell in a Beckman DU spectrophotometer. This cell was thermostated to 25.0 ± 0.1° C. Changes in the concentrations of the reactants were followed by observing the change in optical density of the solution to radiation with a wavelength of 480 mμ.

The reaction was found to be kinetically of the first order with respect to both the cis-dioxalatodiaquochromate-(III) ion and the reacting cerium(IV) species; i.e. second

order overall. The effect on the reaction rate of varying the sulphate ion concentration indicated that the complex ion was being oxidised by $[Ce(SO_4)_3]^{-2}$. The reaction was found to proceed more rapidly in the presence of hydrogen ion than in the presence of a similar concentration of sodium ion. Also, the reaction rate was lower in solutions of higher ionic strength.

At an ionic strength of 2.00, and a temperature of 25.0 ∓ 0.1°C, the following rate law for the reaction was obtained.

$$\frac{d(Ce(IV))}{dT} = \left((0.90\pm0.05+0.025\pm0.002(H^+)\right)\left(Ce(SO_4)_3^{-2}\right)\left(\text{cis-dioxalatodiaquochromate(III)}^{-1}\right)$$

This rate law implies that the reaction proceeds through two alternative paths. Path 1 could involve an activated complex of the composition $\left([Ce(SO_4)_3][H^+][\text{cis-dioxalatodiaquochromate}^-(III)]^{-1}\right)^{-2}$.

A possible mechanism which could involve such an activated complex would be:

$$H^+ + \left[(H_2O)_2(C_2O_4)Cr\begin{matrix}O\text{-}C=O\\O\text{-}C=O\end{matrix}\right]^{-1} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \left[(H_2O)_2(C_2O_4)Cr\text{-}O\text{-}C(=O)\text{-}C(=O)\text{-}OH\right]^0$$

$$\left[(H_2O)_2(C_2O_4)Cr\text{-}O\text{-}C=C\text{-}OH\right]^0 + \left[Ce(SO_4)_3\right]^{-2} \rightarrow \text{reaction products}$$

(see page 8)

Path 2 could involve an activated complex with a composition of $\left([\text{cis-dioxalatodiaquochromate}^-(III)]^{-1}[Ce(SO_4)_3]^{-2}[Na^+]\right)^{-2}$ or- $\left([\text{cis-dioxalatodiaquochromate}-\right.$

$(III)]\,[Ce(SO_4)_3^{-2}]).^{-3}$

The activated complex containing sodium ion could indicate a mechanism similar to that for path 1, except that the hydrogen ion would be replaced by sodium ion. The second alternative activated complex, not involving sodium ion, could indicate the following possible mechanism for path 2.

$$\left[(H_2O)_2(C_2O_4)Cr\begin{matrix}O\text{-}C{=}O\\ O\text{-}C{=}O\end{matrix}\right]^{-1} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \left[(H_2O)_2(C_2O_4)Cr\text{-}O\text{-}\underset{O}{\overset{O}{C}}\text{-}\underset{O}{\overset{O}{C}}\text{-}O\right]^{-1}$$

$$\left[(H_2O)_2(C_2O_4)Cr\text{-}O\text{-}\underset{O}{\overset{O}{C}}\text{-}\underset{O}{\overset{O}{C}}\text{-}O\right]^{-1} + Ce(SO_4)_3^{-2} \xrightarrow{slow} \text{reaction products}$$

It is suggested that the temperature dependence of the oxidation of cis-dioxalatodiaquochromate(III) ion by cerium(IV) should be determined in the future. This would enable the entropy and the heat of activation of the reaction to be calculated. These data should help to elucidate the nature of the activated complexes involved.

This work could then be extended to a wide variety of transitional metal complexes containing oxidisable ligands. The data obtained from such studies, could give some further indication of the state of the bonding within these complexes.

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