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THE KINETICS OF THE REDUCTION OF PERCHLORATE ION IN DILUTE SOLUTION

by

Paul R. Quinney

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INTRODUCTION

The reactions and uses of perchloric acid as a strong oxidizing agent in concentrated solutions are well known (1,2,3,4). However, in dilute solutions it appears to act only as an acid, the perchlorate ion being relatively unreactive. Because of this unreactivity of the perchlorate ion in dilute solutions perchlorates are used considerably, for example, as a means of maintaining constant ionic strength in solutions, in electromotive force studies, or, in general, under conditions where an inert ion is required. Also, perchlorate ion does not form complexes in aqueous solutions and so perchlorate salts are used to study the formation of complex ions such as chlorides and sulfates by means of electromotive force measurements. Investigations of this nature give an insight into the manner in which ions are coordinated in solutions. This further aids in explaining the mechanisms by which reactions take place in aqueous media.

Perhaps less well known are the reactions in which perchlorate ion is reduced in dilute solutions. Sjollema (5) reduced perchlorate with ferrous hydroxide and Tommasi (6) reportedly reduced it with hyposulfurous acid. Rothmund (7) demonstrated that the salts of trivalent titanium as well as the salts of the lower oxidation states of vanadium and molybdenum were oxidized with considerable speed by perchloric acid in dilute aqueous solutions. The lower salts of tungsten and chromium also react but extremely slowly.

Since perchlorate ions are quite stable and do not tend to form complexes in aqueous solutions, the question arises as to the mechanism of electron transfer during the course of the reduction process. In order for an oxidation-reduction reaction to take place there must be, of course, some means by which an electron may transfer from one reactant to the other. In general, this transfer may occur by two different processes: 1) direct transfer of electron upon collision of the two reactants, and 2) transfer of electron after the formation of coordinated complex ions as an intermediate. The former process takes place as a result of a direct collision of the reactants. The second is the result of an electrostatic attraction between ionic species to form a coordinated complex which may react to yield the end products.

If the process takes place by a direct collision of the reactants, then they must possess sufficient energy to cause an interaction of their atomic orbitals allowing an electron transfer to take place. The nature of this reaction would require fairly high energies, those normally found in the gas phase at elevated temperatures where the reacting species would possess the required energy.

For reactions at lower temperatures, such as reactions carried out in the liquid phase, the reactant molecules would not possess a high enough energy to react upon collision. Consequently, a more reasonable explanation must be found, one which requires an intermediate with a lower activation energy so that the reactants can scale the potential hump which exists between reactants and products. The formation of a coordination complex between oxidant and reductant has been proposed. The formation of this complex lowers the activation energy of the reacting species so that a reaction may take place.

Considerable evidence supporting the theory that coordination complexes enter into oxidation reactions may be found in the literature. Manchot and Haunschild (8) and Manchot and Pflaum (9) were earlier proponents of this theory. More recent data are given by Duke (10) and Duke and Bremer (11). A review of the more recent work done on this theory may be found in Bremer's Doctoral thesis (12).

Since perchlorate ion does not tend to form complex ions, undoubtedly due to its stable configuration, the mechanism by which Ti(III) and ClO_4^- do react in dilute solutions becomes of interest. The reacting species are undoubtedly some complexes of Ti(III) as $Ti(OH)^{++}$ or $TiCl_x^{+3-x}$, the latter since the reaction is carried out in Cl^- solutions. Bredig and Michel (13) studied the chemical kinetics of perchloric acid and its salts in aqueous solutions of hydrochloric and sulfuric acids. The reaction of interest in this work which they studied was that of the oxidation of Ti(III) with perchlorate ion in hydrochloric acid-water solutions. They found the kinetics of the reduction of perchlorate ion to be first order in Ti(III) and the rate to be independent of the initial concentration of Ti(III). They reported also that increasing the hydrochloric acid concentration increases the rate, especially at high concentrations, i.e., those of the order of 4-6M. They did not point out that under these conditions both the H^+ and Cl^- concentrations are being increased and that probably both of these do have an effect on the rate. The perchlorate dependence was studied using both $HClO_4$ and $Mg(ClO_4)_2$ indicating that the rate is proportional to the perchlorate concentration whether as $HClO_4$ or $Mg(ClO_4)_2$. However, their data show that the rate is considerably greater when $HClO_4$ is used, thereby indicating that the H^+ does play a role in the reaction kinetics. They do point out later that the dependence of acid is complex, the reaction being less influenced at lower concentrations and increasing to approximately first order. This is one phase of the problem that requires more study. A simple dependence of acid as well as the other ions is not in accord with the stoichiometry of the reaction,

$$8TiCl_3 + 7HCl + HClO_4 \longrightarrow 8TiCl_4 + 4H_2O.$$

Actually, though, this is quite frequently the case, where the actual kinetics of a reaction consists of a series of lower order reactions which make up the over-all process.

One of the mechanisms of the reaction proposed by Bredig and Michel (13) requires that a direct combination of Ti(III) and ClO_4^- takes place to form a complex as an intermediate step which would then react to give Ti(IV). This seems unlikely since direct complexes of perchlorate ion are very rare and probably the Ti(III) is in solution as a complex as mentioned above. Another possible explanation proposed is that in which Ti(III) is oxidized in a slow step to Ti(V), whereupon the Ti(V) immediately reacts with another Ti(III). The ClO_4^- is reduced to Cl^- by a stepwise process. However, this requires the presence of $2H^+$ and also the probability of a quadra-molecular reaction which is highly improbable. A third explanation offered is the reaction between Ti(III) and ClO_4^- to first form an oxygen compound of hexavalent chloride and Ti(IV). This gives a formula for a hypothetical acid H_2ClO_4 analogous to manganic acid. However, the H^+ dependence does not enter into this mechanism and from the data given it must be considered.

In reviewing these mechanisms the possibility of a complex of Ti(III) and Cl^- existing or of a hydrolysis product of Ti(III), $Ti(OH)^{+2}$, have not been considered. These would indeed seem to not only exist in solutions of this kind but also seem to play an important part in considering a kinetic mechanism for this reaction. With the preceding considerations in mind, the work comprising this thesis was undertaken. It was hoped that in the course of this investigation a suitable mechanism for the reduction of perchlorate ion in dilute aqueous solutions could be postulated.

EXPERIMENTAL

Inorganic Materials

The titanium metal powder used to prepare the titanium(III) chloride solutions was obtained from Metal Hydrides, Inc., Beverly, Massachusetts. Previous attempts were made to study the kinetics of this reaction using solutions of $TiCl_3$ made with Ti metal obtained from the Chicago Apparatus Company, Chicago, Illinois. Inconsistent results were obtained and the reaction did not appear to either go to completion or to be first order in Ti(III) as shown by Bredig and Michel (13). Both samples of the Ti metal were analyzed spectrographically. That from the Chicago Apparatus Company was found to contain a rather high percentage of iron, i.e., greater than 1%. The Ti powder obtained from Metal Hydrides, Inc. had less than 0.01%. MacKenzie and Tompkins (14) reported in their study of the auto-oxidation of $TiCl_3$ solutions that Fe^{+2} does interfere. Thus, all solutions of $TiCl_3$ were made from Ti metal powder from the Metal Hydrides, Inc.

Ferrous ammonium sulfate used was Baker and Adamson Company, Reagent Grade, obtained from General Chemical Division of the Allied Chemical and Dye Corporation and was not purified further.

Ceric ammonium sulfate was obtained from the G. Frederick Smith Company, Columbus, Ohio.

Sodium chloride and sodium hydroxide were Baker Analyzed, Reagent Grade, manufactured by the J. T. Baker Chemical Company.

All acids used were the products of the Baker and Adamson Company.

Preparation of Solutions

Titanium(III) chloride solutions were made by dissolving Ti metal powder in approximately 6N HCl. The reaction was carried out at room temperature under an atmosphere of nitrogen to prevent oxidation of the Ti(III) by atmospheric oxygen. The solutions were approximately 0.3N and were standardized as described below. After the reaction was completed (usually 4-6 hours) the solution was filtered and then stored under nitrogen. The nitrogen was passed through a 0.1N vanadyl sulfate trap to remove any residual oxygen. The concentration of Ti(III) underwent no appreciable change over a period of three months.

Solutions of $TiCl_3$ were standardized according to Method I as outlined in the Association of Official Agricultural Chemists, "Methods of Analysis" (15).

The total chloride concentration was determined by the nitrobenzene modification of the Volhard method for soluble chlorides. It was necessary to first oxidize the Ti^{+3} by pipetting a sample into an excess of ceric sulfate solution to prevent the Ti^{+3} from reducing the Ag^{+}.

The hydrogen ion concentration was determined by two different methods. The first of these and the one used was to let it be equal to the difference between the total chloride and the titanium concentration. The second method was to first dilute the concentrated solution down by pipetting five milliliters into a 100 milliliter flask and making up to the mark with water. Then to ten milliliters of this was added an excess of standard NaOH solution. The precipitate formed was filtered off and then the excess base titrated with standard alkali. The two methods agreed within 1%.

Sodium perchlorate solutions were made by neutralizing 72% perchloric acid with sodium hydroxide pellets and then diluting to the desired concentration. The solution was standardized by passing it through a column of acid exchange resin and then titrating the acid produced with standard alkali using phenolphthalein as indicator.

Sodium chloride solutions were made by dissolving a weighed quantity of the salt into a volumetric flask and diluting to volume.

Both the HCl and $HClO_4$ solutions used were standardized with standard alkali using phenolphthalein as indicator.

Ferrous ammonium sulfate was dissolved in approximately 0.05N H_2SO_4 and also stored under nitrogen to prevent oxidation by atmospheric oxygen.

Ceric ammonium sulfate solutions were prepared by dissolving the required amount of the salt in nine normal H_2SO_4.

A solution of Ce(IV) in 9N H_2SO_4 was used as a quenching medium. Five ml samples of the reaction mixture were pipetted into excess Ce(IV) at known intervals of time. The excess Ce(IV) was titrated with standard Fe(II). The amount of Ce(IV) used is equivalent to the amount of Ti(III) present at the time the sample was taken.

DISCUSSION

The Pseudo-Rate Constant

A plot of the natural logarithm of the milliliters of Ce^{+4} used up versus time yielded excellent straight lines for all determinations. In most all cases the values plotted were averages of two or more determinations.

The over-all rate expression for the disappearance of total Ti^{+3} can be written thus,

$$-\frac{d[T_{Ti}{}^{+3}]}{dt} = k[T_{Ti}{}^{+3}]\,F(H^{+})F(Cl^{-})F(ClO_4{}^{-}) \qquad (1)$$

where k is the specific rate constant for the reaction and F represents some function of concentrations as yet to be determined. For any one run the concentration of H^{+} remains constant and if the $ClO_4{}^{-}$ and Cl^{-} concentrations are large compared to the Ti^{+3}, then this expression simplifies to

$$-\frac{d[T_{Ti}{}^{+3}]}{dt} = k'[T_{Ti}{}^{+3}]. \qquad (2)$$

In this equation k' represents a pseudo first order rate constant and is the slope of a plot of $\ln[T_{Ti}{}^{+3}]$ vs. time. Thus, by varying the starting concentrations of H^{+}, Cl^{-}, and $ClO_4{}^{-}$, the rate dependence of each ion can be studied and in this way the nature of the function F is determined. From this it may be possible to propose a mechanism by which this reaction takes place.

Rate Determinations

All determinations were carried out in a distilled water bath using a mercury thermoregulator to control the temperature to ±0.05°C. Except for special determinations to be considered later the majority of runs was made at 40°C. At this temperature the reaction went to completion in about one hour, giving ample time for taking samples. At 60°C the reaction was complete in about ten minutes.

The reactions were carried out in a 100 milliliter volumetric flask with an extra calibration mark at 96 milliliters.

The $NaCl$, $NaClO_4$, $HClO_4$, and HCl, necessary to make up a solution of the desired concentrations were added to the 100 milliliter flask and diluted to the 96 milliliter mark. The flask and contents were then placed into a water bath for 15-30 minutes and allowed to come to temperature. Four milliliters of $TiCl_3$ solution were added, the solution shaken thoroughly, and the timer started. At various intervals of time, depending upon the speed of reaction, five milliliter samples were taken and pipetted into an excess of quenching solution. The time of quenching was taken as that time the meniscus passed a certain mark on the pipette, about the halfway mark.

The quenching solution was a 0.01N solution of ceric ammonium sulfate approximately 9N in H_2SO_4. It was found necessary to adjust the acidity of this solution to the most optimum conditions. If the pH were too high then basic salts of cerium precipitated, whereas if the acid concentration was too high then NaCl precipitated, and tended to obscure the end point. A concentration of about 9N H_2SO_4 was found to give the best results. Ten milliliters of the Ce(IV) solution were used and the excess was titrated with 0.01N ferrous ammonium sulfate using ferroin as the indicator. For these concentrations the indicator blank is quite high and a large error was anticipated but by using a constant volume of indicator good consistent results were obtained. Indicator blank corrections were not made since the errors involved were well within the over-all errors in the rate determinations.

The exact concentrations of the Ce(IV) and Fe(II) solutions were not known, only their titre. The volume of Fe(II) needed to titrate the excess of Ce(IV) after quenching was converted to an equivalent amount of Ce(IV) which in turn is converted to an equivalent amount of Ti(III) present at the time the sample was taken. Thus, when a run was completed a plot of ln(Ce[IV] used up) versus time was made for the first order plot.

The Hydrogen Ion Dependence

Since it was not too clear as to the role that the H^+ played in this reaction from the data of Bredig and Michel (13) it was decided to first study this effect. Runs were made at a chloride concentration equal to 2.0M, $ClO_4^- = 0.5M$, $Ti^{+3} = 0.015M$. Data were also collected at three temperatures, 30°C, 40°C, and 50°C, to study the effect of temperature on the rate constants. The data are shown in Tables 1, 2, and 3, and are plotted in Figures 1, 2, and 3, respectively.

A plot of the pseudo constant k' vs. $[H^+]$ yielded a straight line for temperatures of 30° and 40°C. The best straight line was determined by the Method of Least Squares. Thus, k' may be written,

$$k' = k_{0_H} + k_{1_H}[H^+] \qquad (3)$$

where k_{0_H} and k_{1_H} are the rate constants. The values of k_{0_H} and k_{1_H} were obtained from the graphs, k_{0_H} being the y intercept and k_{1_H} being the slope of the straight line. This equation then represents the function $F(H^+)$ in the

Table 1. Hydrogen Ion Dependence 30°C. Variation of pseudo first order rate constants with $[H^+]$.

$[Ti^{+3}] = 0.015M$ $[Cl^-] = 2.0M$ $[ClO_4^-] = 0.5M$ 49 gr/L

$[H^+]$	$k'x10^3$	$[H^+]$	$k'x10^3$
0.23	8.37	1.2	10.24
0.40	8.75	1.4	10.82
0.60	8.05	1.6	11.47
0.80	9.72	1.8	12.00
1.0	9.97	2.0	12.47

Table 2. Hydrogen Ion Dependence 40°C. Variation of pseudo first order rate constants with $[H^+]$.

$[Tl^{+3}] = 0.015M$ $[Cl^-] = 2.0M$ $[ClO_4^-] = 0.5M$

$[H^+]$	$k'x10^2$	$[H^+]$	$k'x10^2$
0.23	2.66	1.2	3.40
0.40	2.84	1.4	3.60
0.60	3.01	1.6	3.77
0.80	3.15	1.8	3.91
1.0	3.29	2.0	4.17

Table 3. Hydrogen Ion Dependence 50°C. Variation of pseudo first order rate constants with $[H^+]$.

$[Ti^{+3}]$ = 0.015M $[Cl^-]$ = 2.0M $[ClO_4^-]$ = 0.5M

$[H^+]$	$k'x10^2$	$[H^+]$	$k'x10^2$
0.23	8.95	1.2	11.22
0.40	9.43	1.4	11.78
0.60	9.86	1.6	12.53
0.80	10.16	1.8	13.52
1.0	10.52	2.0	14.45

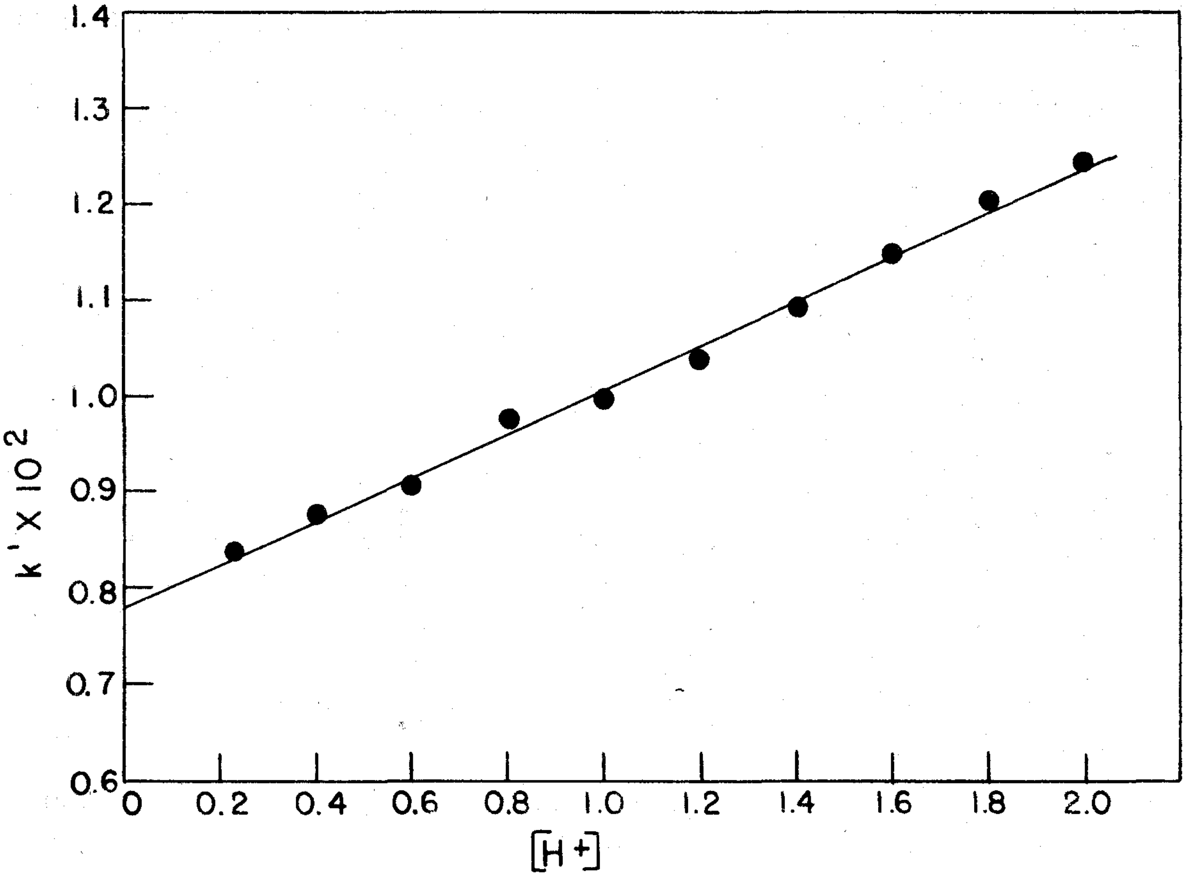

FIG. 1. HYDROGEN ION DEPENDENCE 30° C FIRST ORDER RATE CONSTANTS VERSUS [H+]. [Ti+3] = 0.015 M $[ClO_4^-]$ = 0.5 M $[Cl^-]$ = 2.0 M

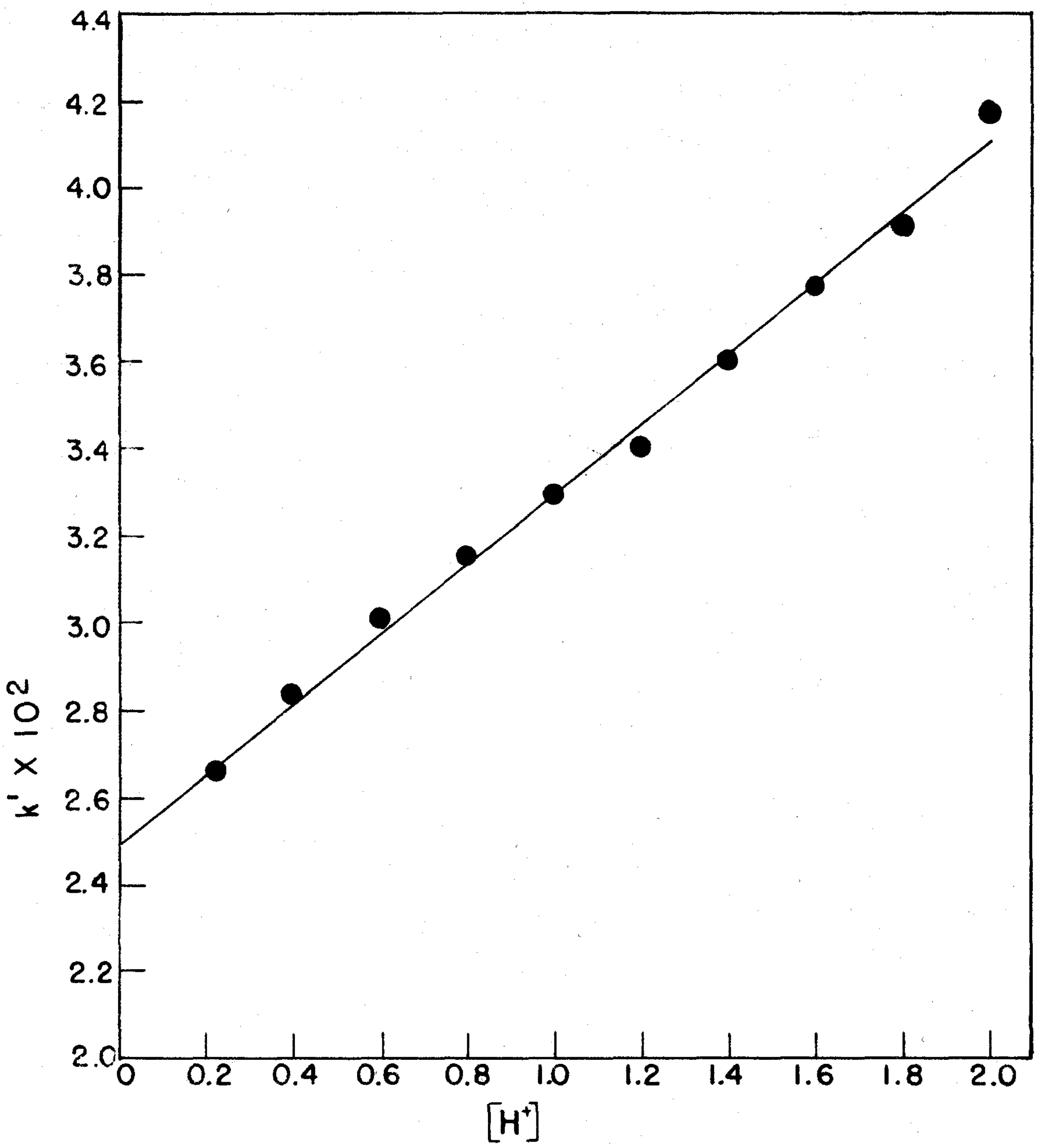

FIG. 2 HYDROGEN ION DEPENDENCE 40°C FIRST ORDER RATE CONSTANTS VERSUS $[H^+]$. $[Ti^{+3}] = 0.015M$ $[ClO_4^-] = 0.5 M$ $[Cl^-] = 2.0 M$

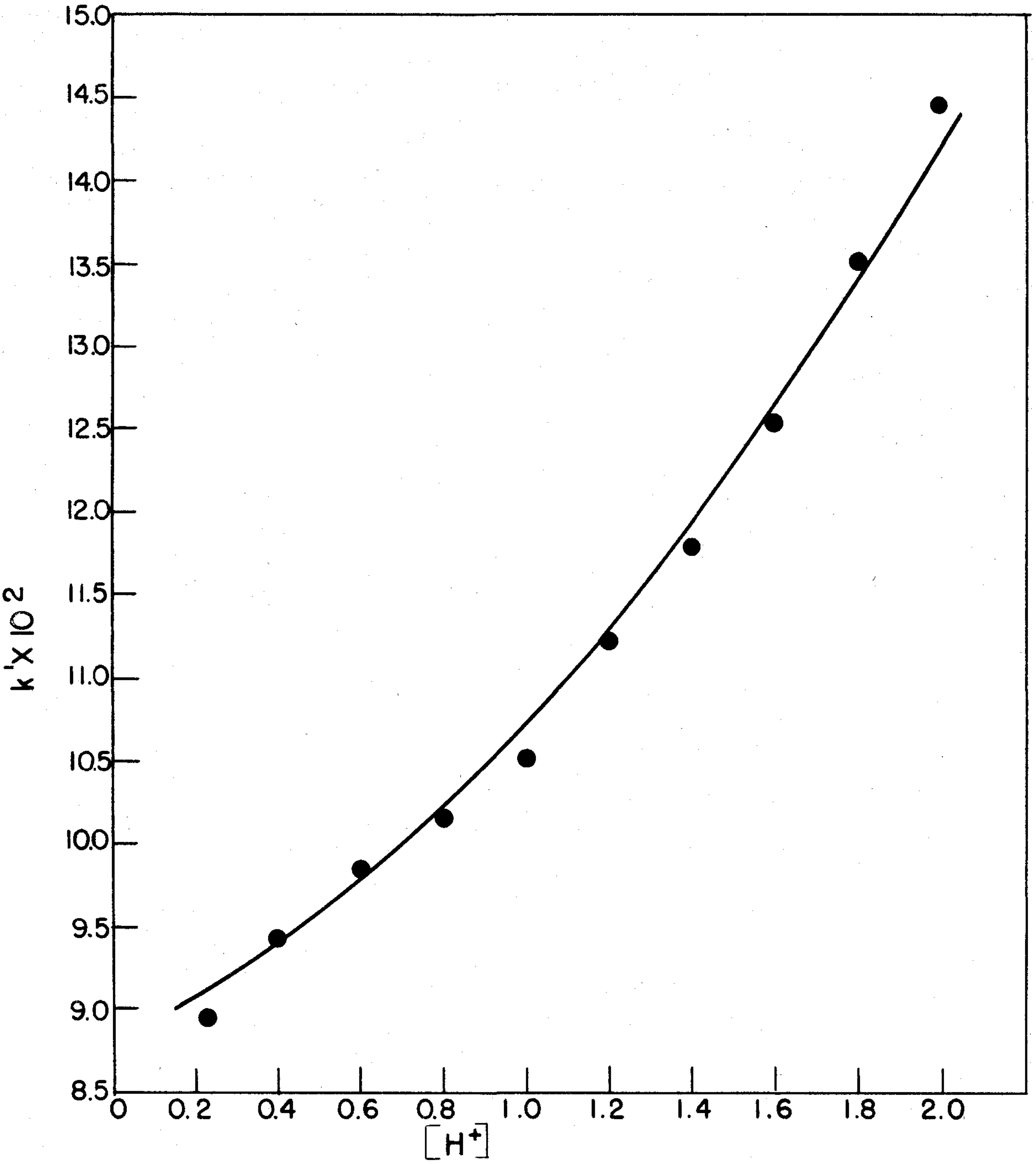

FIG. 3. HYDROGEN ION DEPENDENCE 50°C FIRST ORDER RATE CONSTANT VERSUS $[H^+]$ $[Ti^{+3}] = 0.015M$ $[ClO_4^-] = 0.5 M$ $[Cl^-] = 2.0 M$

original rate equation and the rate expression takes the form,

$$-\frac{d[T_{Tl^{+3}}]}{dt} = (k_{0_H} + k_{1_H}[H^+])F(Cl^-)F(ClO_4^-)[T_{Tl^{+3}}]. \tag{4}$$

Above 40°C the H^+ dependence is no longer linear and at 50°C the function assumes the form,

$$k' = k_{0_H} + k_{1_H}[H^+] + k_{2_H}[H^+]^2. \tag{5}$$

The values of k_{0_H}, k_{1_H}, and k_{2_H} obtained from the graphs of Figures 1, 2, and 3 are given in Table 4.

The significance of the constants k_{0_H} and k_{1_H} may be explained in the following way. The reaction proceeds by two independent paths, one which is hydrogen ion dependent and the other which is hydrogen ion independent. Thus, k_{0_H} represents the rate constant for the reaction if no H^+ were present in the solution, or it is the rate constant for a reaction uncatalyzed by H^+. Then k_{1_H} is the rate constant for the H^+ dependent reaction.

These constants vary with temperature so that the activation energies and entropy changes for these effects can be calculated. The following equations were used,

Table 4. Hydrogen Ion Dependence. Variation of rate constants with temperature.

t °C	$k_{0_H} \times 10^2$	$k_{1_H} \times 10^2$	$k_{2_H} \times 10^2$
30	0.78 ± 0.05*	0.23 ± 0.02	---
40	2.49 ± 0.2	0.81 ± 0.06	---
50	8.80 ± 0.6	1.20 ± 0.08	0.75 ± 0.5

* Errors based on an estimated maximum error of about 7% in determining the pseudo rate constants.

$$\Delta F^{\ddagger} = -2.3\ RT \log \frac{K}{K_B\ T/h}$$

K_B = Boltzmann's Constant

h = Planck's Constant

$$\Delta H^{\ddagger} = 2.3\ R \frac{T_1T_2}{T_2-T_1} \log \frac{K_2}{K_1} - RT$$

$$\Delta S^{\ddagger} = \frac{-\Delta F^{\ddagger} + \Delta H^{\ddagger}}{T} .$$

Using the data shown in Table 4 these quantities were calculated and are shown in Table 5.

The fact that the reaction proceeds both hydrogen ion catalyzed and hydrogen ion uncatalyzed indicates that there must be at least two titanium complexes which can form a coordinated complex with perchlorate ion and will react to give the final products. These complexes could be $Ti(OH)^{++}$ and $TiCl^{++}$, as well as a hydrated complex. Since the reaction is hydrogen ion catalyzed one might expect the following equilibrium to exist,

$$Ti(OH)^{++} + H^{+} \rightleftharpoons Ti^{+3} + H_2O.$$

However, if this were the case then it should be possible to determine an equilibrium constant for this reaction and it should show up in the rate equation. It can be seen that this is not the case; consequently, this equilibrium does not exist, or, at least it does not enter into the kinetics

Table 5. Rate Constants and Thermodynamic Functions for the Hydrogen Ion Dependence.

$$-\frac{d[Ti^{+3}]}{dt} = (k_{0_H} + k_{1_H}[H^{+}])[Ti^{+3}]$$

Uncatalyzed reaction	30°C	40°C
$k_{0_H} \times 10^2$	0.78 ± 0.5	2.49 ± 0.2

$\Delta F^{\ddagger}_{313} = 20.7 \pm 0.1$ kcal

$\Delta H^{\ddagger} = 21.3 \pm 12\%$ kcal

$\Delta S^{\ddagger} = 21.3 \pm 50\%$ e.u.

Catalyzed reaction	30°C	40°C
$k_{1_H} \times 10^2$	0.23 ± 0.02	0.81 ± 0.06

$\Delta F^{\ddagger}_{313} = 21.3 \pm 0.1$ kcal

$\Delta H^{\ddagger} = 24.2 \pm 8\%$ kcal

$\Delta S^{\ddagger} = 9.27 \pm 50\%$ e.u.

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of this reaction. This would then lead to the supposition that either the $TiCl^{++}$ or the hydrated Ti^{+3} is one of the reacting species.

The next phase of the problem then was to study the effect of chloride ion on this reaction.

The Chloride Ion Dependence

Although chloride ion is one of the products of this reaction and might not be considered as having too great an effect on the rate since the reaction goes to completion, one would nevertheless expect it to play an important role in the reaction kinetics due to the formation of chloride complexes of Ti^{+3}.

If one assumes the following to be the rate expression,

$$-\frac{d[T_{Ti^{+3}}]}{dt} = k_{1_{Cl}}[Ti^{+3}] + k_{2_{Cl}}[TiCl^{++}] + k_{3_{Cl}}[TiCl_2^{+}] + \dots, \qquad (6)$$

then the total titanium in solution both complexed and non-complexed will be given by,

$$[T_{Ti^{+3}}] = [Ti^{+3}] + [TiCl^{++}] + [TiCl_2^{+}] + \dots \qquad (7)$$

Now for the complexes formed, we may write,

$$Ti^{+3} + Cl^{-} \rightleftharpoons TiCl^{++},$$

$$TiCl^{++} + Cl^{-} \rightleftharpoons TiCl_2^{+}, \text{ etc.}$$

Equilibrium constants for these equilibria may also be written,

$$K_1 = \frac{[TiCl^{++}]}{[Ti^{+3}][Cl^-]}, \qquad K_2 = \frac{[TiCl_2^{++}]}{[TiCl^{++}][Cl^-]}, \text{ etc.}$$

Then, $[TiCl^{++}] = K_1[Ti^{+3}][Cl^-]$,

and $[TiCl_2^{+}] = K_1K_2[Ti^{+3}][Cl^-]^2$, etc.

Substituting in the expression for total titanium, equation 7,

$$[T_{Ti^{+3}}] = [Ti^{+3}] + K_1[Ti^{+3}][Cl^-] + K_1K_2[Ti^{+3}][Cl^-]^2 + \ldots,$$

from which

$$[Ti^{+3}] = \frac{[T_{Ti^{+3}}]}{1 + K_1[Cl^-] + K_1K_2[Cl^-]^2 + \ldots}. \qquad (8)$$

The rate law expression then becomes,

$$-\frac{d[T_{Ti^{+3}}]}{dt} = \frac{k_{1_{Cl}}[T_{Ti^{+3}}] + k_{2_{Cl}}\ K_1[Cl^-][T_{Ti^{+3}}]}{1 + K_1[Cl^-] +}$$

$$\frac{+\ k_{3_{Cl}}\ K_1K_2[Cl^-][T_{Ti^{+3}}] + \ldots}{K_1K_2[Cl^-]^2 + \ldots}$$

or,

$$-d \ln [\mathrm{Tl}^{+3}] = \left[\frac{k_{1_{Cl}} + k_{2_{Cl}} K_1[\mathrm{Cl}^-] + k_{3_{Cl}} K_1K_2[\mathrm{Cl}^-]^2 + \ldots}{1 + K_1[\mathrm{Cl}^-] + K_1K_2[\mathrm{Cl}^-]^2 + \ldots} \right] dt. \tag{9}$$

The expression in the brackets is the pseudo first order rate constant, k', the values of which can be obtained from the plots of $\ln[\mathrm{Tl}^{+3}]$ vs. time. If the expression is simplified to the following,

$$k' = \frac{k_{1_{Cl}} + k_{2_{Cl}} K_1[\mathrm{Cl}^-]}{1 + K_1[\mathrm{Cl}^-]}, \tag{10}$$

thereby disregarding for the time being the higher complexes, one obtains an equation with three unknowns: K_1, the equilibrium constant for the formation of the complex, and the rate constants $k_{1_{Cl}}$ and $k_{2_{Cl}}$. By taking three values of k' vs. Cl^-, three equations can be set up and the unknowns $k_{1_{Cl}}$, $k_{2_{Cl}}$, and K_1, determined. The theory can be checked by comparing the experimentally determined data with that calculated using the newly determined constants $k_{1_{Cl}}$, $k_{2_{Cl}}$, and K_1.

The chloride dependence of the reaction was studied at four different values of H^+ concentration and at two temperatures. In this way it was possible to determine not only the effects of chloride ion at various H^+ but also the temperature dependence as well.

The data obtained are shown in Tables 6, 7, 8, and 9, and are plotted in Figures 4, 5, 6, 7, respectively. These data show quite clearly the decrease in rate upon increasing the Cl^- concentration. This is in contrast to the data of Bredig and Michel (13) who found an increase in rate upon increasing the HCl concentration. Although these runs were at lower Cl^- than those of Bredig and Michel (13), determinations made at higher concentrations, i.e., 4M, showed no increase in rate. It would seem that increasing the HCl concentration should produce a decrease in rate since the decrease due to Cl^- is far greater than the increase produced by H^+.

For all four determinations the theory was tested by first calculating the constants $k_{1_{Cl}}$, $k_{2_{Cl}}$, and K_1, from the data obtained, using equation 10. These are shown in Table 10. Then the constants were substituted back into equation 10 for k', and for given values of Cl^-, the corresponding values of k' were calculated. The theoretical and observed values so obtained are compared in Table 11. It can be seen that agreement with theory is excellent for Cl^- concentrations less than about two molar. Beyond this concentration higher Cl^- complexes of Ti^{+3} must become more

Table 6. Chloride Ion Dependence 40°C. Variation of pseudo first order constants with $[Cl^-]$.

$[Ti^{+3}] = 0.015M$ $[H^+] = 0.22M$ $[ClO_4^-] = 0.5M$

$[Cl^-]$	$k'x10^2$	$[Cl^-]$	$k'x10^2$
0.24	3.87	1.6	2.58
0.40	3.47	1.8	2.59
0.60	3.24	2.0	2.51
0.80	3.02	2.4	2.53
1.0	2.85	2.6	2.47
1.2	2.74	3.0	2.52
1.4	2.63		

Table 7. Chloride Ion Dependence 40°C. Variation of pseudo first order rate constant with $[Cl^-]$.

$[Ti^{+3}] = 0.015M$ $[H^+] = 0.5M$ $[ClO_4^-] = 0.5M$

$[Cl^-]$	$k' \times 10^2$	$[Cl^-]$	$k' \times 10^2$
0.24	4.13	1.6	2.80
0.40	3.75	1.8	2.75
0.60	3.47	2.0	2.72
0.80	3.26	2.4	2.67
1.0	3.10	2.6	2.64
1.2	2.94	3.0	2.65
1.4	2.87		

Table 8. Chloride Ion Dependence 40°C. Variation of pseudo first order rate constants with $[\mathrm{Cl}^-]$.

$[\mathrm{Tl}^{+3}] = 0.015M$ $[\mathrm{H}^+] = 0.75M$ $[\mathrm{ClO}_4^-] = 0.5M$

$[\mathrm{Cl}^-]$	$k' \times 10^2$	$[\mathrm{Cl}^-]$	$k' \times 10^2$
0.26	4.50	1.8	2.99
0.40	4.23	2.0	2.98
0.60	3.81	2.2	2.99
0.80	3.60	2.4	2.97
1.0	3.32	2.6	2.93
1.2	3.26	2.8	2.99
1.4	3.13	3.0	3.05
1.6	3.05		

Table 9. Chloride Ion Dependence 40°C. Variation of pseudo first order rate constants with $[Cl^-]$.

$[Ti^{+3}] = 0.015M$ $[H^+] = 1.0M$ $[ClO_4^-] = 0.5M$

$[Cl^-]$	$k' \times 10^2$	$[Cl^-]$	$k' \times 10^2$
0.51	4.31	1.6	3.36
0.60	4.02	1.8	3.29
0.80	3.88	2.0	3.18
1.0	3.67	2.4	3.18
1.2	3.53	2.6	3.14
1.4	3.44	3.0	3.11

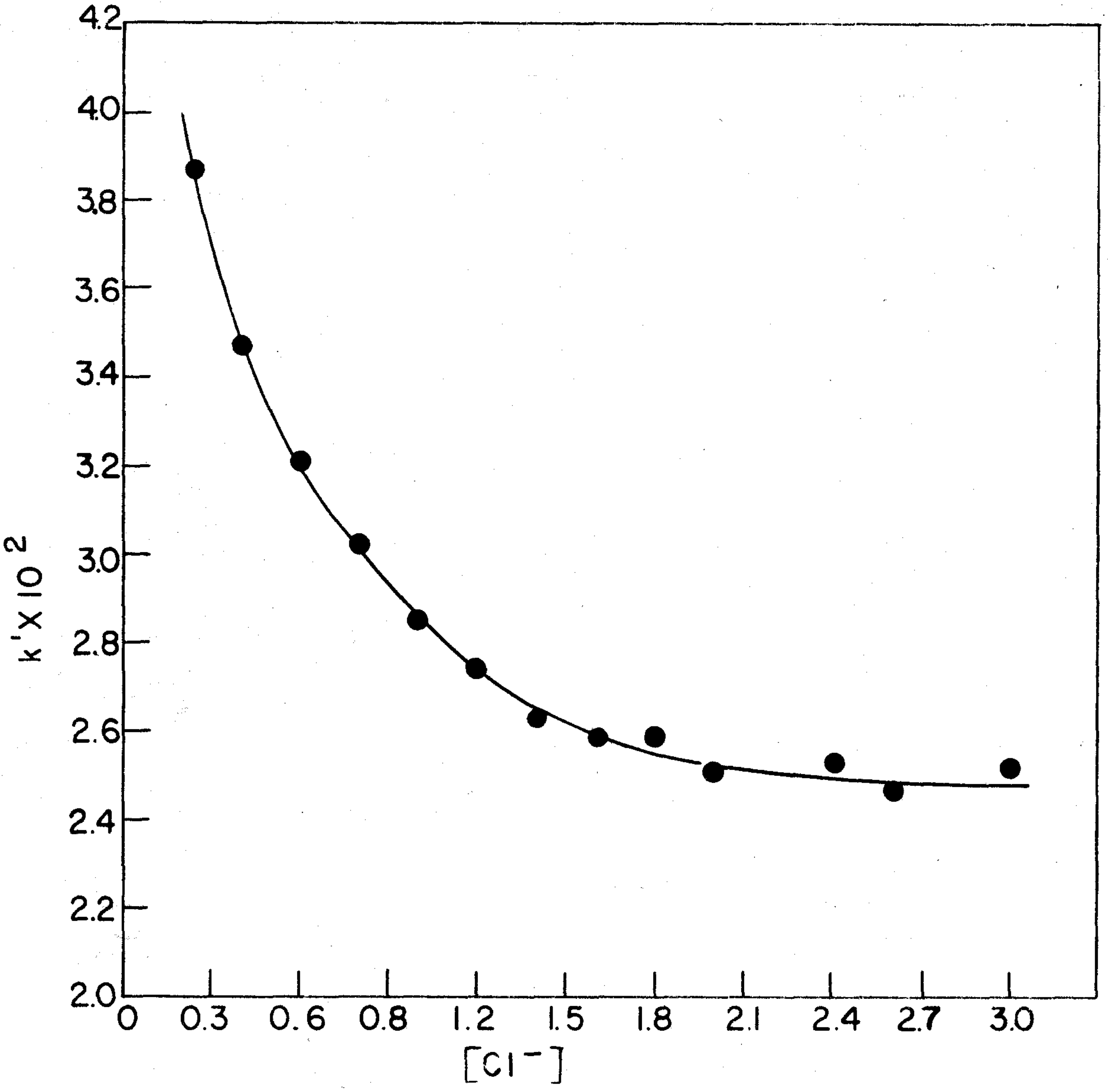

FIG. 4. CHLORIDE ION DEPENDENCE 40°C FIRST ORDER RATE CONSTANTS VERSUS $[Cl^-]$ · $[Ti^{+3}]$ = 0.015M $[ClO_4^-]$ = 0.5M $[H^+]$ = 0.22M

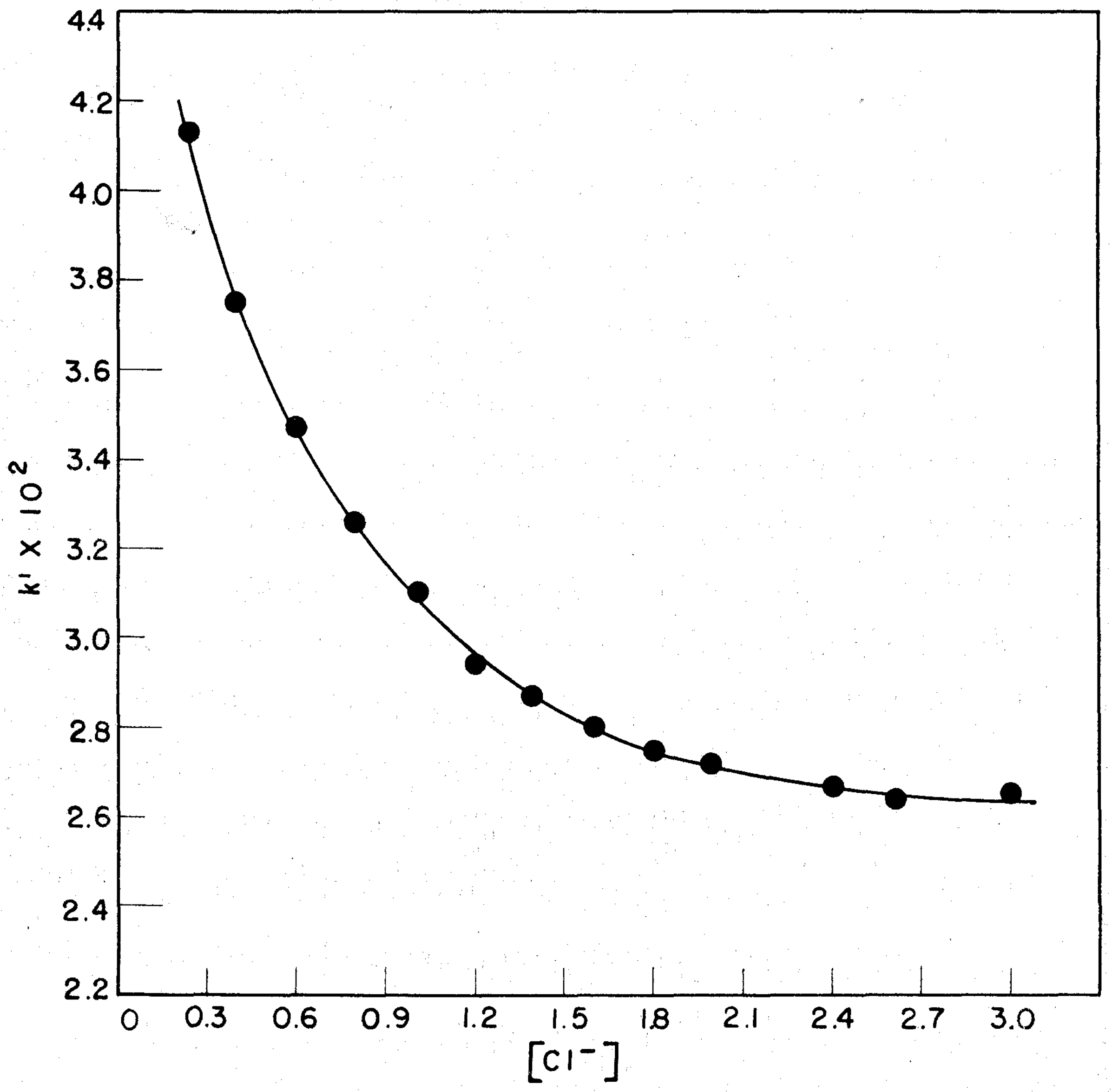

FIG. 5. CHLORIDE ION DEPENDENCE 40°C FIRST ORDER RATE CONSTANTS VERSUS $[Cl^-]$ $[Ti^{+3}] = 0.015$ M $[ClO_4^-] = 0.5$ M $[H^+] = 0.5$ M

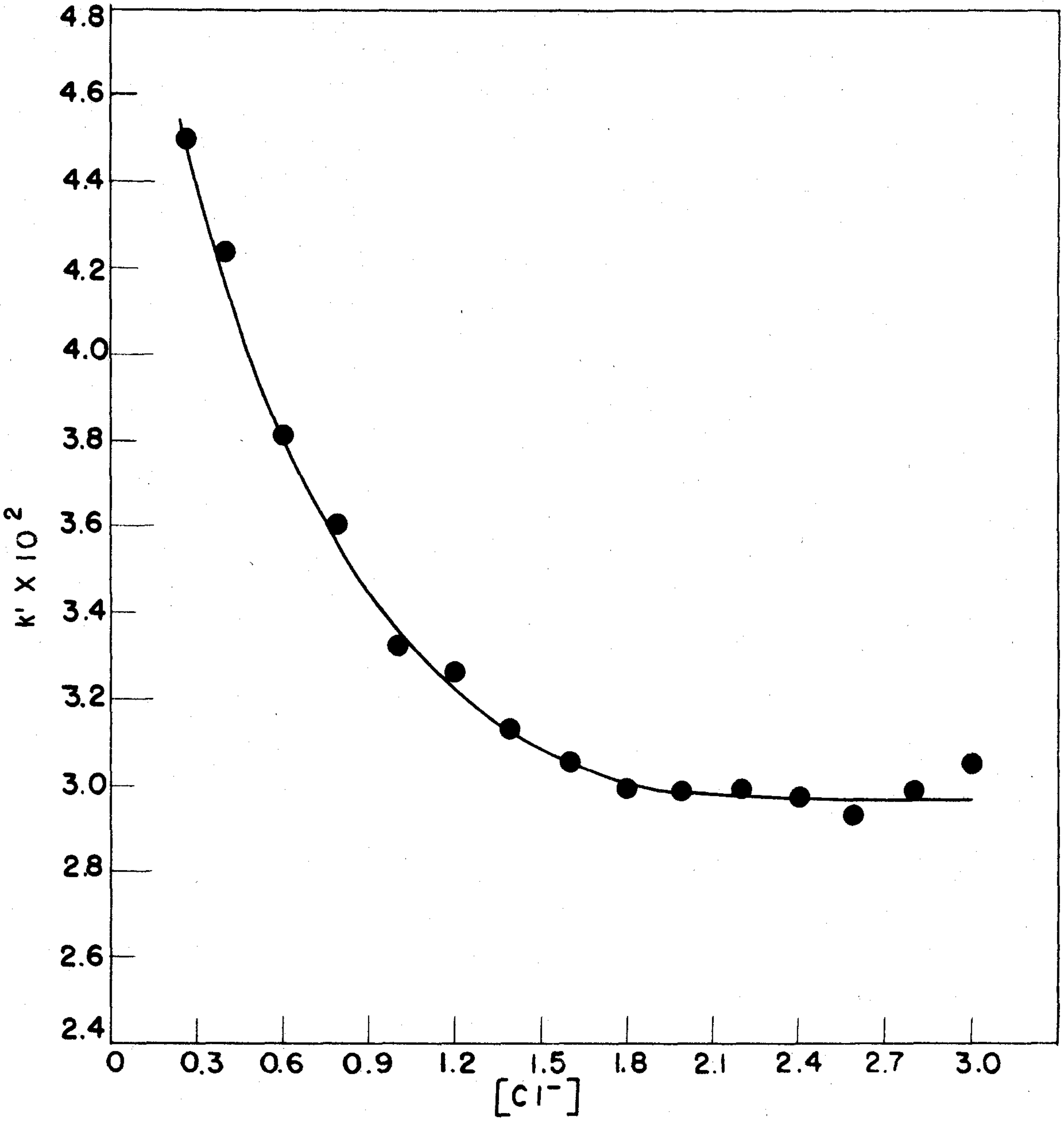

FIG. 6. CHLORIDE ION DEPENDENCE 40°C FIRST ORDER RATE CONSTANTS VERSUS $[Cl^-]$ $[Ti^{+3}] = 0.015\,M$ $[ClO_4^-] = 0.5\,M$ $[H^+] = 0.75\,M$.

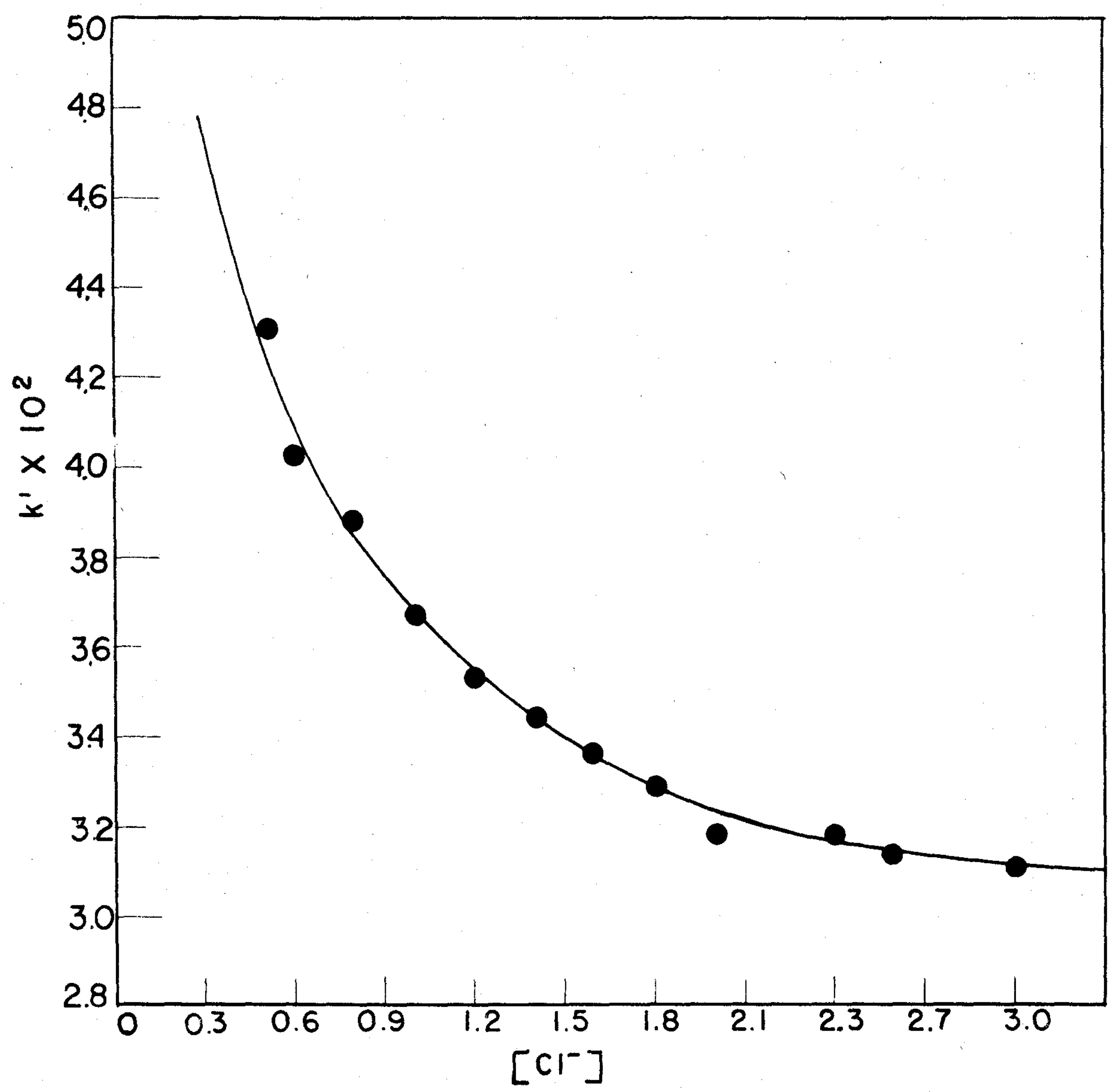

FIG. 7. CHLORIDE ION DEPENDENCE 40 °C FIRST ORDER RATE CONSTANTS VERSUS $[Cl^-]$ $[Ti^{+3}] = 0.015\ M$ $[ClO_4^-] = 0.5\ M$ $[H^+] = 1.0\ M$.

Table 10. Chloride Ion Dependence 40°C. Variation of rate and equilibrium constants with $[H^+]$.

$[Ti^{+3}] = 0.015M$ $[ClO_4] = 0.5M$

$[H^+]$	$k_{1_{Cl}} x10^2$	$k_{2_{Cl}} x10^2$	K_1
0.22	4.86±0.5	1.97±0.2	2.24±0.4
0.50	5.13±0.5	2.12±0.2	2.12±0.4
0.75	5.84±0.6	2.26±0.2	2.25±0.4
1.0	5.99±0.6	2.56±0.3	2.11±0.4

Table 11. Chloride Ion Dependence. Comparison of theoretical and experimental pseudo first order rate constants with variation in $[H^+]$.

	$[H^+] = 0.22M$		$[H^+] = 0.50M$		$[H^+] = 0.75M$		$[H^+] = 1.0M$	
$[Cl^-]$	$k'_c x10^2$ [a]	$k'_e x10^2$ [b]	$k'_c x10^2$	$k'_e x10^2$	$k'_c x10^2$	$k'_e x10^2$	$k'_c x10^2$	$k'_e x10^2$
0.24	3.94	3.87	4.12	4.13	4.52[c]	4.50	----	----
0.4	3.49	3.47	3.75	3.75	4.15	4.23	4.21[d]	4.31
0.6	3.20	3.24	3.45	3.47	3.78	3.81	4.07	4.02
0.8	3.00	3.02	3.24	3.26	3.54	3.60	3.99	3.88
1.0	2.86	2.85	3.09	3.10	3.36	3.32	3.66	3.67
1.2	2.75	2.74	2.97	2.94	3.23	3.26	3.53	3.53
1.4	2.67	2.63	2.88	2.87	3.12	3.13	3.42	3.44
1.6	2.60	2.58	2.81	2.80	3.04	3.05	3.34	3.36
1.8	2.54	2.59	2.75	2.75	2.97	2.99	3.27	3.29
2.0	2.50	2.51	2.69	2.72	2.91	2.98	3.21	3.18
2.2	2.47[e]	2.51[c]	2.65[e]	2.68[e]	2.86	2.99	3.17[e]	3.20[e]
2.4	2.42	2.53	2.61	2.67	2.82	2.97	3.12	3.18
2.6	2.39	2.47	2.58	2.64	2.79	2.93	3.08	3.14
2.8	2.36[e]	2.48[e]	2.56[e]	2.64[e]	2.75	2.99	3.06[e]	3.13[e]
3.0	2.34	2.52	2.53	2.65	2.72	3.05	3.02	3.11

[a] Calculated from equation 10.

[b] Experimental values.

[c] $Cl^- = 0.26$

[d] $Cl^- = 0.51$.

[e] Taken from graphs.

evident and consequently the pseudo first order rate constant expression can no longer be simplified in the manner indicated above for the lower concentrations of Cl^-.

The calculated values of the equilibrium constant in Table 10 appear to be in good agreement, within experimental error (±7%). The increasing values of $k_{1_{Cl}}$ and $k_{2_{Cl}}$ for increasing H^+ show that the chloride complexes become more evident at higher H^+.

Because the reaction is retarded considerably due to increasing Cl^-, there must be a series of equilibria of the form shown previously, i.e.,

$$Ti^{+3} + Cl^- \rightleftharpoons TiCl^{++}$$
$$TiCl^{++} + Cl^- \rightleftharpoons TiCl_2{}^+$$
$$TiCl_2{}^+ + Cl^- \rightleftharpoons TiCl_3, \text{ etc.}$$

At lower concentrations the complexes most likely present are $TiCl^{++}$ and $TiCl_2{}^+$, along with small concentrations of the others.

The chloride dependence was also run at 50°C to determine the effect of increased temperature on the rate and equilibrium constants. The data obtained are shown in Tables 12, 13, 14, and 15, and are plotted in Figures 8, 9, 10, and 11. The constants for these determinations were calculated and are shown in Table 16.

Table 12. Chloride Ion Dependence 50°C. Variation of pseudo first order rate constants with $[Cl^-]$.

$[Ti^{+3}] = 0.015M$ $[H^+] = 0.23M$ $[ClO_4^-] = 0.5M$

$[Cl^-]$	$k' \times 10^2$	$[Cl^-]$	$k' \times 10^2$
0.24	12.38	1.8	8.72
0.40	11.32	2.0	8.21
0.60	10.55	2.2	8.21
0.80	9.84	2.4	8.08
1.0	9.34	2.6	8.25
1.2	9.02	2.8	8.29
1.4	8.72	3.0	8.17
1.6	8.58		

Table 13. Chloride Ion Dependence 50°C. Variation of pseudo first order rate constants with $[Cl^-]$.

$[Ti^{+3}] = 0.015M$ $[ClO_4^-] = 0.5M$ $[H^+] = 0.5M$

$[Cl^-]$	$k' \times 10^2$	$[Cl^-]$	$k' \times 10^2$
0.24	13.83	1.2	9.77
0.4	10.61	1.4	9.66
0.6	11.72	1.8	9.33
0.8	11.03	2.0	8.88
1.0	10.28		

Table 14. Chloride Ion Dependence 50°C. Variation of pseudo first order rate constants with $[Cl^-]$.

$[Ti^{+3}] = 0.015M$ $[ClO_4^-] = 0.5M$ $[H^+] = 0.75M$

$[Cl^-]$	$k' \times 10^2$	$[Cl^-]$	$k' \times 10^2$
0.26	13.94	1.2	9.78
0.40	13.25	1.4	9.83
0.60	12.06	1.6	9.62
0.80	11.11	1.8	9.58
1.0	10.40	2.0	9.12

Table 15. Chloride Ion Dependence 50°C. Variation of pseudo first order rate constants with $[Cl^-]$.

$[Ti^{+3}] = 0.015M$ $[ClO_4^-] = 0.5M$ $[H^+] = 1.0M$

$[Cl^-]$	$k' \times 10^2$	$[Cl^-]$	$k' \times 10^2$
0.51	13.00	1.4	10.45
0.6	12.42	1.6	10.17
0.8	11.72	1.8	10.17
1.0	11.22	2.0	10.03
1.2	10.72		

Table 16. Chloride Ion Dependence 50°C. Variation of rate constants with $[H^+]$.

$[H^+]$	$k_{1_{Cl}} \times 10^2$	$k_{2_{Cl}} \times 10^2$	K_1
0.23	17.04 ± 1	6.65 ± 0.5	2.83 ± 0.2
0.50	17.53 ± 1	7.15 ± 0.5	2.25 ± 0.2
0.75	18.48 ± 1	7.24 ± 0.5	2.46 ± 0.2
1.0	18.76 ± 1	7.90 ± 0.5	2.38 ± 0.2

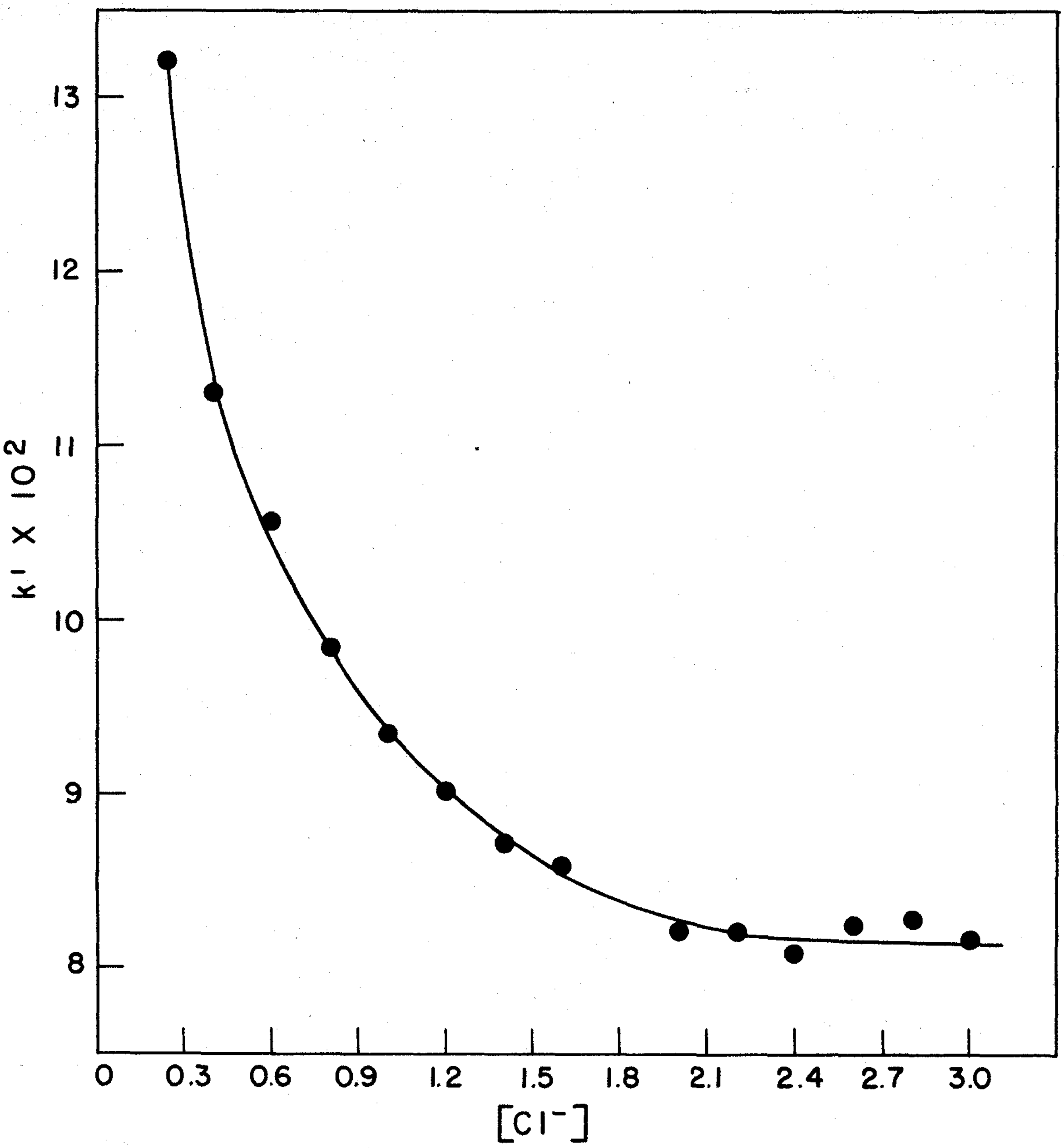

FIG.8 CHLORIDE ION DEPENDENCE 50° C FIRST ORDER RATE CONSTANTS VERSUS $[Cl^-]$ $[Ti^{+3}]$ = 0.015 M $[ClO_4^-]$ = 0.5 M $[H^+]$ = 0.23 M

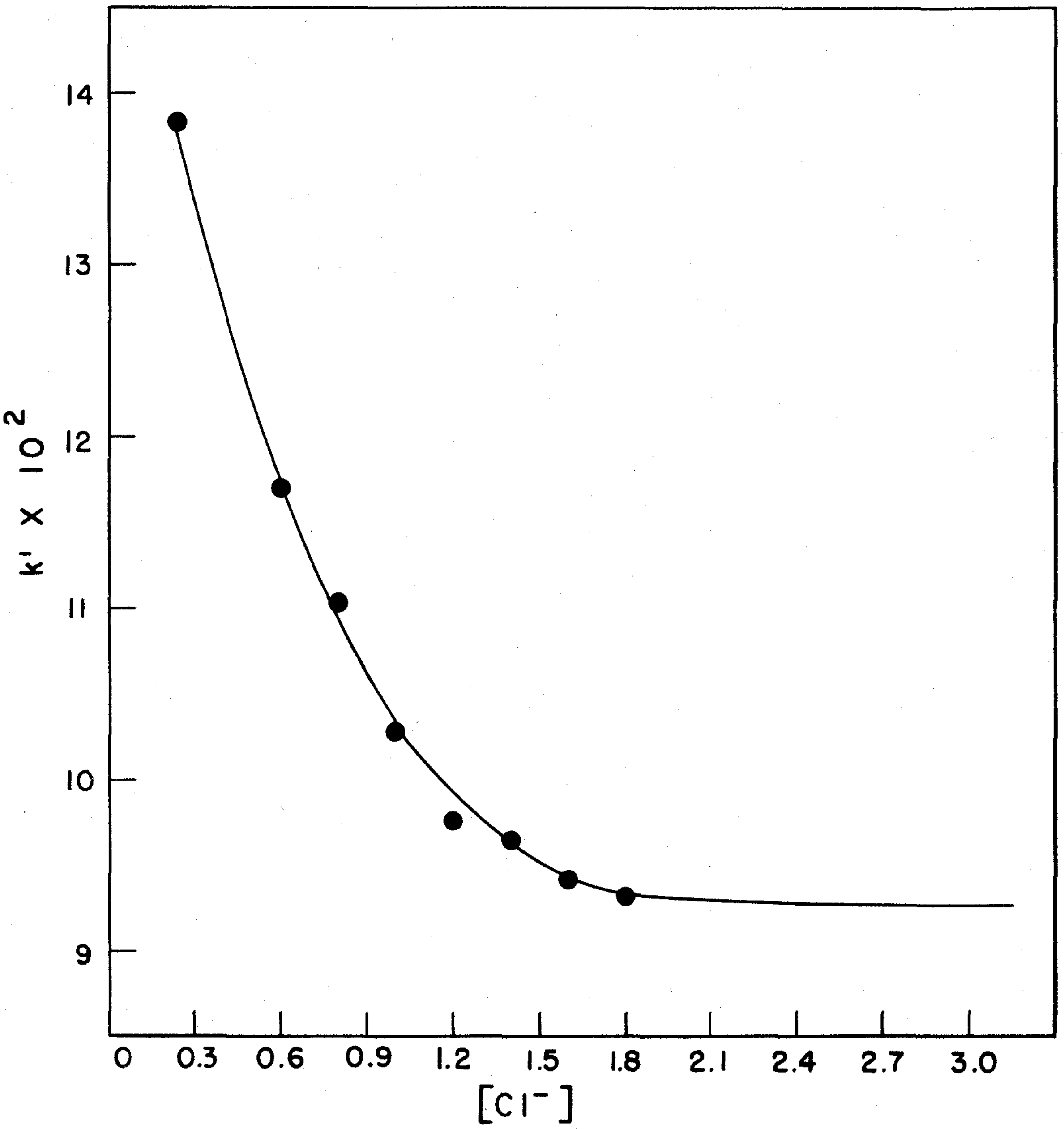

FIG. 9 CHLORIDE ION DEPENDENCE 50°C FIRST ORDER RATE CONSTANTS VERSUS [Cl$^-$][Ti^{+3}] = 0.015M [ClO$_4^-$] = 0.5 M [H$^+$] = 0.5 M .

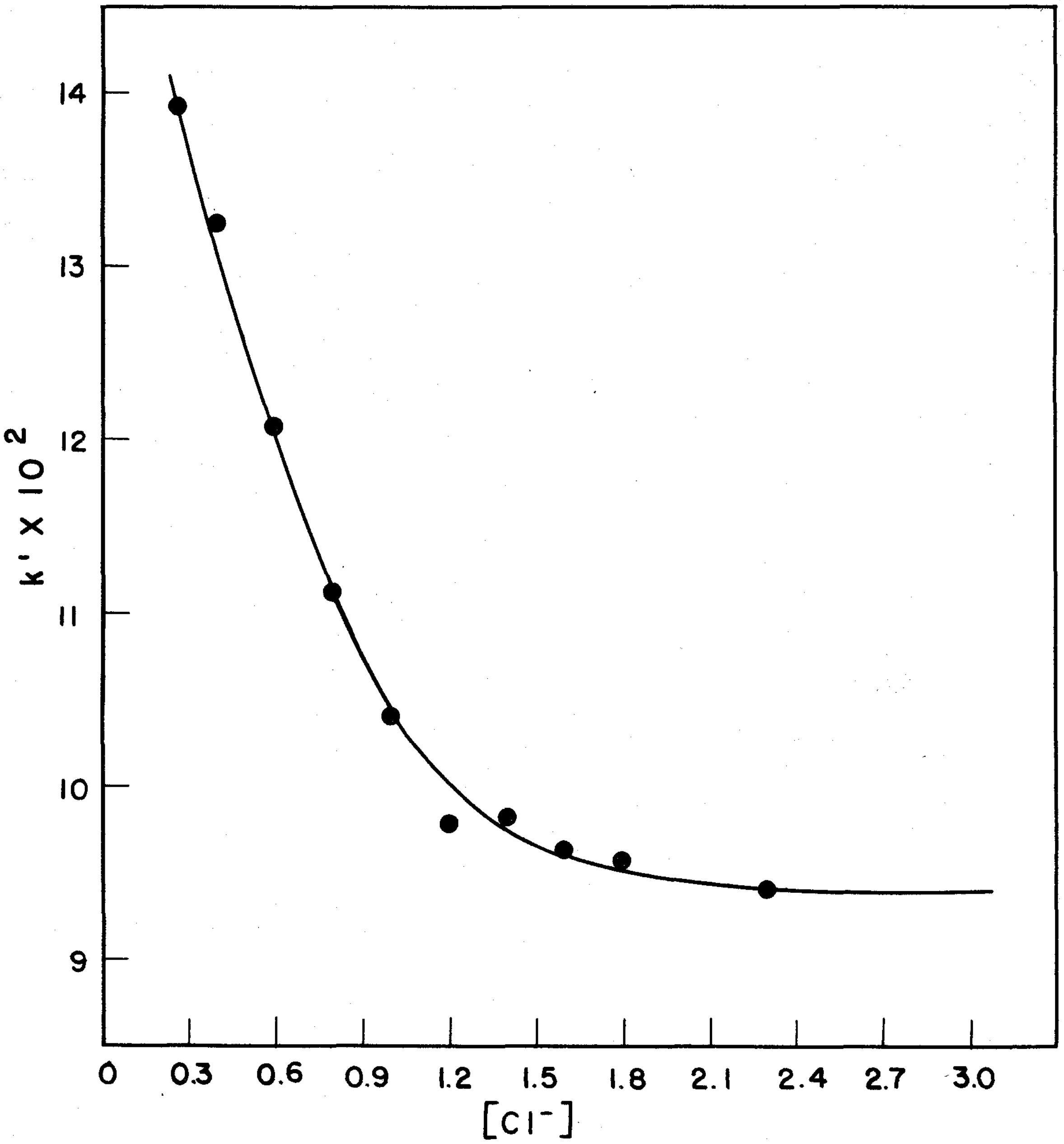

FIG. 10 CHLORIDE ION DEPENDENCE 50° C FIRST ORDER RATE CONSTANTS VERSUS $[Cl^-]$ $[Ti^{+3}] = 0.015 M$ $[ClO_4^-] = 0.5 M$ $[H^+] = 0.75 M$

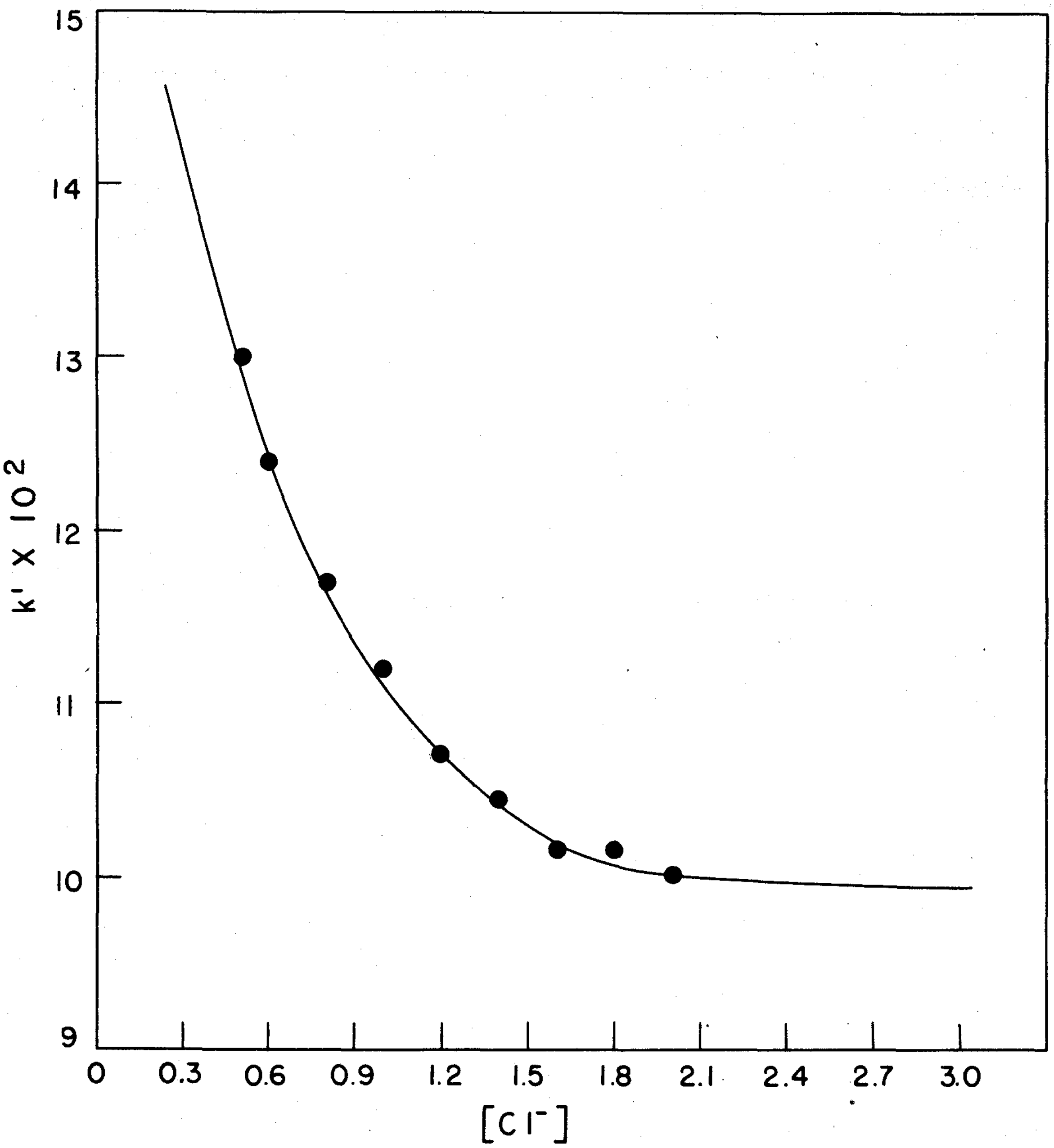

FIG. 11 CHLORIDE ION DEPENDENCE 50°C FIRST ORDER RATE CONSTANTS VERSUS $[Cl^-][Ti^{+3}] = 0.015\,M$ $[ClO_4^-] = 0.5\,M$ $[H^+] = 1.0\,M$

The thermodynamic functions for the chloride dependence of the reaction were calculated using the same equations as for the H^+ dependence. In this case the effect of temperature on the equilibrium constant for the formation of chloride complex was determined and so the thermodynamic functions for this equilibrium could also be calculated. The results obtained are shown in Table 17. The quantity k_1 can be interpreted as the rate constant for the reaction at zero chloride concentration. Consequently, similar to that found for the H^+ dependence, there is a phase of the reaction which proceeds independently of the Cl^-. This seems to indicate that the hydrated Tl^{+3} is the most important reacting species.

In considering the over-all rate expression for this reaction the function $F(Cl^-)$ was found to be,

$$\frac{k_{1_{Cl}} + k_{2_{Cl}} K_1[Cl^-]}{1 + K_1[Cl^-]},$$

for Cl^- concentrations less than two molar. Thus, the original rate law expression, equation 1, may be written,

$$-\frac{d[T_{Tl^{+3}}]}{dt} = [k_{0_H} + k_{1_H} H^+] \frac{k_{1_{Cl}} + k_{2_{Cl}} K_1[Cl^-]}{1 + K_1[Cl^-]} F(ClO_4^-)[T_{Tl^{+3}}] .$$

Table 17. Chloride Ion Dependence. Rate constants and thermodynamic functions for the chloride ion dependence.

<u>Uncatalyzed reaction</u>	<u>40°C</u>	<u>50°C</u>
$k_{1_{Cl}} \times 10^2$	5.13±0.5	17.5±1
$\Delta F^{\ddagger}_{313}$ = 20.2±0.1 kcal		
$\Delta H^{\ddagger}$ = 24.0±13% kcal		
$\Delta S^{\ddagger}$ = 12.1±50% e.u.		
<u>Catalyzed reaction</u>	<u>40°C</u>	<u>50°C</u>
$k_{2_{Cl}} \times 10^2$	2.12±0.2	7.15±0.5
$\Delta F^{\ddagger}_{313}$ = 20.7±0.1 kcal		
$\Delta H^{\ddagger}$ = 23.8±14% kcal		
$\Delta S^{\ddagger}$ = 9.9±50% e.u.		
<u>Equilibrium constant</u>	<u>40°C</u>	<u>50°C</u>
$K_{1 average}$	2.18±0.2	2.48±0.2
ΔF_{313} = 17.8±0.1 kcal		
ΔH = 2366±50% cal.		
ΔS = -49.3±100% e.u.		

This leaves the perchlorate ion function to be determined.

The Perchlorate Ion Dependence

The results of Bredig and Michel (13) showing a linear dependence for perchlorate ion were confirmed in a study of the effects of varying the perchlorate ion concentration. This was found to be true only at concentrations less than one molar, however. Above this value the rate becomes higher than first order.

In most kinetic studies it is desirable to carry out reactions either at low ionic strength where the effects of other ions on the rate are negligible, or at some high value which does not change appreciably during the course of a determination. The latter process is more applicable in an investigation such as this since the ionic strength tends to change as the concentrations of the various reacting ions are changed. Since perchlorates are used quite frequently to maintain constant ionic strength and since perchlorate ion is one of the reactants, one is confronted with a variable which cannot be controlled.

These determinations were carried out at NaCl = 2.0M so that at low $[ClO_4^-]$ the ionic strength was maintained at about two. However, at higher perchlorate the ionic strength is no longer constant but varies with increasing

$[ClO_4^-]$. It was at these high ClO_4^- concentrations that the ClO_4^- dependence deviated from first order. Consequently, this effect may be attributed to the changing ionic strength, rather than a change in the kinetics of the reaction.

The data obtained are shown in Tables 18, 19, 20, and 21, and are plotted in Figures 12 through 15. The determinations were made at three different hydrogen ion concentrations to observe the effect of increasing H^+ on the perchlorate ion dependence. The slopes of these curves are shown in Table 22. The rate of reaction increases with H^+ as was expected.

At low perchlorate ion the pseudo first order rate constant varies directly with the perchlorate ion concentration, and may be written as,

$$k' = k_{1_{ClO_4^-}} [ClO_4^-]. \qquad (11)$$

The function $F(ClO_4^-)$ is then written as $k_{1_{ClO_4^-}} [ClO_4^-]$.

The possibility of the presence of any Ti(III)-perchlorate ion complexes was investigated. Runs were made varying the perchlorate concentration up to 6M. These determinations were carried out at 20°C, since the rate of reaction is too fast at such high ClO_4^- concentrations to be followed by the techniques described earlier. The reaction was found to be first order in Ti^{+3} over the whole

Table 18. Perchlorate Ion Dependence 40°C. Variation of pseudo first order rate constants with $[ClO_4^-]$.

$[Ti^{+3}] = 0.015M$ $[H^+] = 0.22M$ $[Cl^-] = 2.0M$

$[ClO_4^-]$	$k' \times 10^2$	$[ClO_4^-]$	$k' \times 10^2$
0.02	0.0927	0.40	1.97
0.04	0.234	0.60	2.96
0.06	0.283	0.80	4.02
0.08	0.380	1.0	5.18
0.10	0.485	1.1	5.71
0.20	0.935	1.2	6.45

Table 19. Perchlorate Ion Dependence 40°C. Variation of pseudo first order rate constants with $[ClO_4^-]$.

$[Tl^{+3}] = 0.015M$ $[H^+] = 0.23M$ $[Cl^-] = 2.0M$

$[ClO_4^-]$	$k' \times 10^2$	$[ClO_4^-]$	$k' \times 10^2$
0.10	0.493	0.90	4.85
0.20	0.717	1.0	5.56
0.30	1.57	1.2	6.90
0.40	2.03	1.4	8.35
0.50	2.61	1.6	9.77
0.60	3.17	1.8	11.35
0.70	3.69	2.0	13.45
0.80	4.34		

Table 20. Perchlorate Ion Dependence 40°C. Variation of pseudo first order rate constant with $[ClO_4^-]$.
$[Ti^{+3}] = 0.015M$ $[H^+] = 0.50M$ $[Cl^-] = 2.0M$

$[ClO_4^-]$	$k' \times 10^2$	$[ClO_4^-]$	$k' \times 10^2$
0.10	0.564	0.91	5.30
0.20	1.06	1.0	5.69
0.30	1.62	1.2	7.31
0.40	2.12	1.4	8.91
0.50	2.84	1.6	10.00
0.60	3.20	1.8	11.93
0.70	3.94	2.0	13.71
0.80	4.51		

Table 21. Perchlorate Ion Dependence 40°C. Variation of pseudo first order rate constants with $[ClO_4^-]$.

$[Ti^{+3}] = 0.015M$ $[H^+] = 1.0M$ $[Cl^-] = 2.0M$

$[ClO_4^-]$	$k' \times 10^2$	$[ClO_4^-]$	$k' \times 10^2$
0.10	0.677	1.0	6.72
0.20	1.25	1.2	8.44
0.30	1.91	1.4	10.35
0.40	2.51	1.6	12.05
0.50	3.16	1.8	13.70
0.60	4.22	2.0	15.88
0.80	5.32		

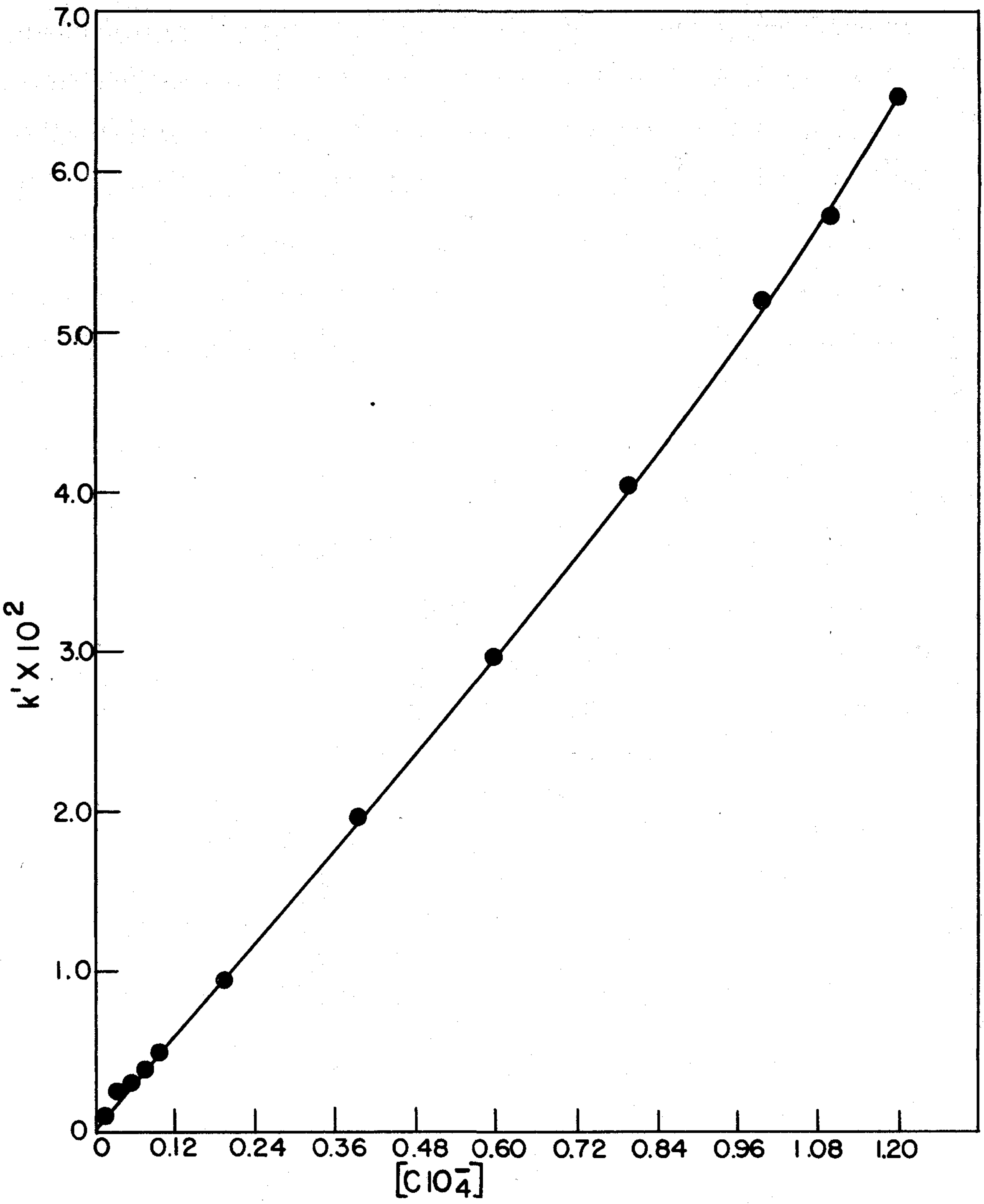

FIG. 12 PERCHLORATE ION DEPENDENCE 40°C FIRST ORDER RATE CONSTANTS VERSUS [ClO$_4^-$] [Ti^{+3}] = 0.015M [Cl$^-$] = 2.0M [H$^+$] = 0.22M

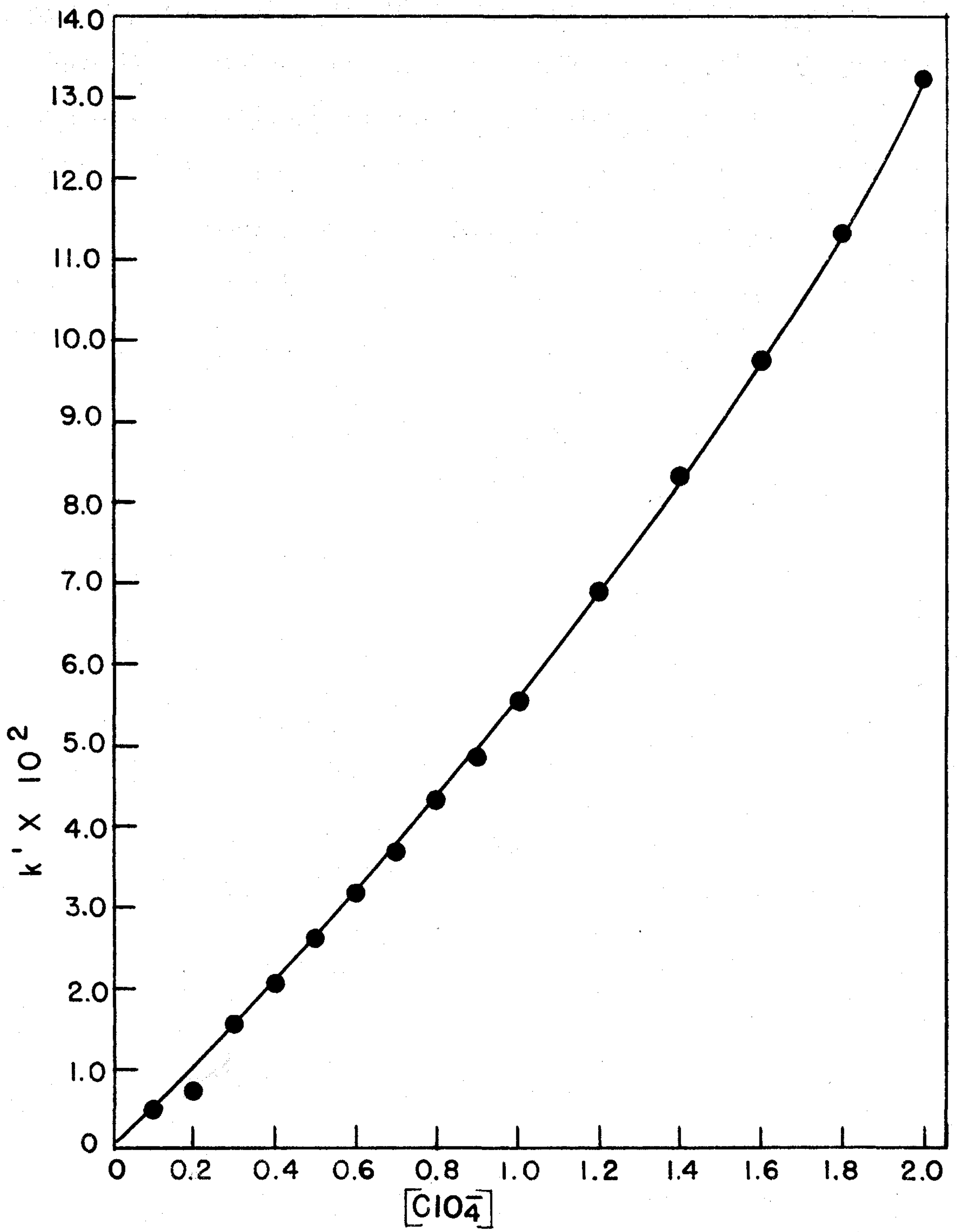

FIG. 13. PERCHLORATE ION DEPENDENCE 40°C FIRST ORDER RATE CONSTANTS VERSUS $[ClO_4^-]$ $[Ti^{+3}]$ $= 0.015$ $[Cl^-] = 2.0$ M $[H^+] = 0.23$ M

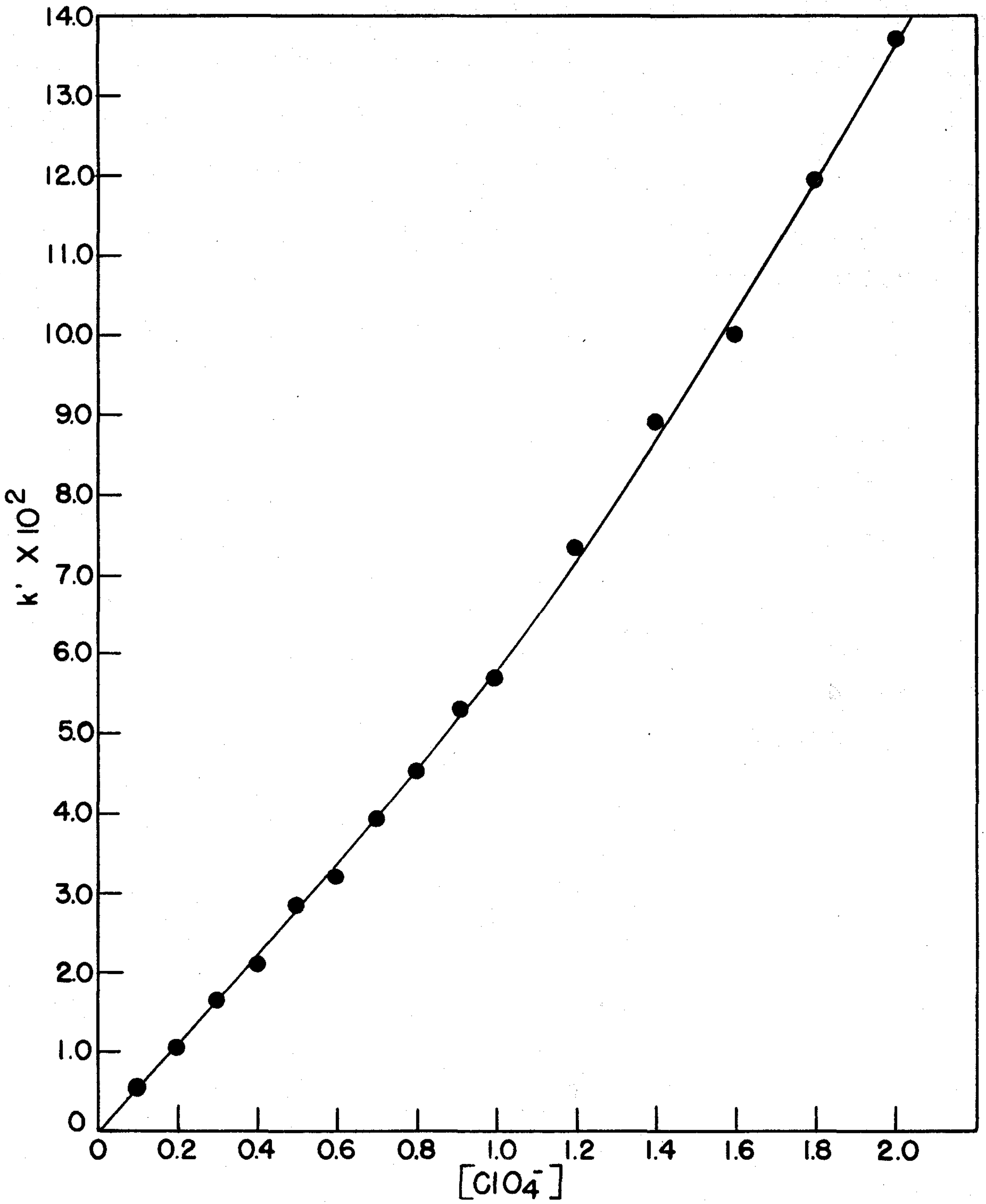

FIG. 14 PERCHLORATE ION DEPENDENCE 40° C FIRST ORDER RATE CONSTANTS VERSUS [ClO$_4$] [Ti^{+3}]=0.015 M [Cl$^-$] = 2.0 M [H$^+$] = 0.5 M.

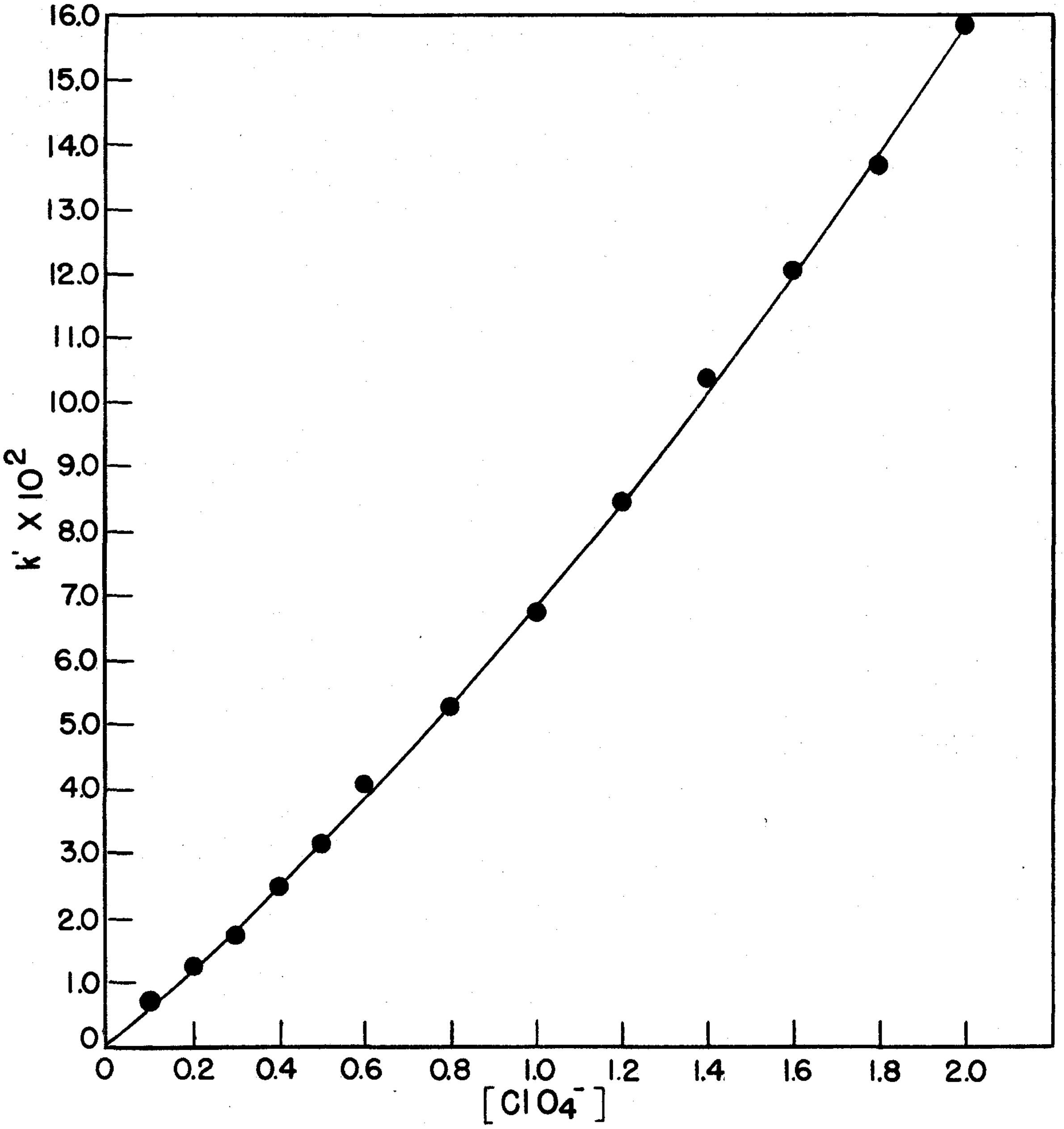

FIG. 15. PERCHLORATE ION DEPENDENCE 40° C FIRST ORDER RATE CONSTANTS VERSUS $[ClO_4^-]\cdot[Ti^{+3}] = 0.015\,M$ $[Cl^-] = 2.0\,M$ $[H^+] = 1.0\,M$

range indicating that no such complexes exist. The data for these runs are shown in Table 23 and are plotted in Figure 16. At a concentration greater than 2M the ClO_4^- dependence is no longer linear.

It was first thought that the deviation from linearity was due perhaps to the increasing ionic strength. However, the results seem to indicate an effect much larger than would be expected solely on the basis of increasing ionic strength. Rather, the large increase in rate is thought to be caused by a decrease in the activity of the solvent water at such high perchlorate ion concentrations. Robinson and Baker (16) studied the vapor pressures of $HClO_4$-H_2O solutions reporting their data as the activity of water at various $HClO_4$ concentrations. The water activity decreases from 0.96 at 1M $HClO_4$ to 0.63 at 6M. At ten molar it is only 0.32. On the other hand the activity coefficients of $HClO_4$ increase from 2.08 to 4.75 at 4M and 6M respectively. This, then, leads to a reasonable explanation for the large increase in rate at high $HClO_4$ concentrations.

The complete rate expression for the reaction between Tl^{+3} and ClO_4^- may be written as the following,

$$
\begin{aligned}
-\frac{d[Tl^{+3}]}{dt} = [k_{0_H} + k_{1_H}\,H^+]\;\frac{k_{1_{Cl}} + k_{2_{Cl}}\,K_1[Cl^-]}{1 + K_1[Cl^-]} \\
k_{1_{ClO_4^-}}[ClO_4^-][Tl^{+3}].
\end{aligned}
$$

Table 22. Perchlorate Ion Dependence. Variation of perchlorate ion dependence with $[H^+]$.

$[Ti^{+3}] = 0.015M$ $[Cl^-] = 2.0M$

$[H^+]$	$k_{1ClO_4^-}x10^2$
0.23	5.26±0.04
0.50	5.56±0.04
1.0	6.35±0.04

Table 23. Perchlorate Ion Dependence 20°C. Variation of pseudo first order rate constants with $[ClO_4^-]$.

$[Ti^{+3}] = 0.015M$ $[H^+] = 0.23M$ $[Cl^-] = 0.24M$

$[ClO_4^-]$	$k'x10^2$	$[ClO_4^-]$	$k'x10^2$
0.25	0.252	3.5	3.08
0.50	0.472	4.0	4.33
1.0	0.804	4.5	5.57
1.5	1.05	5.0	7.17
2.0	1.56	5.5	9.37
2.5	2.01	6.0	11.67
3.0	2.60		

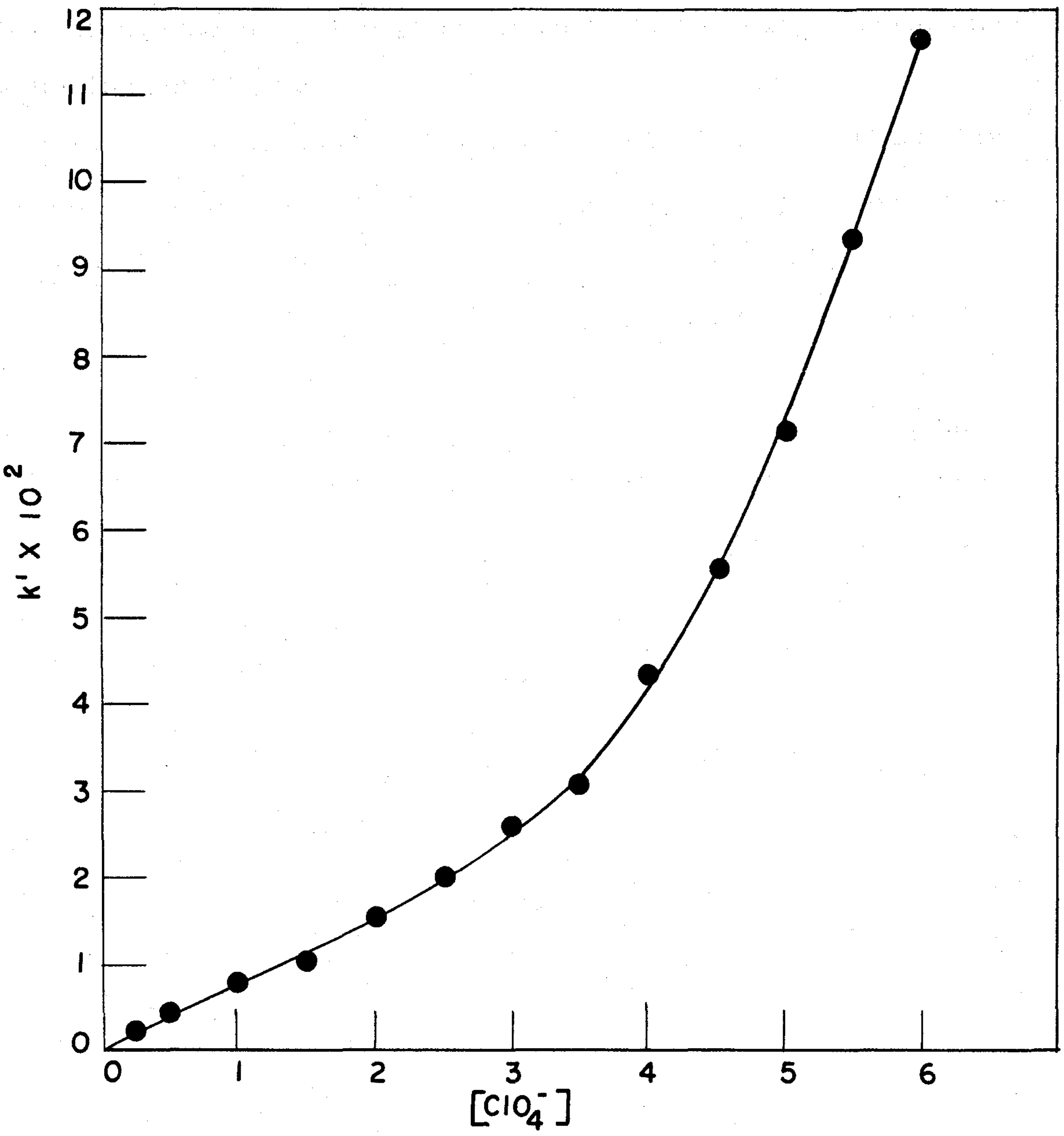

FIG. 16 PERCHLORATE ION DEPENDENCE 20 °C
FIRST ORDER RATE CONSTANTS VERSUS [ClO_4^-],
[Ti^{+3}]=0.015 M [Cl^-] = 0.24 M [H^+] = 0.23 M

or, combining constants,

$$-\frac{d[Tl^{+3}]}{dt} = \frac{k_1 + k_2\, K_1[Cl^-] + k_3[H^+] + k_4\, K_1[H^+][Cl^-]}{1 + K_1[Cl^-]}\, [ClO_4^-][Tl^{+3}] . \qquad (12)$$

The Rate Constants and the Thermodynamic Function

The rate constants k_1, k_2, k_3, and k_4, in the rate equation

$$-\frac{d[Tl^{+3}]}{dt} = \frac{k_1 + k_2\, K_1[Cl^-] + k_3[H^+] + k_4\, K_1[H^+][Cl^-]}{1 + K_1[Cl^-]}\, [ClO_4^-][Tl^{+3}]$$

can be determined and since the rate of reaction was studied at two temperatures it is possible to calculate the activation energies for this reaction. For the reactions at constant ClO_4^- the pseudo first order rate constant will be given by,

$$\frac{k'}{[ClO_4^-]} = \frac{k_1 + k_2\, K_1[Cl^-] + k_3[H^+] + k_4\, K_1[Cl^-][H^+]}{1 + K_1[Cl^-]} . \qquad (13)$$

For any one run the $[H^+]$ remains constant and this expression becomes,

$$\frac{k'}{[ClO_4^-]} = \frac{k_1' + k_2' K_1[Cl^-]}{1 + K_1[Cl^-]},$$

where,

$$k_1' = k_1 + k_3[H^+], \text{ and} \qquad (14)$$

$$k_2' = k_2 + k_4[H^+]. \qquad (15)$$

A plot of k_1' and k_2' vs. $[H^+]$ should yield two straight lines the first having a slope of k_3 and y-intercept of k_1, the second having a slope of k_4 and a y-intercept of k_2. In each case an average value of K_1 was used. The values of the various constants at 40°C are summarized in Table 24. Using a value of $K_1 = 2.18$, k_1' and k_2' vs. $[H^+]$ are plotted in Figure 17. The constants k_1, k_2, k_3, and k_4, obtained from the plots were found to be, $k_1 = 8.78 \times 10^{-2}$, $k_2 = 3.57 \times 10^{-2}$, $k_3 = 3.46 \times 10^{-2}$, and $k_4 = 1.36 \times 10^{-2}$.

These constants can also be determined by considering the pseudo first order rate expression at constant $[Cl^-]$ and $[ClO_4^-]$. Under these conditions,

$$\frac{k'(1 + K_1')}{[ClO_4^-]} = k_1'' + k_2''[H^+], \qquad (16)$$

Table 24. Hydrogen Ion Dependence 40°C. Variation of rate constants with $[H^+]$.

$[Tl^{+3}] = 0.015M$ $[ClO_4^-] = 0.5M$ $K_1 = 2.18$

$[H^+]$	$k_{1_{Cl}} x10^2$	$k_{2_{Cl}} x10^2$	$k_1' x10^2$	$k_2' x10^2$
0.22	4.86	1.97	9.72	3.94
0.50	5.13	2.12	10.26	4.24
0.75	5.84	2.26	11.68	4.52
1.0	5.99	2.56	11.98	5.12

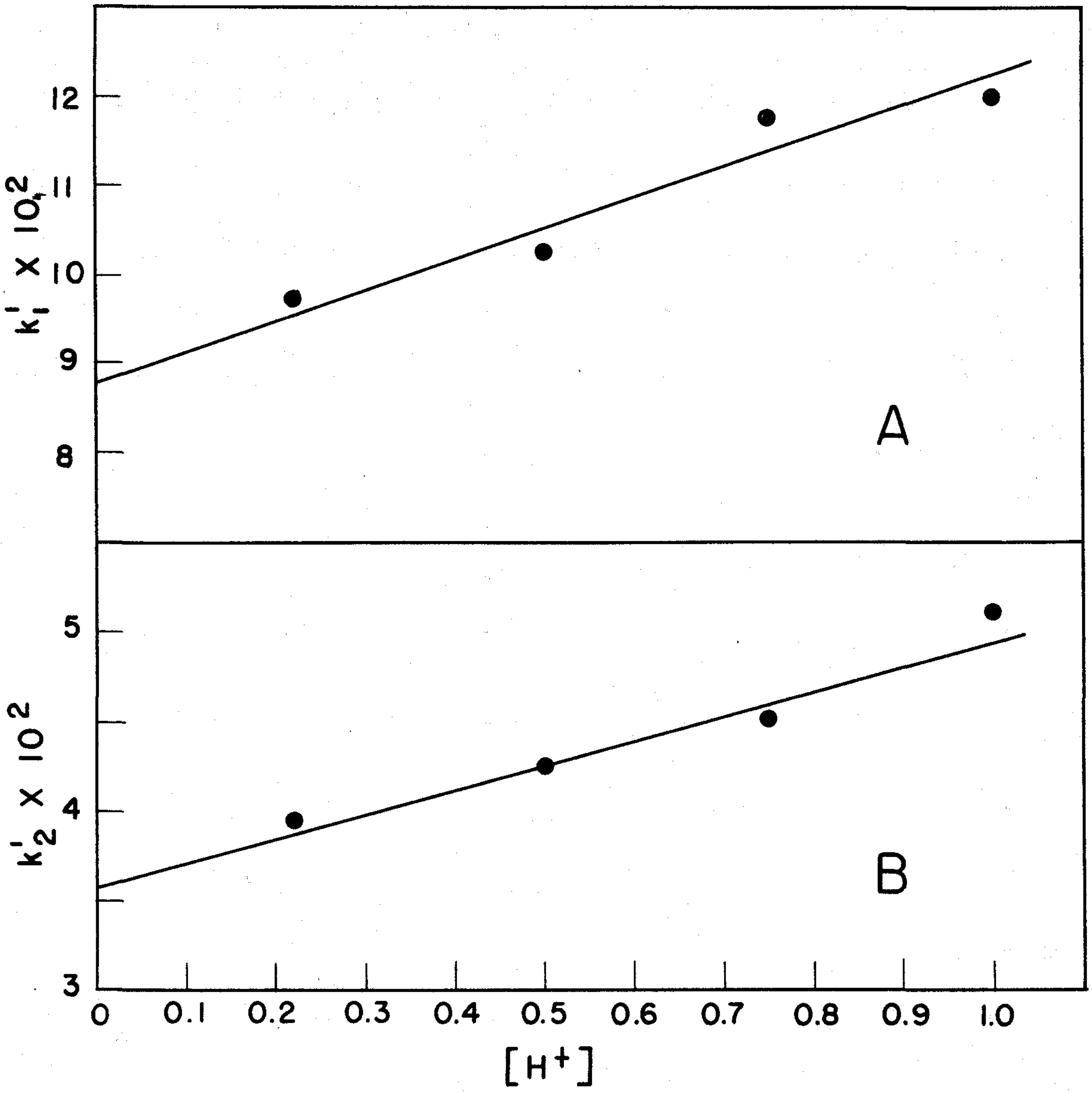

FIG. 17 HYDROGEN ION DEPENDENCE. 40°C
A – k_1' VERSUS $[H^+]$
B – k_2' VERSUS $[H^+]$

where,

$$K_1' = K_1[Cl^-], \tag{17}$$

$$k_1'' = k_1 + k_2\, K_1[Cl^-], \tag{18}$$

and

$$k_2'' = k_3 + k_4\, K_1[Cl^-]. \tag{19}$$

By plotting k' vs. $[H^+]$ at various $[Cl^-]$ a series of straight lines are obtained which have slopes of $\frac{k_2''[ClO_4^-]}{(1 + K_1')}$ and intercepts of $\frac{k_1''[ClO_4^-]}{(1 + K_1')}$. For the reaction at 40°C the data obtained are shown in Table 25 and are plotted in Figure 18. The values of k_1'' and k_2'' as a function of $[Cl^-]$ are given in Table 26 and are plotted in Figure 19. The constants k_1, k_2, k_3, and k_4, for this method were found to be, $k_1 = 8.99\times10^{-2}$, $k_2 = 3.61\times10^{-2}$, $k_3 = 3.34\times10^{-2}$, and $k_4 = 1.37\times10^{-2}$. These agree very well with those calculated above. The average of these values is then, $k_1 = (8.89\pm0.1)\times10^{-2}$, $k_2 = (3.59\pm0.1)\times10^{-2}$, $k_3 = (3.40\pm0.1)\times10^{-2}$, and $k_4 = (1.36\pm0.1)\times10^{-2}$. The errors shown are the standard deviations of the average values.

The same series of calculations was carried out for the reaction at 50°C. The variation of the rate constants as a function of the hydrogen ion which were obtained from

Table 25. Chloride Ion Dependence 40°C. Variation of pseudo first order rate constant with $[Cl^-]$ at various $[H^+]$.

$[ClO_4^-] = 0.5M$ $[Ti^{+3}] = 0.015M$

$[Cl^-]$	$[H^+]=0.22M$ $k' \times 10^2$	$[H^+]=0.5M$ $k' \times 10^2$	$[H^+]=0.75M$ $k' \times 10^2$	$[H^+]=1.0M$ $k' \times 10^2$
0.30	3.70	3.98	4.39	4.73
0.45	3.40	3.68	4.05	4.36
0.60	3.24	3.46	3.81	4.08
0.75	3.06	3.30	3.61	3.88
0.90	2.93	3.07	3.43	3.74

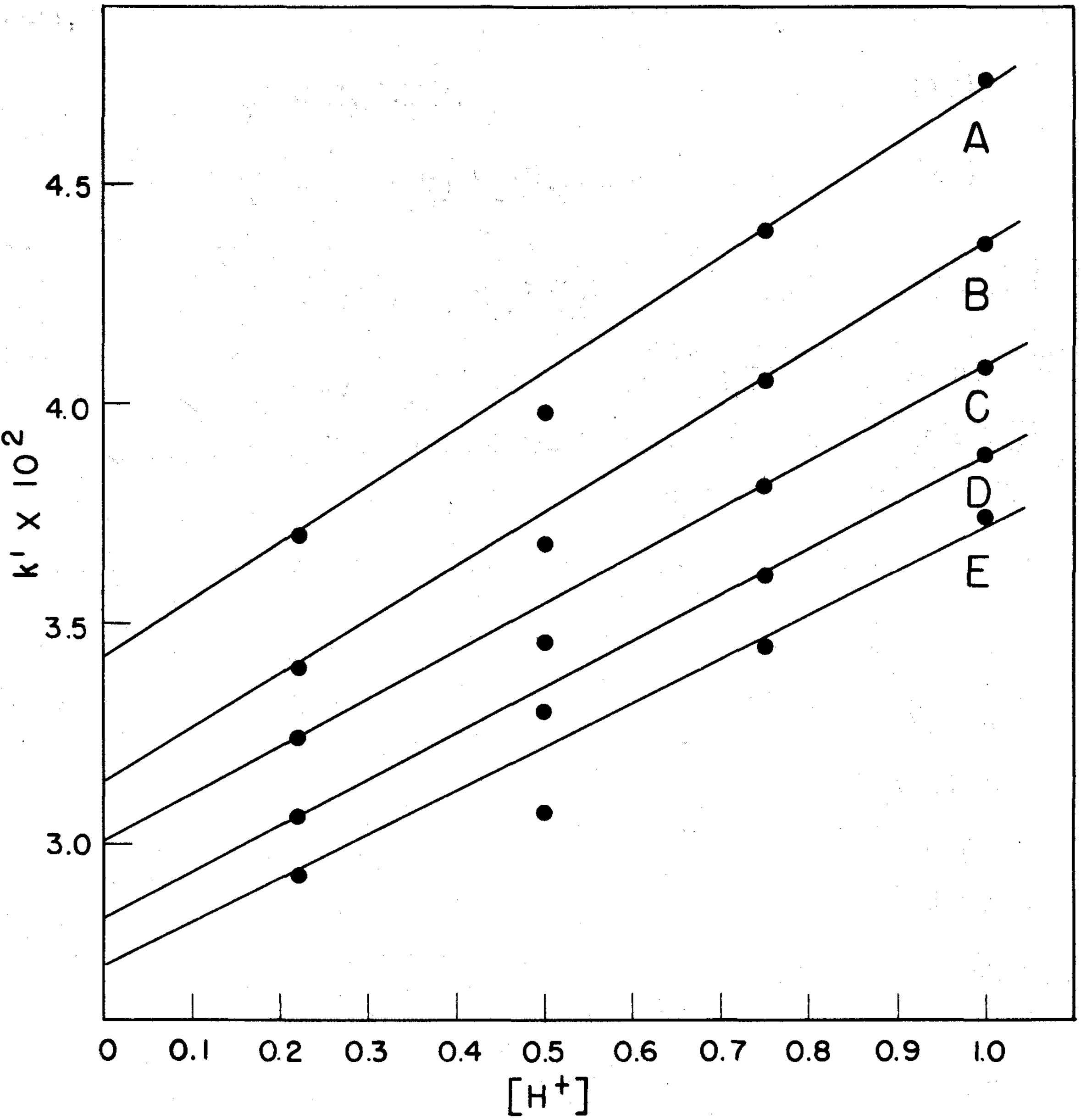

FIG. 18 PSEUDO FIRST ORDER RATE CONSTANTS VERSUS [H$^+$] AT VARIOUS [Cl$^-$] 40°C.

A - [Cl$^-$] = 0.30 M
B - [Cl$^-$] = 0.45 M
C - [Cl$^-$] = 0.60 M
D - [Cl$^-$] = 0.75 M
E - [Cl$^-$] = 0.90 M

Table 26. Chloride Ion Dependence 40°C. Variation of rate constants k_1'' and k_2'' with $[Cl^-]$.
$[Ti^{+3}] = 0.015M$ $[ClO_4^-] = 0.5M$

$[Cl^-]$	$k_1''x10^2$	$k_2''x10^2$
0.30	11.31	4.31
0.45	12.42	4.84
0.60	13.91	4.98
0.75	14.90	5.54
0.90	16.10	5.92

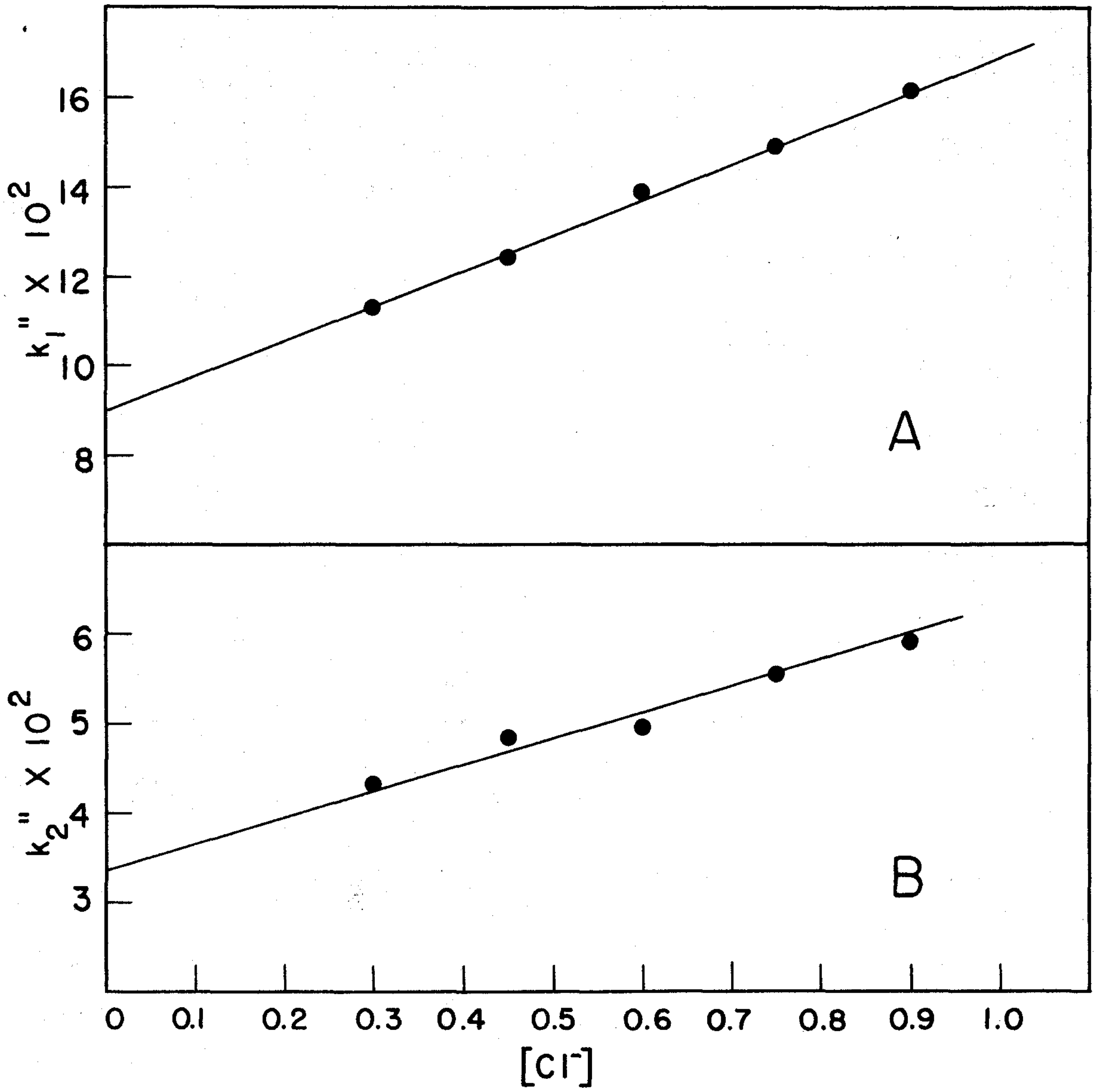

FIG. 19 CHLORIDE ION DEPENDENCE 40°C
VARIATION OF RATE CONSTANTS k_1'' AND k_2'' WITH $[Cl^-]$

A - k_1'' VERSUS $[Cl^-]$
B - k_2'' VERSUS $[Cl^-]$

the chloride ion dependence curves are summarized in Table 27, and are plotted in Figure 20. The rate constants determined in this way are, $k_1 = 33.14\times10^{-2}$, $k_2 = 12.95\times10^{-2}$, $k_3 = 4.41\times10^{-2}$, and $k_4 = 2.33\times10^{-2}$. For the pseudo rate constant expression at constant Cl^- the values of the pseudo rate constant as a function of $[H^+]$ and $[Cl^-]$ are shown in Table 28. These are plotted in Figure 21. The constants k_1'' and k_2'' as a function of $[Cl^-]$ at 50°C are shown in Table 29 and are plotted in Figure 22. The rate constants determined from this graph are $k_1 = 34.12\times10^{-2}$, $k_2 = 13.90\times10^{-2}$, $k_3 = 4.40\times10^{-2}$, and $k_4 = 1.80\times10^{-2}$. The average values of the rate constants obtained for both 40°C and 50°C are summarized in Table 30. The activation energies and entropies for the rate determining steps were calculated and are shown in Table 31.

The Temperature Dependence

The Arrhenius activation energy for this reaction was determined by studying the effects of temperature on the reduction of ClO_4^- by Ti^{+3}. This assumes that the activation energy is constant over the temperature range chosen. The data obtained are shown in Table 32 and are plotted in Figure 23.

The Arrhenius equation is given by,

$$\frac{d \ln k}{dt} = \frac{E_a}{RT^2}, \text{ where } E_a = \text{activation energy.}$$

Table 27. Hydrogen Ion Dependence 50°C. Variation of rate constants with $[H^+]$.

$[Ti^{+3}] = 0.015M$ $[ClO_4^-] = 0.5M$ $K_1 = 2.48$

$[H^+]$	$k_{1_{Cl}}x10^2$	$k_{2_{Cl}}x10^2$	$k_1'x10^2$	$k_2'x10^2$
0.23	17.04	6.65	34.08	13.30
0.50	17.53	7.15	35.06	14.30
0.75	18.48	7.24	36.96	14.48
1.0	18.76	7.90	37.52	15.80

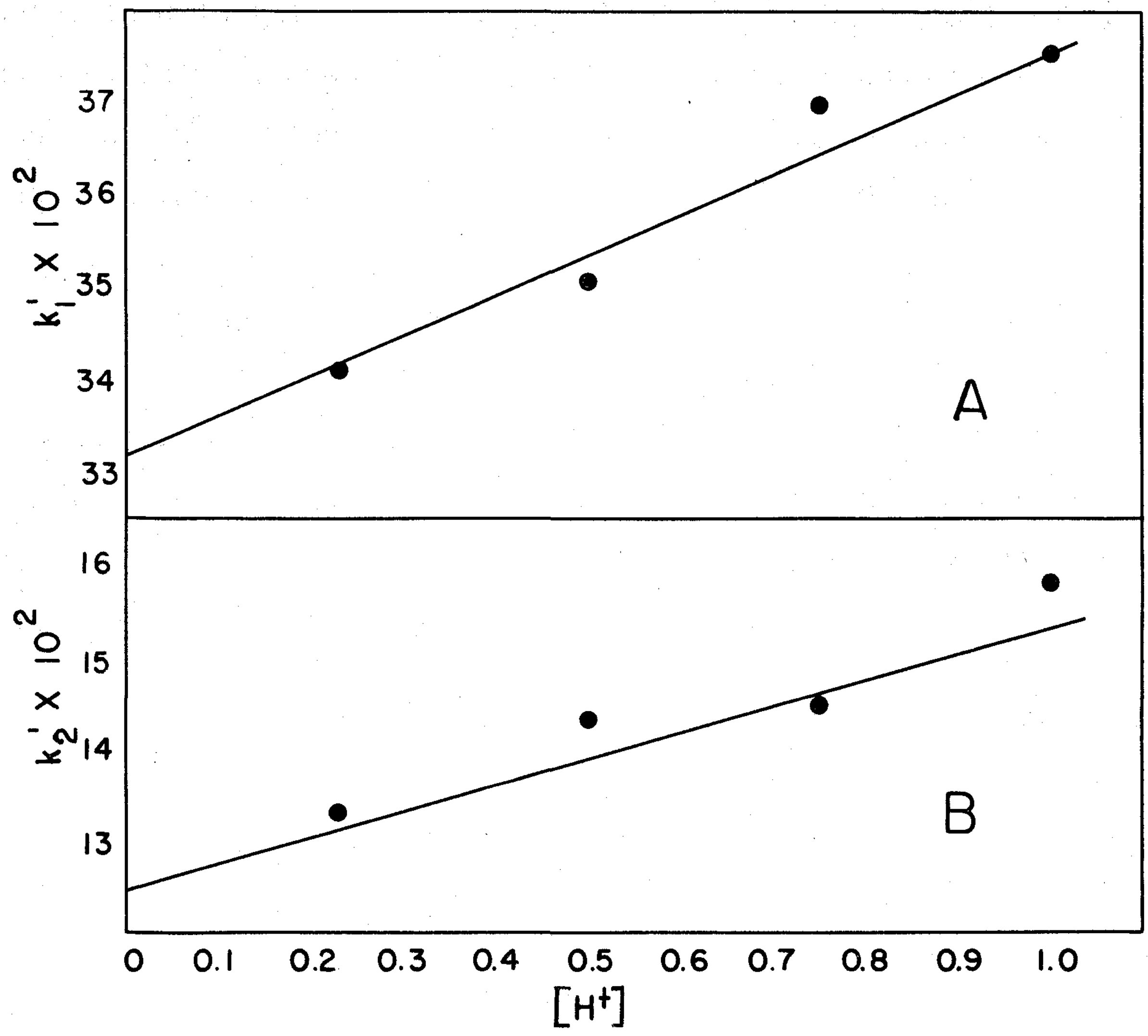

FIG. 20 HYDROGEN ION DEPENDENCE 50°C.

A – k_1' VERSUS $[H^+]$

B – k_2' VERSUS $[H^+]$

Table 28. Chloride Ion Dependence 50°C. Variation of pseudo first order rate constants with $[Cl^-]$ at various $[H^+]$.

$[Ti^{+3}] = 0.015M$ $[ClO_4^-] = 0.5M$

$[Cl^-]$	$[H^+]$=0.23M $k' \times 10^2$	$[H^+]$=0.50M $k' \times 10^2$	$[H^+]$=0.75M $k' \times 10^2$	$[H^+]$=1.0M $k' \times 10^2$
0.30	12.28	13.35	13.70	14.23
0.45	11.08	12.49	12.83	13.25
0.60	10.45	11.72	12.05	12.44
0.75	9.97	11.10	11.32	11.82
0.90	9.58	10.59	10.74	11.36

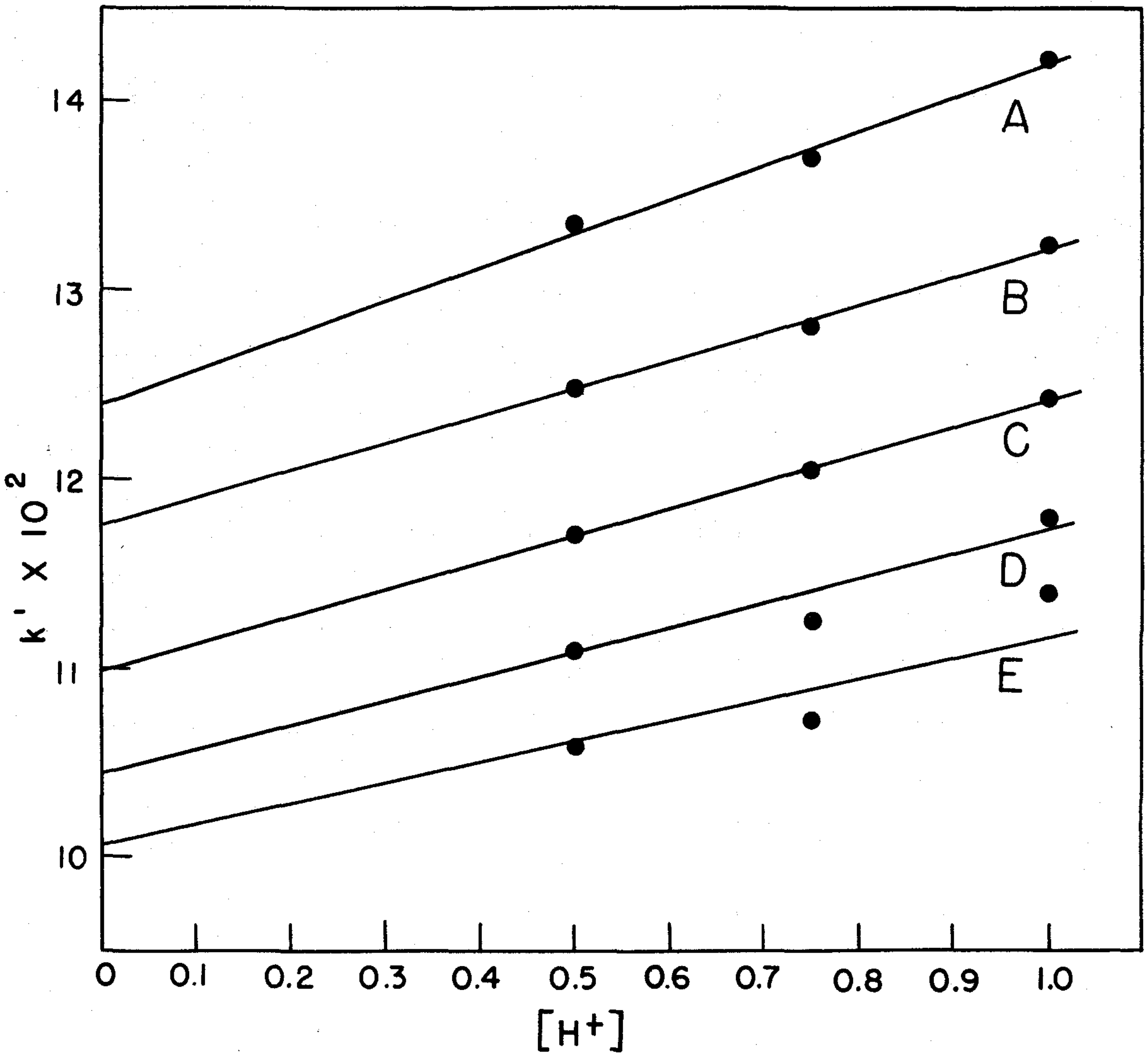

FIG. 21 PSEUDO FIRST ORDER RATE CONSTANTS VERSUS [H⁺] AT VARIOUS [Cl⁻] 50°C

A – [Cl⁻] = 0.30 M
B – [Cl⁻] = 0.45 M
C – [Cl⁻] = 0.60 M
D – [Cl⁻] = 0.75 M
E – [Cl⁻] = 0.90 M

Table 29. Chloride Dependence 50°C. Variation of k_1'' and k_2'' with $[Cl^-]$.

$[Tl^{+3}] = 0.015M$ $[ClO_4^-] = 0.5M$

$[Cl]$	$k_1''\times 10^2$	$k_2''\times 10^2$
0.30	43.3	6.28
0.45	49.7	6.27
0.60	54.7	7.23
0.75	59.7	7.55
0.90	64.9	7.24

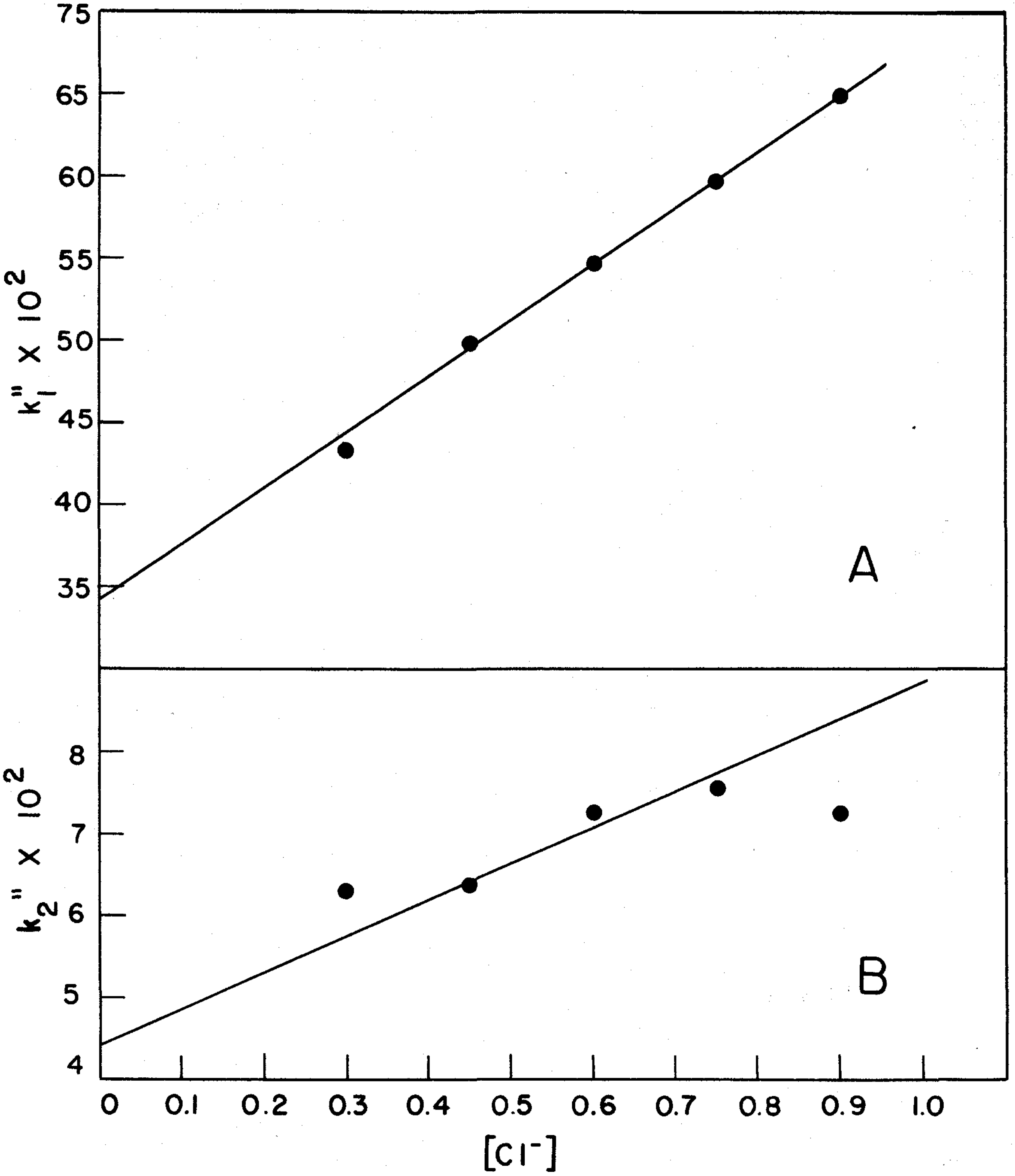

FIG. 22 CHLORIDE ION DEPENDENCE 50°C
VARIATION OF RATE CONSTANTS k_1'' AND k_2'' WITH $[Cl^-]$

A – k_1'' VERSUS $[Cl^-]$
B – k_2'' VERSUS $[Cl^-]$

Table 30. Rate Constants as a Function of Temperature.

$[\mathrm{Tl}^{+3}] = 0.015\mathrm{M}$ $[\mathrm{ClO}_4^-] = 0.5\mathrm{M}$

t	$k_1 \times 10^2$	$k_2 \times 10^2$	$k_3 \times 10^2$	$k_4 \times 10^2$	K_1
40°C	8.89±0.9*	3.59±0.4	3.40±0.3	1.36±0.2	2.18±0.2
50°C	33.6±3	13.4±1.3	4.41±0.4	2.04±0.2	2.48±0.2

---

*Errors for rate constants are based on an estimated error of 10%.

Table 31. Activation Energies and Entropies for the Rate Determining Steps 40°C to 50°C.

	40°C	50°C
$k_1 x 10^2$	8.89±0.9	33.6±3
$\Delta F^{\neq}_{313}$	19.9±1 kcal	
$\Delta H^{\neq}$	26.1±15% kcal	
$\Delta S^{\neq}$	20.8±50% e.u.	
$k_2 x 10^2$	3.59±0.4	13.4±1
$\Delta F^{\neq}_{313}$	20.4±0.1 kcal	
$\Delta H^{\neq}$	25.9±14% kcal	
$\Delta S^{\neq}$	17.6±50% e.u.	
$k_3 x 10^2$	3.40±0.3	4.41±0.4
$\Delta F^{\neq}_{313}$	20.4±0.1 kcal	
$\Delta H^{\neq}$	5.8±50% kcal	
$\Delta S^{\neq}$	-46.5±50% e.u.	
$k_4 x 10^2$	1.36±0.2	2.04±0.2
$\Delta F^{\neq}_{313}$	21.0±0.1 kcal	
$\Delta H^{\neq}$	9.7±50% kcal	
$\Delta S^{\neq}$	-36.2±50% e.u.	
K_1	2.18±0.2	2.48±0.2
ΔF_{313}	17.8±0.1 kcal	
ΔH	2366±50% cal.	
ΔS	-49.3±100% e.u.	

Table 32. Temperature Dependence. Variation of pseudo first order rate constant with temperature.

$[Ti^{+3}]$ = 0.015M $[H^{+}]$ = 0.5M $[ClO_4^{-}]$ = 0.5M
$[Cl^{-}]$ = 2.0M

t °C	k'x10^2	ln k'	$\frac{1}{T}$ x 10^3
30.2	0.885	-4.728	3.296
40.0	2.66	-3.628	3.193
50.0	8.77	-2.434	3.094
60.0	24.3	-1.415	3.001

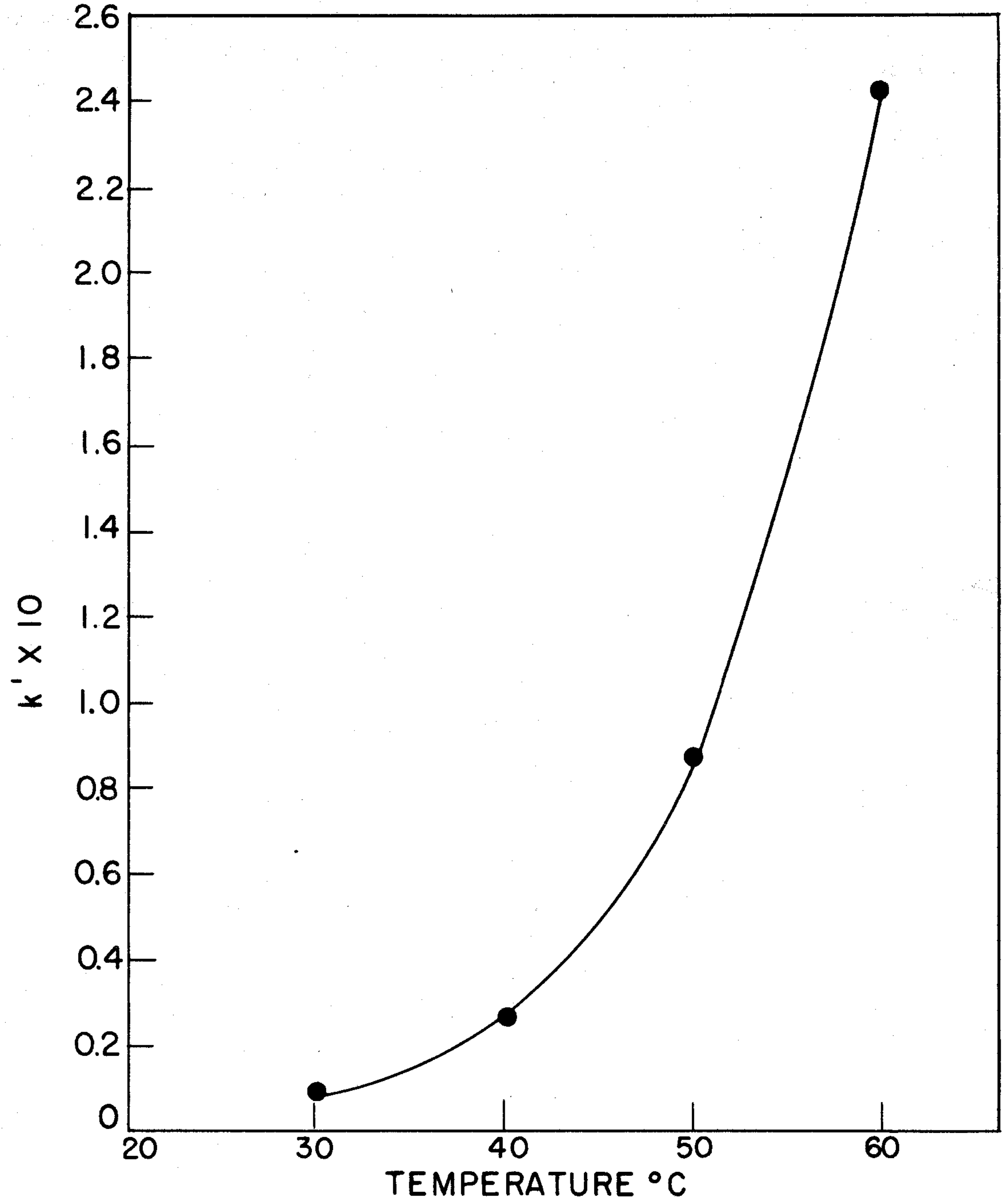

FIG. 23. TEMPERATURE DEPENDENCE FIRST ORDER RATE CONSTANTS VERSUS TEMPERATURE $[Ti^{+3}]$ = 0.015M $[ClO_4^-]$ = 0.5M $[Cl^-]$ = 2.0M $[H^+]$ = 0.5M

Integration of this equation yields,

$$\ln k = -\frac{E_a}{RT} + \text{constant.} \qquad (20)$$

If this is the form of the temperature dependence on the rate, then a plot of ln k vs. $\frac{1}{T}$ should give a straight line with a negative slope $\frac{E_a}{R}$. The data are shown plotted in Figure 24 which is, by inspection, a straight line plot. The slope was found to be -11,750 which gives a value of the activation energy of 23.3±0.1 kcal.

Proposed Mechanism

According to Frost and Pearson (17, p.2)

> A mechanism of a reaction is understood to mean all the individual collisional or other elementary processes involving molecules (atoms, radicals, and ions, included) which take place simultaneously or consecutively in producing the observed over-all reaction.

Included in this definition may be the idea of the concept of the stereochemical picture of the reaction process. A kinetic mechanism is really a theory to explain the facts, which in turn are obtained by experimental procedures. Like all theories they are subject to modification as new and perhaps more pertinent data are obtained. As stated above a theory is proposed to explain the facts and is not necessarily all conclusive. One might very well say, that any relationship of the proposed theory to the actual

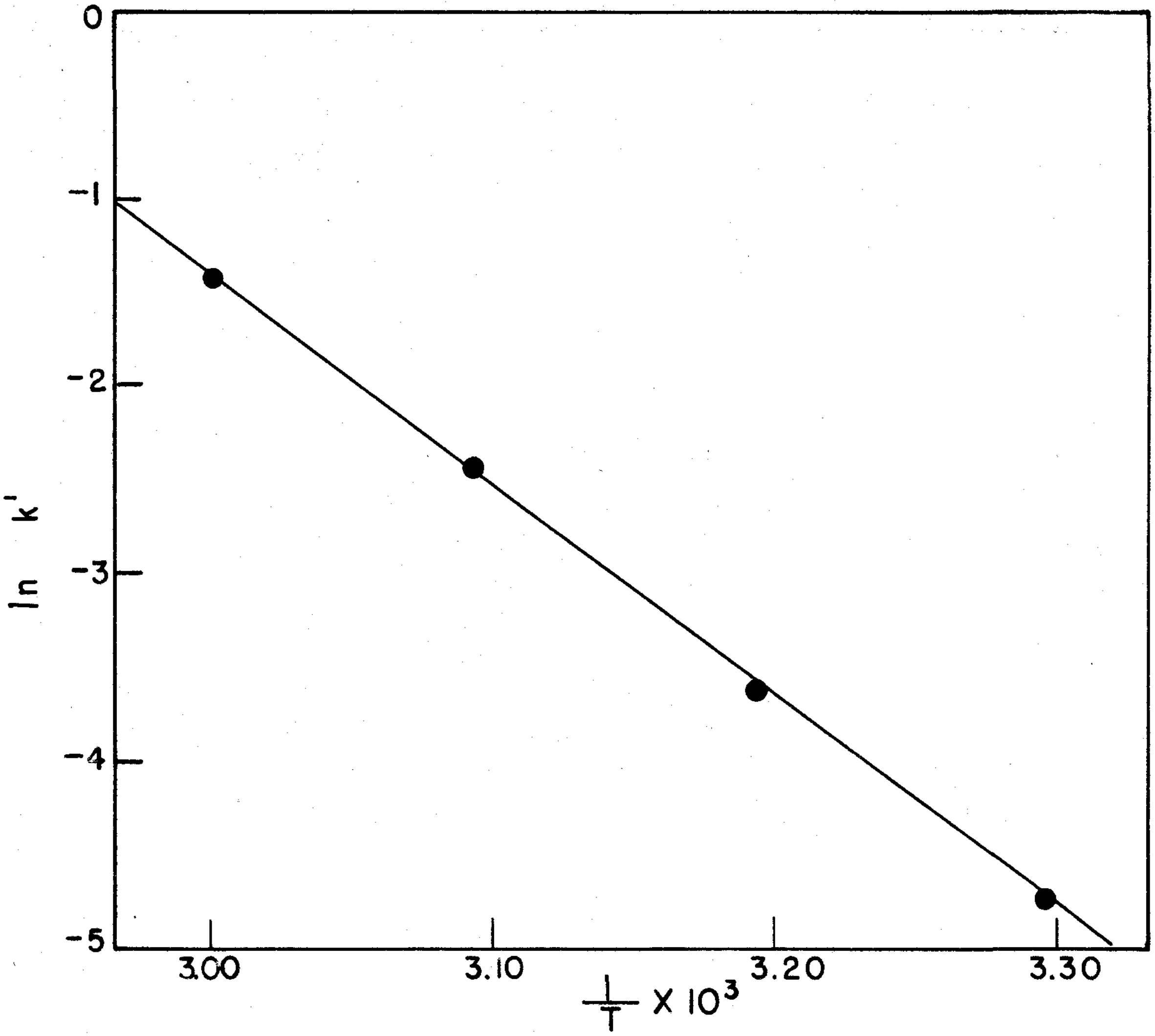

FIG.24.TEMPERATURE DEPENDENCE FIRST ORDER RATE CONSTANTS VERSUS RECIPROCAL ABSOLUTE TEMPERATURE $[Ti^{+3}] = 0.015M$ $[ClO_4^-] = 0.5M$ $[Cl^-] = 2.0M$ $[H^+] = 0.5M$

process being carried on is the principal aim of a chemical kineticist.

In proposing a mechanism for this reaction the following facts found from experimental data must be considered:

1. The rate of reaction is first order in Ti^{+3}.
2. The rate of reaction is first order in perchlorate ion deviating toward higher order at concentrations above 1M.
3. The reaction is both hydrogen uncatalyzed and catalyzed, being first order in H^+ for the latter.
4. The rate of reaction decreases with increasing Cl^-, quite rapidly up to 2M and then seems to become constant at higher concentration.
5. No perchlorate ion complexes of Ti^{+3} were found to exist in solution.

Since the reaction is first order in H^+, then complexes of the form $Ti(OH)^{++}$ would seem to enter into the kinetics. The presence of these complexes in Ti^{+3} solutions was first reported by Yost and Zabaro (18). However, the presence of an equilibrium constant involving these complexes does not appear in the experimentally determined rate expression as was the case for the $TiCl^{++}$ complex. Also if the equilibrium $Ti^{+3} + H_2O \rightleftharpoons Ti(OH)^{++} + H^+$ did exist in solution at low pH one would expect to find a leveling off or a slowing down of the rate at high H^+ and this was not observed experimentally. Consequently, $Ti(OH)^{++}$ complexes do not appear to enter into the reaction kinetics. This leaves then for the reacting species, the hydrated Ti^{+3} and the chloride complex $TiCl^{++}$. Thus, one may write for the over-all rate of disappearance of total titanium,

$$-\frac{d[T_{Ti^{+3}}]}{dt} = k_1[Ti^{+3}][ClO_4] + k_2[TiCl^{+2}][ClO_4] + k_3[Ti^{+3}][ClO_4][H^+] + k_4[TiCl^{++}][ClO_4][H^+]. \qquad (20)$$

The total titanium in solution both complexed and uncomplexed is given by,

$$[T_{Ti^{+3}}] = [Ti^{+3}] + [TiCl^{++}].$$

The equilibrium constant for the formation of $TiCl^{++}$ may be written from,

$$Ti^{+3} + Cl^- \rightleftharpoons TiCl^{++},$$

$$K_1 = \frac{[TiCl^{++}]}{[Ti^{+3}][Cl]} .$$

Thus,

$[TiCl^{++}] = K_1[Ti^{+3}][Cl^-]$ and the total titanium is

$$[T_{Ti^{+3}}] = [Ti^{+3}] + K_1[Ti^{+3}][Cl^-] = (1+K_1[Cl^-])[Ti^{+3}]$$

and

$$[Ti^{+3}] = \frac{[T_{Ti^{+3}}]}{1 + K_1[Cl^-]} ; \quad [TiCl^{++}] = \frac{K_1[Cl^-][T_{Ti^{+3}}]}{1 + K_1[Cl^-]}.$$

Substituting in the rate expression, equation 20,

$$-\frac{d[T_{Ti^{+3}}]}{dt} = k_1 \frac{[ClO_4^-][\quad_{Ti^{+3}}]}{1 + K_1[Cl^-]} + k_2 \frac{K_1[Cl^-][ClO_4^-][\quad_{Ti^{+3}}]}{1 + K_1[Cl^-]} +$$

$$k_3 \frac{[H^+][ClO_4^-][T_{Ti^{+3}}]}{1 + K_1[Cl^-]} +$$

$$k_4 \frac{K_1[Cl^-][ClO_4^-][H^+][T_{Ti^{+3}}]}{1 + K_1[Cl^-]} \qquad (21)$$

or, simplified,

$$-\frac{d[T_{Ti^{+3}}]}{dt} = \frac{k_1 + k_2 K_1[Cl^-] + k_3[H^+] + k_4 K_1[Cl^-][H^+]}{1 + K_1[Cl^-]}$$

$$[ClO_4^-][T_{Ti^{+3}}]. \qquad (22)$$

Equation 22 is the same as the rate expression found from experiment.

The following equations may be considered as a mechanism for the reduction of Ti^{+3} by ClO_4^- in dilute solutions:

$$Ti^{+3} + ClO_4^- \longrightarrow TiO^{++} + ClO_3$$

$$Ti^{+3} + ClO_4^- + H^+ \longrightarrow Ti(OH)^{+3} + ClO_3$$

$$TiCl^{++} + ClO_4^- \longrightarrow TiO^{++} \text{ (or } TiOCl^+\text{)} + ClO_3$$

$$Ti^{+3} + ClO_4^- + H^+ \longrightarrow Ti(OH)^{+3} \text{ (or } TiOHCl^+\text{)} + ClO_3.$$

The reaction is thought to proceed by the formation of a coordinated complex the disproportionation of which is the rate determining step:

$$TiCl^{++} + ClO_4^- \overset{\text{slow}}{\rightleftharpoons} [\text{complex}] \xrightarrow{\text{fast}} \text{products.}$$

Since the reaction involves an eight electron transfer, further reduction of ClO_3 must proceed by a series of rapid steps involving a one electron transfer.

SUMMARY

The kinetics of the reduction of perchlorate ion by Ti^{+3} in dilute solutions has been studied. The rate of reaction has been determined at various concentrations of H^+, ClO_4^-, and Cl^-. The pseudo first order rate constants were calculated from plots of $\ln[T_{Ti^{+3}}]$ vs. time and the nature of the H^+, ClO_4^-, and Cl^- dependences was also determined.

The reaction appears to proceed by more than one path. There is a reaction which is independent of both H^+ and Cl^-. The reaction was also found to be first order in H^+ and to be retarded considerably by addition of chloride. No Ti^{+3}-ClO_4^- complexes were found to exist even at high concentrations of ClO_4^-.

The rate of disappearance of total titanium was found to follow the rate expression,

$$-\frac{d[T_{Ti^{+3}}]}{dt} = \frac{k_1 + k_2 K_1[Cl^-] + k_3[H^+] + k_4 K_1 [Cl^-][H^+]}{1 + K_1[Cl^-]} [ClO_4^-][T_{Ti^{+3}}].$$

The rate constants were determined at two temperatures and the activation energies and entropies were calculated. The

most favorable mechanisms appear to be those which involve perchlorate ion reacting with hydrated Ti^{+3} and the complex $TiCl^{++}$.

The following kinetic mechanisms have been proposed:

$Ti^{+3} + ClO_4^- \rightleftharpoons$ [complex] $\longrightarrow ClO_3 + TiO^{++}$,

$Ti^{+3} + ClO_4^- + H^+ \rightleftharpoons$ [complex] $\longrightarrow ClO_3 + Ti(OH)^{+3}$,

$TiCl^{+2} + ClO_4^- \rightleftharpoons$ [complex] $\longrightarrow ClO_3 - TiO^{++} + Cl^-$
(or $TiOCl^+$),

$TiCl^{+2} + ClO_4^- + H^+ \rightleftharpoons$ [complex] $\longrightarrow ClO_3 + Ti(OH)^{+3} + Cl^-$
(Or $TiOHCl^+$).

In each case the rate determining step is the disproportionation of the coordinated complex. The radical ClO_3 reacts further in a series of rapid one electron transfer reactions to the final product, Cl^-.

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