

7-1951

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Abstract

This work is concerned with the kinetics of the oxidation of chloride ion by cerium (IV) perchlorate. The basic principle of many oxidation-reduction reactions is believed to be the formation of an intermediate in which are combined the oxidant and reductant involved. In the simplest case this intermediate then decomposes to give the products. An increasing number of reactions have been studied and explained on this basis.

Keywords

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Disciplines

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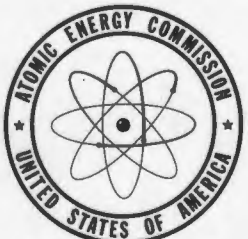
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By
John A. Anderegg
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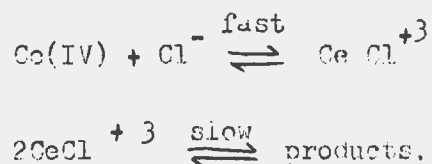
John A. Anderegg and Frederick R. Juce

ABSTRACT

As a preliminary to a study of the cerium(IV) thallous reaction in the presence of chloride it was decided to study the kinetics of the oxidation of chloride with cerium(IV).

Mixtures of Ce(IV) (.005 M) and chloride ion of higher concentration in 4M perchloric acid were prepared and at constant temperature, the disappearance of Ce(IV) was followed. Analyses were done by quenching the reacting mixture in 6M H₂SO₄, which stops the reaction, followed by spectrophotometric determination of the chloride using a Coleman spectrophotometer.

The results showed that at low chloride concentrations (.01 to 0.1 M) the reaction yields chlorate as end product and is second order in cerium. The order in chloride was between first and second. The results were interpreted according to the mechanism.



¹This report was based on an M. S. thesis by John A. Anderegg submitted July 1951.

INTRODUCTION

This work is concerned with the kinetics of the oxidation of chloride ion by cerium (IV) perchlorate. The basic principle of many oxidation-reduction reactions is believed to be the formation of an intermediate in which are combined the oxidant and reductant involved. In the simplest case this intermediate then decomposes to give the products. An increasing number of reactions have been studied and explained on this basis.

Tetravalent cerium has been shown to follow such a path in many of its oxidations. It has a very high standard potential, around 1.75 volts in four molar perchloric acid. It has no unpaired electrons in its ground state. In perchloric acid there seems to be no complexing of the cerium (IV) ion by anything but water.

The total equation is:



The possibility of forming chlorine atoms was considered rather doubtful since the calculated free energy was 40 kilocalories/mole. It was originally felt that in the oxidation of chloride ion by cerium (IV) ion the cerium would complex from one to six chlorides, and that these complexes would then decompose to give finally cerium (III) ion and chlorine gas. A consequence of such a mechanism is that as the chloride concentration increases the complexes containing larger amounts of chloride play an increasingly important part in determining the rate of the reaction. This would lead to an exceedingly complex rate expression. Another aspect is that atomic chlorine might be formed in one of the steps since the standard potential of cerium(IV) is so high.

This investigation is made to increase the knowledge of cerium (IV) oxidations and to study the mechanism of oxidation-reduction reactions in general. It is also desirable to determine whether the decomposition of which of several complexes is rate-determining and if the reaction forms chlorine atoms or chlorine gas first.

HISTORY

Increasing interest has been shown during recent years in the specific mechanisms of oxidation reactions. This interest is evidenced by the extension and application of the intermediate complex concept. Within

this field there have been a large number of studies using cerium (IV) compounds.

One of the early complete studies in which an intermediate complex was postulated was that of Hershey and Bray (1). They studied the reduction of iron (III) with iodide ion and suggested two alternate mechanisms, both of which depended on the formation of some complex between iron (III) ion and iodide ion.

Interaction of a complexing sort has been studied for metalorganic reactions as well as for inorganic reactions. Griegee and others (2) suggested a cyclic lead glycolate as an intermediate in the oxidation of glycol with lead tetracetate. Other oxidants acting similarly were periodate (3), tetravalent cerium (4), and tri- and tetravalent manganese (5). More recently Duke (6) showed that trivalent manganese oxidized oxalate through the disproportionation of oxalate manganate complexes. In another work (7) Duke showed that the periodate-glycol oxidation may also proceed through an intermediate involving the oxidant and reductant.

Other organic-metal bonds in intermediates included the carbon-osmium bond postulated by Zelikoff and Taylor (8) in the oxidation of fumaric and maleic acids with OsO_4 . In a series of studies (9, 10, 11, 12, 13) Westheimer and others proposed a chromic acid ester as the rate-determining intermediate in the chromic acid oxidation of isopropyl alcohol.

Inorganic reactions were represented by Hill's work (14) on the reduction of ozone by cobalt (II) ion; this reaction was supposed to go through a $\text{Co}(\text{AcO})_2$ complex. Other inorganic reactions included the oxidation of cyanide ion by copper(II) ion as studied by Courtney (15). This reaction had a fourth order dependence on cyanide and a first order dependence on Cu(II); the essential step was decomposition of $\text{Cu}(\text{CN})_4^{2-}$ or of $\text{Cu}(\text{CN})_3^-$ with a CN^- . Bottoms (16) investigated the oxidation of sulfite ion by iron(III) ion and tentatively concluded that the reaction proceeded through a $\text{FeSO}_4\text{SO}_3^-$ complex.

Cerium(IV) compounds have gained an increased importance as oxidants for widely varying uses in both organic and inorganic chemistry. Anderson and others (17) carried out the oxidation of arsenite ion with cerium(IV) in HCl solution, and studied the effect of halide ions on the rate. Kolp and Thomas (18) attempted to determine the kinetics of oxidation of water by cerium(IV) perchlorate. This reaction was heterogeneous and photocatalysed. Formation of a Ce(IV) complex with leuco malachite green during its oxidation was postulated by Swann and Hedberg (19).

The specific oxidation of glycol by cerium(IV) in perchloric acid solution to give acetaldehyde and Ce(III) was studied by Duke and Bremer (20). They concluded that the reaction goes through a mono- or a diglycolated cerium(IV) complex, depending on the glycol concentration. The

dependence on $Ce(IV)$ was first order. They also concluded that the perchlorate ion did not complex with cerium(IV) ion in solution. This first order dependence on the oxidant seemed to be a rather general phenomenon for most of the reactions mentioned. The present study was undertaken to determine if the oxidation of chloride ion by cerium(IV) proceeded by a similar path.

EXPERIMENT

All reaction rate studies of the oxidation of chloride ion by cerium(IV) perchlorate were made in amber-colored, stoppered, volumetric 100 ml flasks placed in a water bath at $25.0 \pm .2^\circ C$. The procedure was to make up the solutions in the flasks with the correct amount of perchloric and hydrochloric acids in them, but without the cerium(IV) ion. The flasks were filled nearly to the marks with distilled water, well shaken and placed in the bath until they came to temperature. Meanwhile a number of stoppered 10 ml volumetric flasks with a little less than 5 ml of constant concentration (around four molar) sulfuric acid was prepared. The cerium(IV) perchlorate solution was then added to the reaction flask, the solution was diluted to the mark, shaken and returned to bath. Five ml samples were taken at the proper intervals; care was taken not to introduce any sulfuric acid into the reaction flask. These samples were quenched in the small flasks, and the time was taken as the level passed a marked point on the pipet. This small solution was then diluted to the mark with more sulfuric acid and shaken. The absorbancy of the solution was then read on the spectrophotometer.

All reactions were run at 4.00 M hydrogen ion concentration, coming mostly from perchloric acid, but partially from the hydrochloric acid which supplied the chloride ion and partially from the highly acidic cerium(IV) perchlorate solution. This latter high acidity is necessary for stability. Those runs with constant cerium(IV) were .005 M in Ce^{+4} , and the chloride concentrations varied from .005 to 1.00 M. The perchloric and hydrochloric acids were stock solutions standardized against standard sodium hydroxide. The cerium(IV) perchlorate solution was prepared by electrolysis of pure cerium(III) perchlorate obtained by boiling pure cerium(III) oxalate in perchloric acid. The cerium(IV) was standardized by titrating against ferrous ethylene diamine sulfate in dilute sulfuric acid with ferroin indicator. The 4 M sodium perchlorate used in a few runs to maintain constant ionic strength was prepared by neutralizing 8 M stock perchloric acid with 8 M C.P. sodium hydroxide.

The spectrophotometer used was a Coleman model number 14 with a constant 8.5 volts source for the illuminating lamp. The blank cell contained the same sulfuric acid used in quenching the reaction, and its absorbancy was taken as zero. A calibration run was made duplicating exactly the experimental conditions. A curve was then drawn so that the absorbancy found in a run could be expressed in terms of actual molarity in cerium (IV). Figure 1 shows this curve. The reciprocal and the logarithm of these molarity values were plotted against time to determine order in cerium(IV). The wavelength was 420 millimicrons as suggested by Duke's measurements (21).

The effectiveness of the sulfuric acid for quenching was checked several times by noting the constancy of the reading of a quenched solution over a period of time. Also effect on the color of the solution of dissolved Cl_2 was found to be negligible.

Special care was taken in this experiment to introduce no oxidizable impurities into the reacting solutions since this would obviously lead to more reduction of the cerium(IV) ion than one would expect. In addition the 5 ml pipet used to take samples from the reaction flask was rinsed off with distilled water each time before insertion into the flask to prevent sulfuric acid from getting in and slowing down the reaction. A third special precaution was the keeping of a good 1.5 volt battery in the spectrophotometer at all times to guarantee reproducible readings.

To guard against oxidation of the water by cerium(IV) perchlorate, the reactions were all run in amber flasks at room temperature with high hydrogen ion concentration.

To cerium concentration was chosen for convenient readings on the spectrophotometer.

RESULTS

The main part of the experiment was the variation of chloride ion concentration from .005 M to 1.0 M with the cerium(IV) ion concentration constant at .005 M. Increased Cl^- gave an increased rate; time for completed reaction varied from seven and one half hours for .005 Cl^- to less than two minutes for 1.00 Cl^- . In all the plots of cerium(IV) concentration against time it was found that the data gave a straight line for a second order in cerium(IV) reaction for all concentrations of

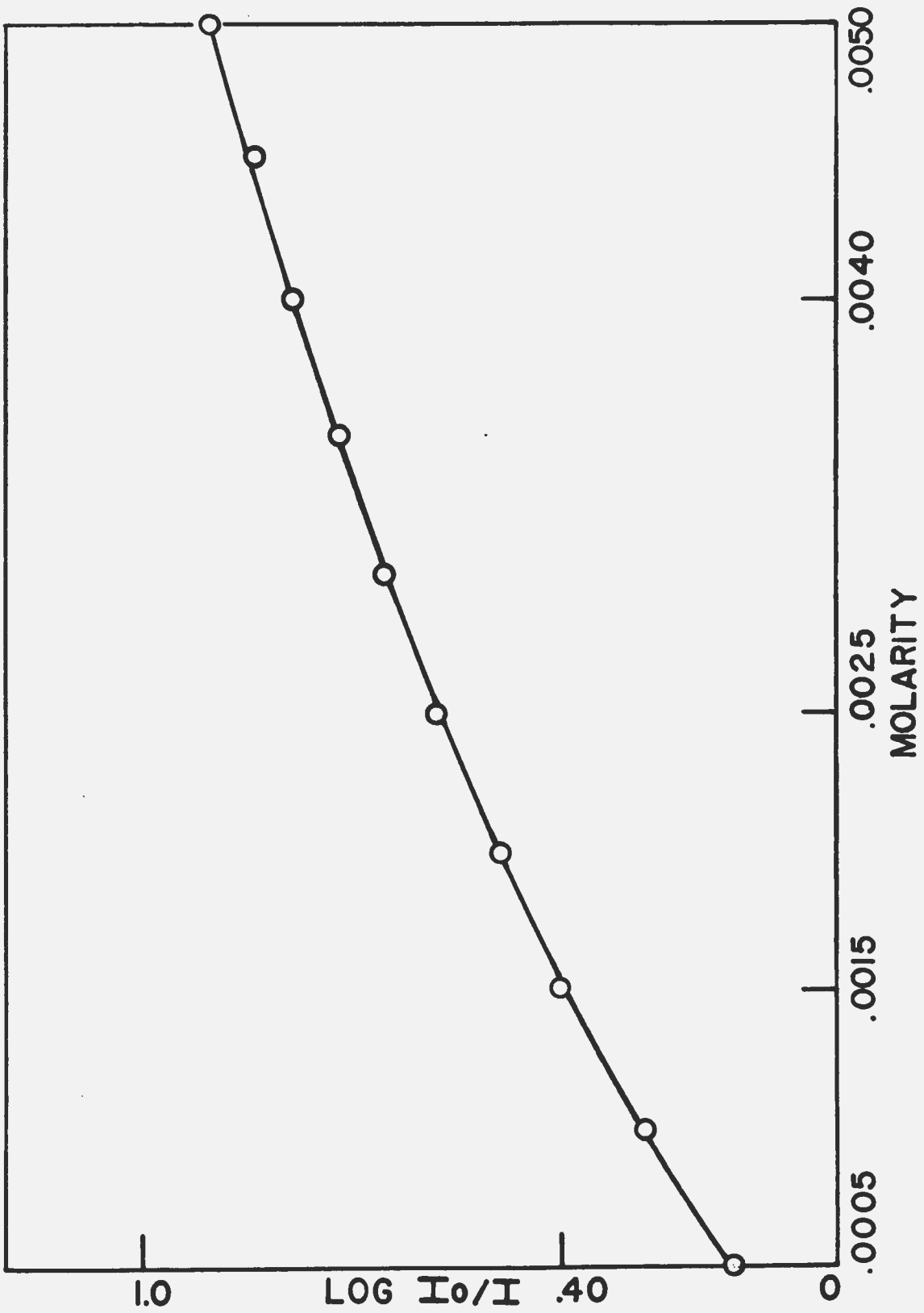
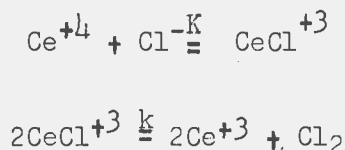


Figure 1--Log I₀/I against Molarity

chloride ion (figure 2). Values of initial slopes of log plots indicated a value close to two for the order of chloride. A mechanism for this was suggested to be:



Here K was the equilibrium constant for the first reaction, and k was the specific rates constant for the second. Then let $A = \text{total Ce(IV)}$

$$-dA/dt = k(\text{CeCl}^{+3})^2$$

and $K = (\text{CeCl}^{+3})/(\text{Ce}^{+4})(\text{Cl}^{-})$, but $A = (\text{Ce}^{+4}) + (\text{CeCl}^{+3})$.

Then $(\text{CeCl}^{+3}) = KA(\text{Cl}^{-})/(1 + K[\text{Cl}^{-}])$.

The second order slope $\equiv R_2 = -dA/dtA^2 = kK^2(\text{Cl}^{-})^2/(1 + K[\text{Cl}^{-}])^2$.

The final expression is

$$1/\sqrt{R_2} = 1/\sqrt{kK}(\text{Cl}^{-}) - 1/\sqrt{k}.$$

A plot of $1/\sqrt{R_2}$ against $1/(\text{Cl}^{-})$ (Figure 3) gave a straight line with a slope of $1/.291$ and an intercept of $.195$. The value of K was then $.0567$ liter/mole and the specific rate constant was 2.27 liter/mole/second. Contrary to most oxidation reactions and to all cerium(IV) oxidations studied, this reaction is second order in the oxidant.

Qualitative results were obtained from runs varying hydrogen ion and ionic strength. Lowering the ionic strength from 4.10 to 3.33 to 2.68 decreased the rate. Hydrogen ion concentrations of three molar and two molar also gave a decreased rate, but not as great a decrease as that for the ionic strength effect.

Table 1 shows a typical run using $.015$ M Cl^{-} and $.005$ M Ce(IV) . The absorbancy is the $\log I_0/I$ value; the concentration values were obtained from the calibration curve. Table 2 gives the values of the slopes of second order plots for all runs made with $.005$ M Ce(IV) .

An explanation of the excellent second order plots obtained at equivalent concentrations of chloride and cerium(IV) was that the chlorine

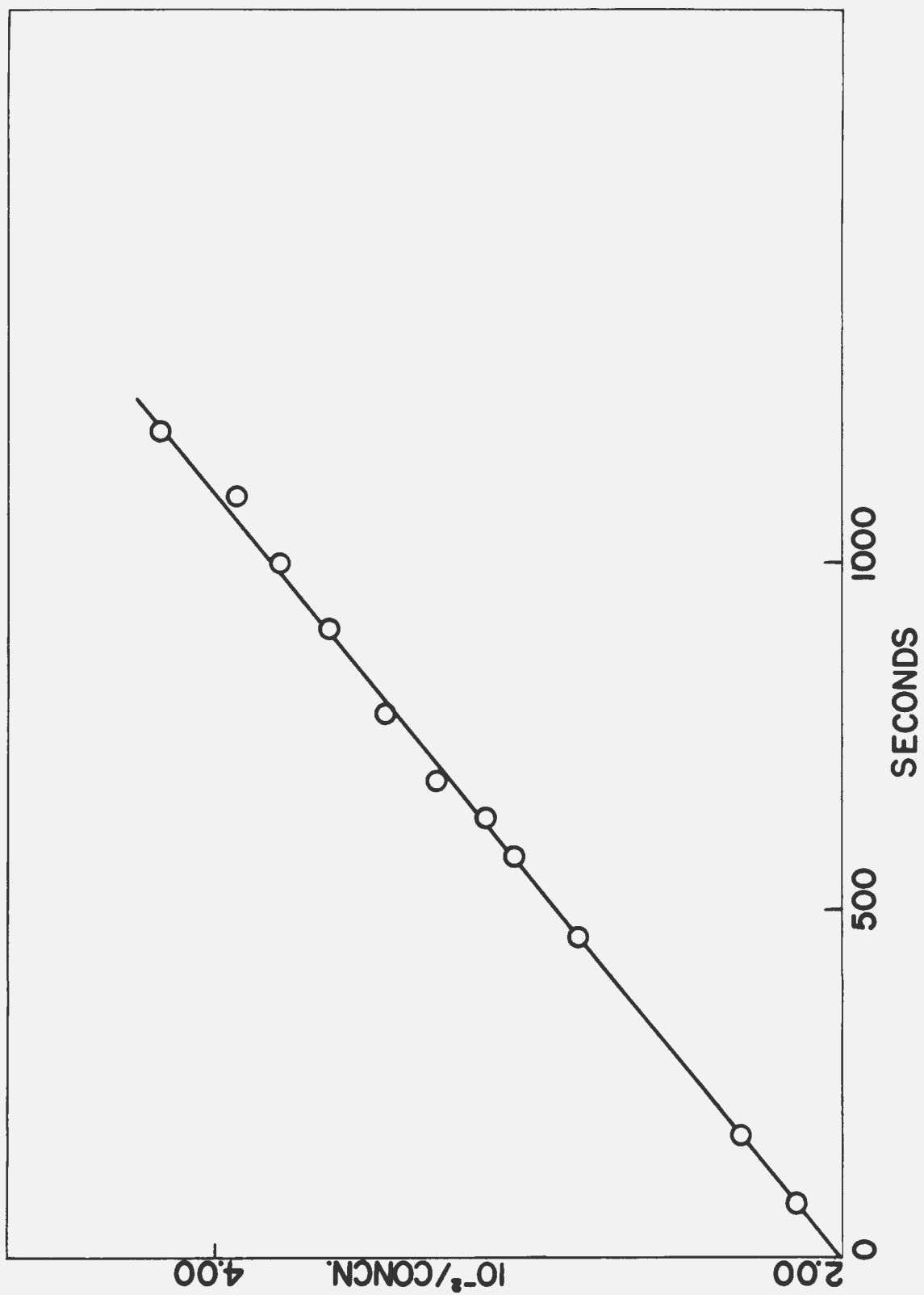


Figure 2--10-2/Concn. against Seconds

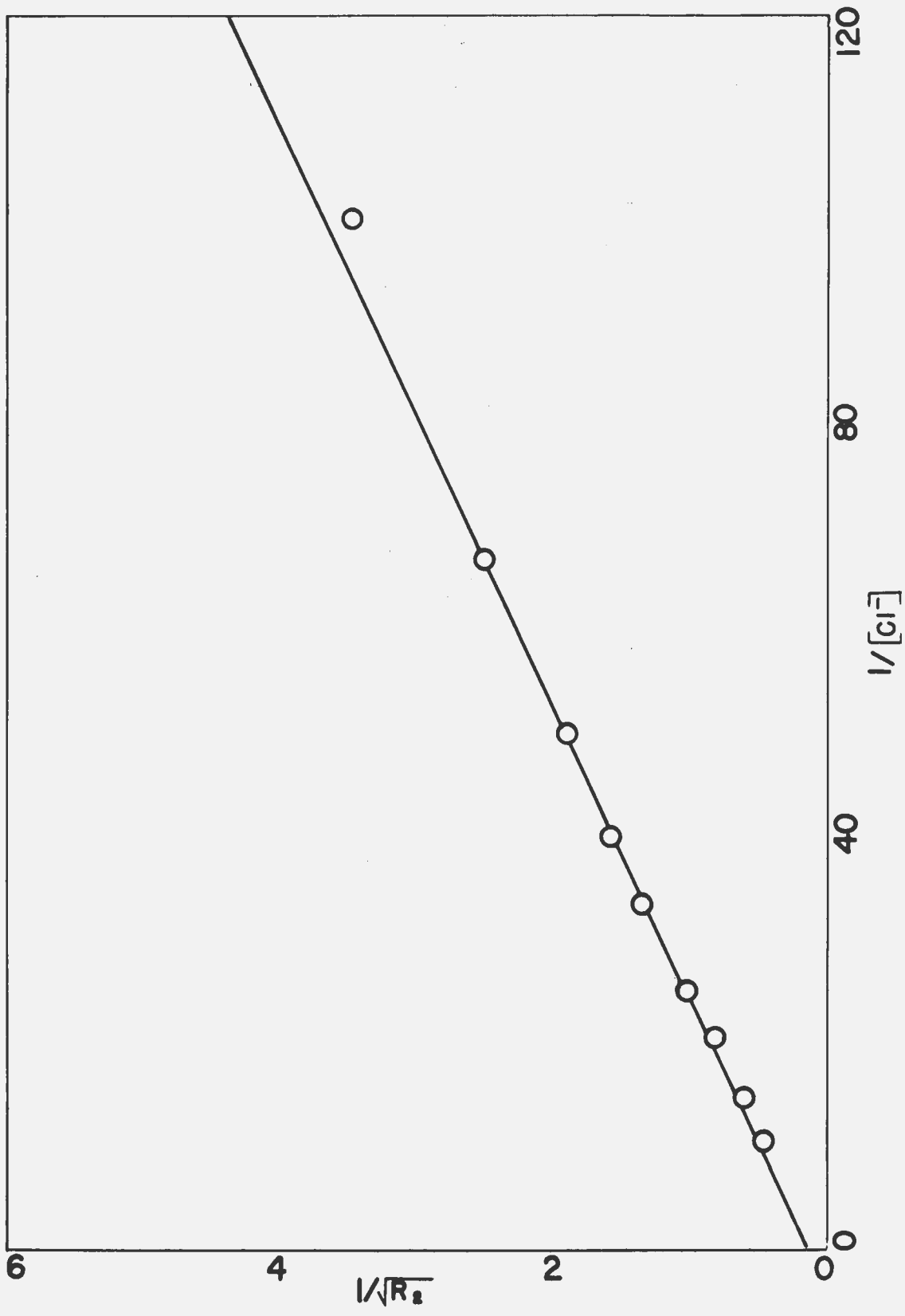


Figure 3--1/√R₂ against I/(Cl⁻)

Table 1

A Typical Run Using .015 M Cl^- and .005 M Ce(IV)
(Run No. 43)

Sec	$\text{Log } I_0/I$	$\text{Concn.} \times 10^{-2}$	$10^{-2}/\text{Concn.}$	$\text{Log concn.} \times 10^3$
76	.860	.470	2.13	0.673
177	.824	.436	2.29	0.640
454	.730	.362	2.76	0.559
577	.701	.340	2.94	0.532
630	.690	.330	3.03	0.519
684	.672	.316	3.17	0.500
788	.651	.302	3.31	0.470
900	.631	.288	3.47	0.459
1002	.613	.277	3.61	0.443
1093	.596	.268	3.73	0.428
1190	.575	.252	3.97	0.402

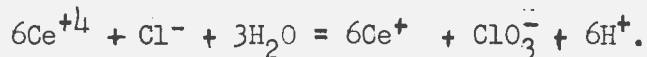
Table 2

Values of the Slopes of Second Order Plots for
All Runs Made with .005 M Ce(IV)

Run	M Cl ⁻	1/M Cl ⁻	Slope \bar{R}_2	$\sqrt{R_2}$	$1/\sqrt{R_2}$
59,60	.005	200.0	.0205	.143	7.00
62-64					
36,37	.010	100.0	.0838	.290	3.45
39,42					
43-46	.015	66.7	.161	.402	2.48
38,47	.020	50.0	.276	.526	1.90
50-54					
55-58	.025	40.0	.399	.632	1.58
73,74	.030	33.3	.560	.749	1.34
75,76	.040	25.0	.922	.960	1.04
77,78	.050	20.0	1.39	1.18	.847
79,80	.070	14.3	2.63	1.62	.616
81,82	.100	10.0	4.39	2.10	.477

gas is tied up in higher oxidation states before it can escape from the solution. To test this idea .03 M Ce(IV) and .005 M Cl⁻ concentrations were made up in 4.00 M perchloric acid; this solution was allowed to react for several days, at the end of which time the solution was completely colorless. Two titers were drawn, AgNO₃ was placed in one, and AgNO₃ and FeSO₄ were placed in the other. The second titer gave considerably more precipitate than the first, indicating some higher oxidation state of chlorine was present.

The two possibilities for obtaining higher oxidation states of chlorine are through disproportionation of the reaction product of the kinetically slow step, or through oxidation of this product with cerium (IV). The present literature data (22) indicate that the oxidation rather than the disproportionation took place. The fact that the experimental data indicated the reaction of two CeCl⁺³ ions to form the activated complex means that the most likely reaction product is Cl₂. This must then be further oxidized to chlorate, the first higher state which would be stable at these concentrations of cerium in 4 M perchloric acid. Thus the most likely kinetic step is the reaction of two complexes to give cerium (III) and Cl₂. The total chemical stoichiometry is



The kinetics of the oxidation of chloride ion by cerium(IV)perchlorate were studied, and the reaction was found to be second order in both Ce(IV) and Cl⁻; the explanation made was that a CeCl⁺³ complex formed and then two of them reacted to give the products.

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