ductions by chromium(II), the greatest effect should appear in the case of the chlorite–chromium(II) stoichiometry. Indeed, in the iron(II)–chlorite[27] and particularly in the uranium(IV)–chlorite[28] systems, the production of chlorate ion occurs to a considerable degree. In all other chromium(II)–chlorine oxidant systems, at best, only a small steady-state concentration of chlorite ion would ever be present.

The production of chlorate ion in the chromium(II)–chlorite reaction *via* paths such as those proposed in reactions 10–12 could presumably be detected by a detailed analysis of the kinetics of both the chromium(II)–chlorate and the chromium(II)–chlorite reactions. The chlorate reaction appears to be much slower than the chlorite reaction. Thus, if significant amounts of chlorate ion are produced in the chlorite–chromium(II) reaction, the kinetics should be consistent with an initial rapid reaction, followed by the slower chlorate–chromium(II) reaction. The stoichiometric data suggest that, if either hypochlorite or chlorine intermediates do react with chlorite, an increased yield of polynuclear species over the yield in the absence of these reactions would result since either the chlorate or the chlorine dioxide product yields more of the polynuclear chromium(III) product than does the corresponding chlorine(I) species.

In conclusion, it should be pointed out that the reactions between chromium(II) and the various chlorine-containing oxidizing agents are quite complex. The relative amounts of the three chromium(III) products which result for these reactions are quite sensitive to both initial hydrogen ion and the initial chloride ion concentrations. The initial step in the reaction probably corresponds to the formation of a chromium–oxidizing agent complex. However, further interpretation of these results will be presented in the paper following[29] with the corresponding kinetic and tracer experiments.

Acknowledgment.—The authors wish to express their appreciation to the Atomic Energy Commission for its generous support of this research through Grant No. AT(40-1)-2858.

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[27] G. Gordon, R. Miyatake, and R. C. Thompson, unpublished results, 1965.

[28] G. Gordon and F. Feldman, *Inorg. Chem.*, **3**, 1728 (1964).

[29] R. C. Thompson and G. Gordon, *ibid.*, **5**, 562 (1966).

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Kinetics of the Reaction between Chromium(II) and the Chlorine Oxidants in Aqueous Perchloric Acid

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The kinetics of the reaction between chromium(II) and chlorate ion have been studied and are consistent with a second-order rate law, first order each with respect to chromium(II) and chlorate ion. The value of the apparent second-order rate constant is 39.0 ± 1.4 M^{-1} sec^{-1} in 0.55 M perchloric acid with an ionic strength of 2.00 M at 20.0°. The same rate is observed in the wavelength region 4100 to 7190 A. The reaction is approximately first order with respect to hydrogen ion in 0.10–1.00 M perchloric acid. Marked medium effects were demonstrated at high ionic strength by substituting zinc and lithium perchlorate for sodium perchlorate. The reaction was also studied as a function of ionic strength, and the data were consistent with an extended form of the Debye–Hückel equation. The activation parameters for the chromium(II)–chlorate reaction in 0.55 M $HClO_4$ and an ionic strength of 2.00 ($NaClO_4$) were $\Delta H^* = 11.2$ kcal and $\Delta S^* = -17$ eu. A survey kinetic study was made on the chlorine dioxide, chlorite, hypochlorite, and chlorine–chromium(II) systems. The lower limits for the second-order rate constants for these systems were 10^3 to 10^5 times greater than the rate constant for the chromium(II)–chlorate system. The interpretation of the stoichiometric and kinetic data suggested an inner-sphere mechanism for all of the chlorine oxidant–chromium(II) reactions. The mechanism of these reactions probably involves the formation of chromium(III)–chlorine oxidant intermediates which are unstable with respect to further reduction by the excess chromium(II) present.

Introduction

The reactions between chromium(II) and the chlorine oxidants are complex in several respects. Three distinct chromium(III) products are formed, and their distribution is markedly a function of initial hydrogen ion and chloride ion concentrations. Further, several reactions between possible intermediates are known to be rapid and might be competitive with the corresponding chromium(II) reaction. For example, the chlorine(III)–chlorine(I), the chlorine(III)–chlorine(0), and the chlorine(I)–chloride reactions (eq 1–4) have been shown to be important in the uranium(IV)–chlorite,[1] iron(II)–chlorite,[2] and vanadium(II)–chlorite[3] reactions.

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[1] G. Gordon and F. Feldman, *Inorg. Chem.*, **3**, 1728 (1964).

[2] G. Gordon, R. Miyatake, P. H. Tewari, and R. C. Thompson, to be published.

[3] G. Gordon and P. Tewari, *J. Phys. Chem.*, **70**, 200 (1966).

$$2HClO_2 + HClO = 2ClO_2 + Cl^- + H_2O + H^+ \qquad (1)$$

$$ClO_2^- + HClO = ClO_3^- + Cl^- + H^+ \qquad (2)$$

$$2HClO_2 + Cl_2 = 2ClO_2 + 2Cl^- + 2H^+ \qquad (3)$$

$$Cl^- + HOCl = Cl_2 + OH^- \qquad (4)$$

Earlier work has suggested that chromium(II) can be oxidized by either one- or two-electron paths.[4] If the unstable chromium(IV) intermediate is produced *via* a two-electron-transfer reaction, it is rapidly reduced by the chromium(II) present to chromium(III). Further evidence for the +4 oxidation state as an intermediate has been obtained from a variety of reactions in which chromium(VI) is reduced to chromium(III).[5–7]

The chromium(II)–chlorine oxidant reactions would appear to be ideal systems in which to study one- and two-electron transfer and atom transfer. The monochloropentaaquochromium(III) ion exchanges chloride ion with solvent at a rate corresponding to a half-life of >40 hr.[8] Thus, any chlorine transferred in these reactions to the chromium(III) product could be detected by the presence of a $(H_2O)_5CrCl^{2+}$ product. Ardon and Plane[4] have proposed that a two-electron transfer from chromium(II) to form chromium(IV) results in the formation of a polynuclear chromium(III) species after the subsequent chromium(IV)–chromium(II) reaction. Thus, the presence or absence of a polynuclear chromium(III) species might be used to distinguish between a one- or a two-electron-transfer reaction.

This paper presents the results of a detailed kinetic investigation of the relatively slow chlorate–chromium(II) reaction and a survey study of the much more rapid oxidation of chromium(II) by chlorine(IV), chlorine(III), chlorine(I), and chlorine(0).[9]

Experimental Section

Reagents.—The preparation and standardization of the chromium(III) perchlorate, chromium(II) perchlorate, sodium chlorate, sodium hypochlorite, chlorine, sodium perchlorate, and perchloric acid solutions have been described earlier.[10] The zinc perchlorate and lithium perchlorate solutions were prepared by dissolving the appropriate amount of the twice recrystallized salt in distilled water.[3] Chlorine dioxide was prepared by the method of Bray.[11] The purified gas was dissolved in distilled water and stored in the dark at 0°.

An improved method of determining the zinc(II) and hydrogen ion concentrations in the chromium(II) solutions was developed. The chromium(II) was converted to the +6 oxidation state by heating an aliquot of the chromium(II) solution with ammonium persulfate in an acid solution which contained a trace amount of silver nitrate.[12] The solution was buffered at pH 10 with ammonium chloride and sodium hydroxide. The zinc(II) concentration was determined by titration with a standard solution of the disodium salt of ethylenediaminetetraacetic acid to the green Eriochrome Black T end point.[13] The hydrogen ion concentration of the chromium(II) solutions was taken to be the difference between the total cation concentration and the sum of the zinc(II) and chromium(II) concentrations. The total cation concentration of the solution was determined by an ion-exchange technique.

The Chromium(II)–Chlorate Reaction.—The reactants were rapidly mixed,[14] and the course of the reaction was monitored spectrophotometrically. The reaction was followed by observing the appearance of the chromium(III) products in the visible wavelength region. The reactions were slow enough to permit the change of transmittance with time data to be recorded on a Moseley 7101A strip chart recorder which had a full scale response time of 0.5 sec. The chart speed was 0.50 in./sec. In several experiments the reaction was monitored by observing the disappearance of chromium(II) at 7190 A. The specifications of the IP28 photomultiplier tube are not favorable at this wavelength, and accordingly a Hamamatsu R136 photomultiplier tube was used.

Typical Experiment.—The sodium chlorate solution was outgassed under a mild vacuum and placed in a small flask. Prepurified nitrogen was bubbled through for 5 min to minimize the oxygen content, and the flask was stoppered with a soft rubber serum cap. The spring-powered syringe was rinsed several times with the same solution, carefully loaded, and secured through the cooling coils; temperature equilibrium was attained within 10 min. To the 2-cm cylindrical absorption cell was added 5.90 ml of a solution containing the appropriate amounts of perchloric acid, the perchlorate salt used to adjust the ionic strength, and in some experiments sodium chloride. This solution was purged of oxygen with prepurified nitrogen, and 0.50 ml of the chromium(II) stock solution was added under a nitrogen atmosphere. The cell was stoppered with a serum cap and immediately placed in the sample compartment of the rapid-mixing apparatus. The sample compartment had previously been filled with distilled water, and temperature equilibrium was attained with the cooling coils surrounding the compartment. The temperature control is estimated to be ±0.1°, even for the 5.0° experiments. In addition to the syringe needle, a small hypodermic needle was inserted through the syringe cap in order to relieve the increased pressure in the cell during the injection. The reaction was initiated by releasing the triggering lever on the loaded syringe which caused the injection of 0.595 ml of the sodium chlorate solution. Previous mixing experiments have shown that a smooth kinetic trace, particularly at the beginning of the reaction, is sufficient evidence of complete and rapid mixing.

Approximately 3 to 4 min after initiation of the reaction, the observed transmittance changed less than 0.002 absorbance unit/min. This time corresponds very closely to that calculated for 99.5% of the reaction.

The Oxidation of Chromium(II) by Chlorine Dioxide, Chlorite, Hypochlorite, and Chlorine.—All of these reactions were complete within a few hundred milliseconds, even with 0.005 *M* chromium(II) at 0° and an ionic strength of 0.10. Thus, all of the kinetic data for these systems were recorded by photographing the trace obtained from a Tektronix 503 oscilloscope which directly monitored the phototube. A triggering device was used to trigger the oscilloscope trace concomitant with injection of one of the reactant solutions. The wavelength used to monitor the reaction and the choice of which reactant was to be injected depended on the particular oxidizing agent. These data are presented later.

Treatment of Kinetic Data.—Preliminary calculations indicated that at constant hydrogen ion concentration the kinetic data were consistent with a second-order rate equation, first

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(4) M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

(5) J. P. Tong and E. L. King, *ibid.*, **82**, 3805 (1960).

(6) J. H. Espenson, *ibid.*, **85**, 3328 (1963).

(7) J. Sullivan, *ibid.*, **87**, 1495 (1965).

(8) H. Taube and E. L. King, *ibid.*, **76**, 4053 (1954).

(9) No attempt will be made to differentiate between the protonated and unprotonated chlorine oxidants. Thus, chlorine(III) refers to chlorite ion and chlorous acid, and chlorine(I) refers to hypochlorite ion and hypochlorous acid. The other chlorine-containing species will be interchangeably referred to as follows: chlorate ion as chlorine(V), dissolved chlorine dioxide as chlorine(IV), and dissolved chlorine as chlorine.

(10) R. C. Thompson and G. Gordon, *Inorg. Chem.*, **5**, 557 (1966).

(11) W. C. Bray, *Z. Physik. Chem.*, **54**, 569 (1906).

(12) C. L. Wilson and D. W. Wilson, "Comprehensive Analytical Chemistry," Vol. 1C, D. Van Nostrand Co., Inc., New York, N. Y., 1959, p 586.

(13) F. Welcher, "The Analytical Uses of Ethylenediamine Tetraacetic Acids," D. Van Nostrand Co., Inc., Princeton, N. J., 1958, p 149.

(14) R. C. Thompson and G. Gordon, *J. Sci. Instr.*, **41**, 480 (1964).

order each with respect to chromium(II) and chlorate ion. The data were analyzed by means of a linear and a nonlinear computer program.[15,16] The best nonlinear least-squares fit[17] of the data with the second-order rate equation was found by minimizing the quantity $(A_{\text{obsd}} - A_{\text{calcd}})^2$ where A_{obsd} is the observed optical density and A_{calcd} is the calculated optical density from the parameters of the second-order rate equation. Each of the measured optical densities was given a weight of 1.00. The program could simultaneously determine variations in as many as six parameters. These parameters were the initial chromium(II) and chlorate ion concentrations, initial and final optical densities, zero time error, and the second-order rate constant, k_1. The most pertinent output data included an estimated standard deviation for each of the parameters and a comparison of the observed and calculated optical density and its standard deviation at each time t. Several different combinations of parameters to be estimated were chosen, and in each case the variations in these parameters were less than the known accuracy of the parameter itself. In each case, the final values of k_1 were identical within the limits of 1 standard deviation.

It should be emphasized that the computer programs provide an empirical fit for the input data. However, essentially identical values are obtained whether the linear or the nonlinear least-squares program is used.[18] Therefore, the nonlinear program with unit weights for each datum point was used.

Experimental Test of the Kinetic Calculations.—For the computations, it was tacitly assumed that the distribution of the chromium(III) products is the same throughout the course of the reaction. If this assumption is correct, the value of the rate constant should be independent of the wavelength used to follow the reaction even though the ratios of the extinction coefficients of the chromium(III) products might vary markedly. The assumption was tested experimentally by repeating the same kinetic run at 4100, 4800, 5400, and 5800 A. The values of the rate constants obtained are the same within the precision of the experiments at each wavelength although the ratios of the extinction coefficients for the three products vary considerably over this wavelength range. These values and the second-order rate constants at the four wavelengths are shown in Table I.

Table I

Molar Extinction Coefficients ($\text{cm}^{-1}\ M^{-1}$) of the Chromium(III) Products and Second-Order Rate Constants at Various Wavelengths

Species	4100 A	4500 A	5400 A	5800 A
$Cr(OH_2)_6^{3+}$	16.2	6.7	9.9	13.8
$(H_2O)_5CrCl^{2+}$	17.4	16.7	6.0	13.3
Polynuclear species[a]	20.7	13.6	12.1	17.5
k_1, M^{-1} sec^{-1}	40.0 ± 0.2	38.9 ± 0.6	37.4 ± 0.2	38.5 ± 1.0

[a] Entries are for the product formed after 1 hr when chromium(II) is oxidized by oxygen. This is not necessarily the same polynuclear product formed in these reactions.

Tracer Techniques.—The chromium(II) and oxidant solutions were mixed under the same conditions used for the stoichiometric experiments. Three minutes after injection, the reaction mixture was rinsed into a beaker, and oxygen gas was bubbled through the solution to oxidize the excess chromium(II) to the polynuclear chromium(III) species. Excess cupferron solution was added to remove the zinc(II) present initially in the chromium(II) solution.[11] The cold filtrate was placed on a column of Dowex-50 resin which was cooled with ice. The $(H_2O)_5CrCl^{2+}$ species was eluted with 0.7 M $HClO_4$ followed by elution of the $Cr(H_2O)_6^{3+}$ with 2.5 M HCl. Gentle suction was applied to speed the flow rate through the column.

The $(H_2O)_5CrCl^{2+}$ was precipitated as the phosphate[19,20] and the $Cr(H_2O)_6^{3+}$ as the fluoride.[21] The precipitates were dried over $CaSO_4$, and the coordinated water was separated from the solids *in vacuo*.[19] This water was converted to carbon dioxide with silver cyanide by the method of Shakhashiri and Gordon.[22] The resulting carbon dioxide was analyzed mass spectrometrically by the double-collector method, and the 46/(44 + 45) ratio was recorded directly.[23]

Appropriate blank experiments showed that neither the $(H_2O)_5CrCl^{2+}$ nor the $Cr(H_2O)_6^{3+}$ was isotopically diluted during the separation and purification and that chlorate only slowly exchanges with solvent.

Oxygen-18-enriched water was obtained from YEDA. Enriched sodium chlorate was prepared by bubbling chlorine gas through a basic solution of sevenfold oxygen-18-enriched water. Silver perchlorate was added to remove chloride ion quantitatively. The sodium chlorate–sodium perchlorate mixture was recrystallized and vacuum dried. The resulting solid contained 23.8% sodium chlorate (6.30-fold enriched) and 76.2% sodium perchlorate (normal isotopic composition). Since perchlorate does not detectably oxidize chromium(II) solution under the conditions of these experiments, the sodium chlorate–perchlorate mixture was used directly.

Results

Form of the Rate Law for the Chromium(II)–Chlorate Reaction.—At a fixed hydrogen ion concentration of 0.55 M and with the ionic strength adjusted to 2.00 M with sodium perchlorate, the reaction was found to obey a second-order rate law, first order each with respect to chromium(II) and chlorate ion

$$d[\text{Cr(III)}]/dt = k_1[\text{Cr(II)}][\text{ClO}_3^-] \tag{5}$$

The results of the kinetic experiments designed to determine the order of the reaction are summarized in Table II. The average value of k_1 from all of the entries in Table II is 39.0 ± 1.4 M^{-1} sec^{-1}. The value of

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(15) The computer time for this project was supported in part through the facilities of the Computer Science Center Laboratory of the University of Maryland.

(16) For the linear least-squares program, since the chromium(III) products, $(H_2O)_5CrCl^{2+}$, $Cr(OH_2)_6^{3+}$, and the polynuclear species, all exhibit very similar absorption spectra in the visible wavelength region but do not show an isosbestic point, an effective extinction coefficient, E_{eff}, was defined as: $E_{\text{eff}} = (A_\infty - A_0)/lN$, where A_∞ = infinite optical density, A_0 = initial optical density, l = path length (cm), and N = normality of reactant *not* in excess. The chromium(III) concentration at any time t, $Cr^{3+}{}_t$, was then calculated from the Beer's law relationship: $Cr^{3+}{}_t = (A_t - A_0)/lE_{\text{eff}}$ where A_t is the optical density at any time t. The chromium(II) and the chlorate ion concentrations were calculated for 30 different values of the recorded transmittances for each run. The initial observed transmittance was corrected for a dilution of the small amount of absorbing chromium(III) in the cell upon injection of the transparent sodium chlorate solution. The A_0 corrected value was calculated from the relationship: $A_0(\text{cor}) = 0.9155[A_0 - A_{\text{cell}}] + A_{\text{cell}}$, where 0.9155 is the ratio of volumes prior to and after injection and A_{cell} is the cell correction for the reaction cell filled with distilled water. These corrections were very small since the initial transmittance was usually >90%, and the injected sodium chlorate diluted the solution by only about 10%. In a typical run, 0.064 and 0.060 absorbance units were the uncorrected and corrected respective initial absorbances. When the chromium(II)–chlorate reaction was followed by observing the disappearance of chromium(II) at 7190 A, the same method of calculating concentrations was used. In this case, however, a somewhat larger dilution correction for the initial absorbance resulted, owing to the larger initial value. The linear least-squares program calculated the rate constant k_1 appropriate to the integrated second-order rate expression: $\ln [\text{Cr(II)}_t/(\text{ClO}_3^-)_t] = [(\text{Cr(II)}_0/6) - (\text{ClO}_3^-)_0]k_1t + \ln [\text{Cr(II)}_0/(\text{ClO}_3^-)_0]$, where k_1 is the second-order rate constant (M^{-1} sec^{-1}), t is the time, and the subscript zero indicates the initial concentration. The best linear fit was determined analytically for the $\ln \{[\text{Cr(II)}]_t/[\text{ClO}_3^-]_t\}$ as a function of time by standard least-squares techniques.

(17) The authors wish to acknowledge the generous assistance of Dr. T. W. Newton and Dr. Roger Moore for making the Los Alamos program available. A detailed description of the program appears in the Los Alamos publication LA-2367.

(18) For example, with 2.17×10^{-2} M Cr(II) and 3.28×10^{-3} M ClO_3^- the k_1 values from the linear and nonlinear program were 38.7 ± 1.2 and 38.5 ± 1.0 at 5800 A and 39.3 ± 1.0 and 38.9 ± 0.6 at 4500 A, respectively.

(19) G. Gordon, *Inorg. Chem.*, **2**, 1277 (1963).

(20) J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954).

(21) R. Kolaczkowski and R. A. Plane, *Inorg. Chem.*, **3**, 332 (1964).

(22) B. Z. Shakhashiri and G. Gordon, *Talanta*, **13**, 142 (1966).

(23) The analysis of the carbon dioxide was performed by Mr. Dale Wilson.

TABLE II

SECOND-ORDER RATE CONSTANTS FOR THE CHROMIUM(II)–CHLORATE REACTION[a]

10^2[Cr(II)]$_0$, M	10^3[ClO$_3^-$]$_0$, M	λ, A	k_1,[b] M^{-1} sec^{-1}
2.17	3.28	5800	38.5 ± 1.0
2.17	3.28	5400	37.4 ± 0.2
2.17	3.28	4500	38.9 ± 0.6
2.17	3.28	4100	40.0 ± 0.2
2.17	4.97	4100	38.2 ± 0.6
2.17	1.65	4100	37.0 ± 0.3
2.17	2.48	4100	38.5 ± 1.3
3.23	3.30	4100	39.9 ± 0.5
4.33	3.30	4100	40.3 ± 0.7
4.33	1.65	4100	37.0 ± 0.4
2.39	2.39	4100	41.2 ± 0.8
2.39	3.57	4100	41.4 ± 0.5
2.39	2.67	4100	38.7 ± 1.1
2.39	2.67	7190[c]	39.6 ± 0.6

[a] At $I = 2.00$ M, $T = 20.0°$, and 0.55 M HClO$_4$. Each rate constant represents the average of a triplicate set of experiments. [b] The values of k_1 represent the average of triplicate experiments for up to 75% reaction. The deviations are the average deviations of the arithmetic mean of the triplicate set. [c] The IP28 photomultiplier tube was replaced by a Hamamatsu R136 photomultiplier tube.

k_1 was not very sensitive to the type of computer program used,[18] and the standard deviation for each experiment was always less than 2%. The entries in Table II are for up to 75% reaction, but in general the second-order plots were linear for 90% reaction with only slight changes in the rate constants and standard deviations.

The last entry in Table II summarizes a triplicate set monitored by following the disappearance of chromium(II). The excellent agreement between k_1 values for these runs and the average value of k_1 for all of the experiments in which the appearance of chromium(III) was followed indicates that the reactant chromium(II) disappears at the same rate that the product chromium(III) appears.

The Effect of Chloride Ion.—Experiments were carried out in triplicate with 2.4 × 10^{-3} M Cr(II), 2.7–3.6 × 10^{-3} M ClO$_3^-$, 1.1–1.3 M NaCl, 0.55 M HClO$_4$, an ionic strength of 2.00 M, and 20.0°, to discern the effect of chloride ion on the rate of the reaction. The rate constant, k_1, was 36.1 ± 1.2 which is in good agreement with the average k_1 values for the experiments listed in Table II. Thus, it is concluded that even high concentrations of chloride ion have at most a small effect on the rate-determining step in the chlorate–chromium(II) reaction. This result also suggests that the chloride ion produced during the reaction has a negligible effect on the observed kinetics.

The Effect of Hydrogen Ion.—The effect of the hydrogen ion concentration on the apparent second-order rate constant was also investigated. Sodium perchlorate was used to maintain constant ionic strength, and these results are summarized in Table III. Since the values of k_1 increase as the hydrogen ion concentration increases, the rate constant k_2 was calculated where

$$k_1 = k_2(\mathrm{H}^+) \qquad (6)$$

and the constants k_2' and k_3' were calculated where

$$k_1 = k_2'(\mathrm{H}^+) + k_3'(\mathrm{H}^+)^2 \qquad (7)$$

The results of these calculations are summarized in Table III; the value of the apparent rate constant, k_2, was 98.1 ± 6.3 M^{-2} sec^{-1}, the value of k_2' was 56.1 ± 2.9 M^{-2} sec^{-1}, and k_3' was 29.5 ± 2.0 M^{-3} sec^{-1}. Deviations from a single hydrogen ion term are not unusual with a tenfold or greater change in concentration at high ionic strengths. In order to determine whether a mechanistic interpretation for the deviations from first-order hydrogen ion dependence in this system was justified, possible medium effects were tested by substituting lithium perchlorate and zinc perchlorate for sodium perchlorate at two different hydrogen ion concentrations. Essentially the same rate constants were obtained in the presence of zinc perchlorate (20.5 M^{-1} sec^{-1} in 0.30_0 M HClO$_4$ and 89.1 M^{-1} sec^{-1} in 1.00 M HClO$_4$) and sodium perchlorate (see Table III). This result shows that the rate of the reaction is not sensitive to the perchlorate ion concentration.

TABLE III

THE EFFECT OF HYDROGEN ION ON THE CHROMIUM(II)–CHLORATE REACTION[a]

Hydrogen ion concn, M	Measd rate constant, M^{-1} sec^{-1}	k, calcd with eq 6	k, calcd with eq 7
0.10_0	8.24	9.81	5.9
0.30_0	21.0	29.4	19.5
0.55_0	39.0	54.0	39.8
1.00	84.9	89.1	85.6
1.70	181	167	181

[a] $I = 2.00$ (NaClO$_4$); $T = 20.0°$.

However, with lithium perchlorate a marked increase in the value of the rate constant at the same hydrogen ion concentration was observed (29.7 M^{-1} sec^{-1} in 0.300 M HClO$_4$ and 110 M^{-1} sec^{-1} in 1.00 M HClO$_4$). Since there is a significant change in the apparent rate constant when lithium perchlorate is substituted for either zinc or sodium perchlorate at high ionic strength, it is concluded that the data do not differentiate between a minor path with a hydrogen ion dependence different from first order and an activity effect where the pertinent activity coefficients are changing at a constant ionic strength.[24]

The Effect of Ionic Strength.—Possible medium effects were investigated by studying the effect of ionic strength on the rate of the reaction. Sodium, lithium, and zinc perchlorate were used to maintain constant ionic strength. The effect of ionic strength on the apparent second-order rate constant is summarized in Table IV. The experimental results are consistent with an extended form of the Debye–Hückel equation[25]

$$\log k_1 = \log k_0 + \Delta Z^2 \alpha I^{1/2}/(1 + \beta I^{1/2}) + \gamma I \qquad (8)$$

A nonlinear least-squares program[17] was used to calculate the best values of log k_0, β, and γ. The values of

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(24) T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

(25) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co. Ltd., London, 1949, p 237.

$\alpha = 0.5046$ appropriate to the temperature of 20.0° and -2 for ΔZ^2 appropriate to the equation

$$\mathrm{Cr(II)} + \mathrm{ClO_3^-} + \mathrm{H^+} = [\mathrm{CrClO_3H^{2+}}]^{\ddagger} \qquad (9)$$

were used. The results of these calculations are compared with the experimental rate constants in Table IV. The computed values for the parameters log k_0, β, and γ are tabulated in Table V. The second-order rate constant is not very sensitive to the ionic strength in the range 0.50–2.00 M at a constant hydrogen ion concentration of 0.30 M. The effect is largest in the case of lithium perchlorate and considerably less for sodium and zinc perchlorate.

TABLE IV

THE EFFECT OF IONIC STRENGTH ON THE CHROMIUM(II)–CHLORATE REACTION[a]

Salt	I	k_{exptl}, M^{-1} sec^{-1}	k_{calcd}, M^{-1} sec^{-1} [b]
$NaClO_4$	2.00	21.0	20.9
	1.60	18.2	18.3
	1.20	16.5	16.6
	0.80	16.0	15.8
	0.50	16.3	16.3
$LiClO_4$	2.00	29.7	30.0
	1.60	24.9	24.6
	1.20	20.8	20.6
	0.80	17.6	18.0
	0.50	17.2	17.0
$Zn(ClO_4)_2$	2.00	18.4	18.5
	1.69	17.6	17.2
	1.29	15.3	16.8
	0.89	15.5	15.1
	0.54	15.1	15.2

[a] 0.30_0 M $HClO_4$; $T = 20.0°$. [b] Calculated from eq 8 with simultaneous solution for log k_0, β, and γ, which are given in Table V.

TABLE V

COMPUTED PARAMETER VALUES FROM EQ 8[a]

Salt	Log k_0	β	γ
$NaClO_4$	1.61 ± 0.02	0.45 ± 0.13	$0.29_1 \pm 0.04_0$
$LiClO_4$	1.52 ± 0.05	0.89 ± 0.39	$0.29_3 \pm 0.05_3$
$Zn(ClO_4)_2$	1.52 ± 0.11	0.99 ± 0.08	$0.17_2 \pm 0.09_8$

[a] 0.30 M $HClO_4$; $T = 20.0°$.

Temperature Dependence.—Rate constants were determined at five different temperatures in the range 5.0 to 25.0°. These results are given in Table VI.

The Oxidation of Chromium(II) by Chlorine Dioxide, Chlorite, Hypochlorite, and Chlorine.—The kinetics of the oxidation of chromium(II) by the other chlorine oxidants was studied in a series of survey experiments. The integrated second-order rate expression

$$\ln \frac{[\mathrm{Cr(II)}]_t}{[\mathrm{oxidant}]_t} = \frac{[\mathrm{Cr(II)}_0 - a[\mathrm{oxidant}]_0}{a} k_{\mathrm{A}} t + \ln \frac{[\mathrm{Cr(II)}]_0}{[\mathrm{oxidant}]_0} \qquad (10)$$

was used for the calculation appropriate to the reaction

$$a\mathrm{H^+} + a\mathrm{Cr(II)} + \text{oxidant} = a\mathrm{Cr(III)} + \mathrm{Cl^-} + (a/2)\mathrm{H_2O} \qquad (11)$$

where k_A is the second-order rate constant, t is the time in seconds, and a is the stoichiometric coefficient for the reactant chromium(II) (*i.e.*, in the reaction with ClO_2^-, a is 4). These results are summarized in Table VII. Since the mixing time was competitive with the reaction time for the systems studied, the rate constants obtained can be considered only lower limits. The data were consistent with the second-order rate expression to the extent that a standard deviation of 10% or less was observed in all cases. No hydrogen ion dependence was detected for these systems in the range of 0.10 to 0.50 M perchloric acid.

TABLE VI

THE APPARENT SECOND-ORDER RATE CONSTANT FOR THE CHROMIUM(II)–CHLORATE REACTION AT VARIOUS TEMPERATURES[a]

Temp, °C	No. of runs	k, M^{-1}, sec^{-1}
5.0	6	13.6
10.0	5	19.1
15.0	6	27.4
20.0	42	39.0
25.0	6	54.9

[a] 0.55 M $HClO_4$; $I = 2.00$ M ($NaClO_4$).

Tracer Results.—A series of tracer experiments was carried out in which chromium(II) contained in normal water[26] was rapidly mixed with 6.30-fold enriched sodium chlorate contained in normal water. In the case of the chromium(II)–chlorate reaction, water from both the $Cr(OH_2)_6^{3+}$ and the $(H_2O)_5CrCl^{2+}$ was analyzed, and the resulting enrichments[27] were 1.28 ± 0.004 and $1.00_0 \pm 0.00_1$. No tracer results are available for the other chromium(II)–chlorine oxidant reactions.

Although the $[(H_2O)_5CrCl^{2+}]$ was found to be of normal isotopic composition, since excess chromium(II) was present, this does *not* preclude initial transfer of chlorate oxygen to the $(H_2O)_5CrCl^{2+}$. Taube and King[8] have measured the rate of the Cr(II)–$CrCl^{2+}$ electron-exchange reaction and observed a second-order rate constant of ≈8.3 M^{-1} sec^{-1}. Since excess chromium(II) is present in the reaction mixture for several minutes, it is not surprising that the observed enrichment was 1.00.

An attempt was also made to precipitate rapidly all of the chromium(III) products with Na_2HPO_4 subsequent to the removal of zinc. Only incomplete precipitation resulted. A blank experiment in which air-oxidized chromium(II) was precipitated with Na_2HPO_4 indicated, however, that the product of this reaction is quantitatively precipitated. The precipitate which was obtained from partial precipitation of a chromium(II)–chlorate reaction was analyzed and was found to be 1.08_8-fold enriched.

Discussion

The data in Tables II and III are consistent with a principal net activation process for the chlorate–chromium(II) reaction

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(26) Normal water is defined as 1.00-fold enriched.

(27) The experiment utilized 6.30-fold enriched 0.0266 M ClO_3^-, 0.199 M Cr(II), 0.371 M Zn(II), and 0.55 M $HClO_4$ contained in 1-fold enriched water at 5°. The concentration and enrichments are calculated from the solution immediately upon mixing, but prior to the start of the reaction.

TABLE VII

APPARENT SECOND-ORDER RATE CONSTANTS FOR THE REACTION BETWEEN CHROMIUM(II) AND VARIOUS CHLORINE OXIDANTS[a]

Reaction	Halate concn, M	[Cr(II)], M	k_A,[b] M^{-1} sec^{-1}	Method used to follow reaction
Cr(II) added to ClO_2	$1.8–2.4 \times 10^{-4}$	$1.0–1.4 \times 10^{-3}$	$(3.5 \pm 0.3)10^5$	Disappearance of ClO_2 at 3600 A, ϵ 1120[c]
ClO_2 added to Cr(II)	$0.9–1.2 \times 10^{-3}$	$6.0–7.0 \times 10^{-3}$	$(4.8 \pm 0.3)10^4$	Appearance of Cr(III) at 5800 A, ϵ 21.1
ClO_2^- added to Cr(II)	$4.1–5.2 \times 10^{-4}$	$4.6–5.2 \times 10^{-3}$	$(8.1 \pm 0.8)10^4$	Appearance of Cr(III) at 4100 A, ϵ 24.9
OCl^- added to Cr(II)	$1.0–1.5 \times 10^{-3}$	$6.0–7.0 \times 10^{-3}$	$(2.1 \pm 0.1)10^4$	Appearance of Cr(III) at 4100 A
Cr(II) added to Cl_2	$4.0–4.6 \times 10^{-3}$	$4.0–6.0 \times 10^{-3}$	$(9.7 \pm 0.3)10^3$	Disappearance of Cl_2 at 3500 A, $\epsilon \approx 50$

[a] 0.1–0.5 M $HClO_4$; $I = 0.1–0.5$ M; $T = 5.0°$. [b] The deviation corresponds to one standard deviation. [c] ϵ is the extinction coefficient (M^{-1} cm^{-1}) of the absorbing species.

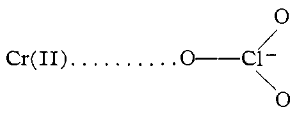
$$Cr(II) + ClO_3^- + H^+ = [CrClO_3H^{2+}]\ddagger \qquad (12)$$

The determination of the exact order of the reaction with respect to hydrogen ion is complicated by medium effects. At high hydrogen ion concentrations (1.70 M perchloric acid), it is possible that a term in the rate law with a hydrogen ion dependence higher than first order is significant, but the interpretation of the data cannot distinguish between this proposal and the alternative explanation of a first-order dependence obscured by a medium effect. The difficulty of evaluating the effect of hydrogen ion in reaction rate studies which are carried out at high ionic strengths is not unique to this system.[24,28] In the vanadium(II)–chlorate reaction,[3] a small positive hydrogen ion dependence was observed at $I = 0.70$ M with sodium perchlorate, but a small negative dependence was found under the same conditions if lithium perchlorate was substituted for sodium perchlorate.

The role of the proton in the activated complex is not clear. The corresponding iron(II)–chlorate reaction has a similar rate law,[2] but the vanadium(II)–chlorate reaction[3] does not appear to include a proton in the principal activation process. The rates of oxy anion reactions frequently exhibit orders of one or two in hydrogen ion concentrations.[29] Edwards[29] suggests that in the equilibrium

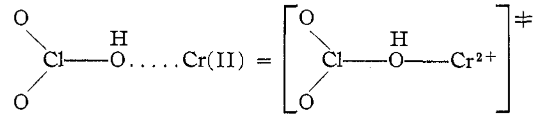
$$ClO_3^- + H^+ = HClO_3 \qquad (13)$$

the role of the proton is to weaken the strong bond between the negative oxygen atom and the positive central chlorine atom. A relevant question concerns the point of attack on the chlorate by the chromium(II) in the rate-determining step. The preliminary oxygen-18 tracer studies reported here indicate that some chlorate oxygen is transferred to the $[Cr(OH_2)_6^{3+}]$ product in the chlorate–chromium(II) reaction,[30] If one of the chlorate oxygens were transferred to the chromium(III) product concomitant with or immediately following the rate-determining step



(14)

then the role of the proton might be to labilize the oxygen atom for transfer



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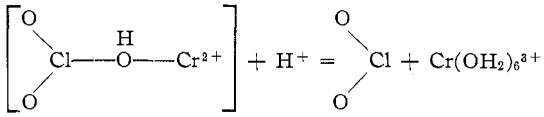
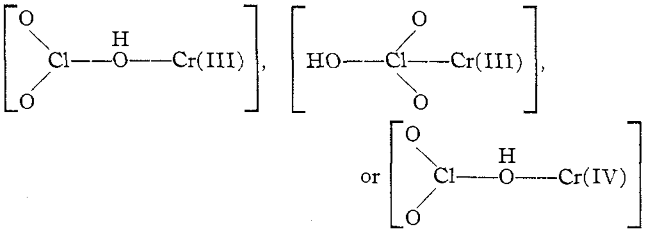
The next step could then correspond to the hydrolysis of an intermediate



(16)

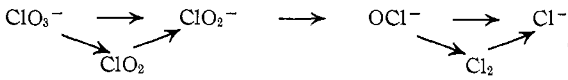
One hexaaquochromium(III) ion and a chlorine dioxide molecule would be the products. However, the stoichiometry data[10] are not consistent with the initial formation of *only* these two products.[31]

Three alternative mechanisms which would include the intermediates



are consistent with all of the data.

The last intermediate requires an initial two-electron attack resulting in the formation of chromium(IV), followed by a rapid attack by chromium(II) to yield *less* than 100% polynuclear species. The significant point about all of these mechanisms is that *none* predicts a step-by-step reduction of the chlorate ion



(17)

but rather invoke unstable chromium(III)–chlorine oxidant intermediates. This concept is substantiated by the other Cr(II) kinetic and stoichiometric results.

The product chloride ion does not appear to act as a nonbridging ligand or as a bridging ligand in the rate-determining step of the chromium(II)–chlorate reaction. This follows since chloride ion does not catalyze the rate, and the equilibrium concentration of $(H_2O)_5$-

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(28) B. Perlmutter-Hayman and G. Stein, *J. Chem. Phys.*, **40**, 848 (1964).

(29) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 137, 138.

(30) If all of the chlorate oxygen was transferred to the $[Cr(OH_2)_6^{3+}]$ product, a maximum of 1.89-fold enriched water would be found. The observed average value of 1.287 corresponds on the average to only 0.32 chlorate oxygen transferred to each $[Cr(H_2O)_6^{3+}]$.

(31) The above mechanism requires $ClO_3^- + Cr(II) = Cr(OH_2)_6^{3+} + ClO_2$ and $ClO_2 + 5Cr(II) = 5Cr(III) + Cl^-$, but the calculations based on the stoichiometry of the ClO_2 reaction (from Table I, ref 10) indicate that (2.2–2.7)$[Cr(OH_2)_6^{3+}]$ and (1.2–1.6)$[(H_2O)_5CrCl^{2+}]$ should be found if he equations were correct. The stoichiometric results for the chlorate reaction show that only 2.01$[Cr(OH_2)_6^{3+}]$ and 1.08$[(H_2O)_5CrCl^{2+}]$ are formed. The excess $[(H_2O)_5CrCl^{2+}]$ and $[Cr(OH_2)_6^{3+}]$ required by the above mechanism is definitely outside of the experimental error reported for the stoichiometric determinations.

$CrCl^+$ is quite small in all of these reactions.[32] This interpretation substantiates the tentative conclusion reached in the stoichiometric study of the system.[10] It was found that added chloride ion appears in the product to a remarkable extent. However, the kinetic data obtained do *not* preclude the possible role of chloride ion as a nonbridging ligand or a bridging ligand in the fast steps of the chromium(II)–chlorate reaction. Unfortunately, the effect of chloride ion on the rate of the other chromium(II) reactions could not be determined since the rates were near the limit of detection with our apparatus.[33]

The rate of the chlorate–chromium(II) reaction in solutions of sodium perchlorate, lithium perchlorate, and zinc perchlorate at ionic strengths in the range 0.50 to 2.00 M are consistent with an extended form of the Debye–Hückel[25] equation. Theoretically, the log k_0 values obtained should be independent of the salt added, but substantial differences occurred (see Table V). The deviations are not surprising since in all of the experiments 0.30 M perchloric acid was present, and necessarily the reaction was not studied at low ionic strength.

The activation enthalpies and entropies for the principal net activation process shown in eq 12 in sodium perchlorate at $I = 2.00$ M and 0.55 M $HClO_4$ were calculated from the temperature dependence data by means of a nonlinear least-squares computer program.[17] Eyring's[34] absolute reaction rate theory

$$k_1 = (k_b/h)T \exp(\Delta S^*/R) \exp(\Delta H^*/RT) \quad (18)$$

was used in the calculations. The values of $\Delta H^* = 11.2 \pm 0.1$ kcal/mole and $\Delta S^* = -17 \pm 0.4$ eu were obtained.[35]

These values of ΔH^* and ΔS^* are close to the values obtained for the corresponding vanadium(II)–chlorate reaction,[3] where $\Delta H^* = 9.9$ kcal/mole and $\Delta S^* = -23$ eu. The activated complexes are formally the same with the exception that a proton is present in the chromium(II) system. The extensive chlorate oxygen and chlorate chlorine transfer to the chromium(III) products suggests an inner-sphere activated complex.

The rate constants measured for the chlorine dioxide–, chlorite–, hypochlorite–, and chlorine–chromium(II) reactions can only be considered as lower limits. All of these reactions are at least 10^3 to 10^5 times faster than the corresponding chlorate–chromium(II) reaction. It is possible that the difference in rates arises from an inner-sphere chlorate–chromium(II) reaction and an outer-sphere reaction for the other chlorine oxidant–chromium(II) reactions. However, the efficient chlorine transfer to the $(H_2O)_5CrCl^{2+}$ product for all of the oxidizing agents suggests an inner-sphere mechanism for all of these reactions. Whatever the reason, the difference in rates is quite striking.

The data also indicate that in the chlorine dioxide–chromium(II) reaction, the chlorine dioxide disappears about 10 times faster than the chromium(III) products appear. This factor is surely outside experimental error. The observation is consistent with a chromium(II)–chlorine dioxide intermediate that is less absorbing at 3600 A than chlorine dioxide and also less absorbing at 4100 A than the chromium(III) products. The possibility of various chromium(III)–oxidizing agent complexes which are unstable with respect to further reduction by the excess chromium(II) present is indeed consistent with the stoichiometric data.

In the uranium(IV)–chlorite reaction, Gordon and Feldman[1] propose the mechanism

$$\text{U(IV)} + \text{Cl(III)} = \text{U(VI)} + \text{Cl(I)} \quad (19)$$

$$\text{Cl(I)} + \text{Cl(III)} = \text{Cl(V)} + \text{Cl}^- \quad (20)$$

The reaction between the product chlorate ion and uranium(IV) is very slow. Table VIII lists the rates of other reactions of the type

$$6H^+ + ClO_3^- + (9 - 1.5n)M^{n+} = (9 - 1.5n)M^{4-(n/2)} + Cl^- + 3H_2O \quad (21)$$

where M is the metal ion.

TABLE VIII

SECOND-ORDER RATE CONSTANTS FOR METAL ION–CHLORATE REACTIONS[a]

Metal ion	Rate constant, K^{-1}, M^{-1} sec^{-1}	Ref
U(IV)	Very slow	*b*
Fe(II)	2×10^{-2}	2
V(II)	18.2	3
Cr(II)	39.0	This work

[a] 0.5–0.6 M $HClO_4$; $I = 2.0$–3.0 M; $T = 20.0°$. [b] L. Federova and E. Kanevskii, *Kinetika i Kataliz*, **3,** 332 (1962).

The wide range of rates observed for reaction 21 suggests that, in some of the reactions, the metal ion–hypochlorite reaction might be competitive with the hypochlorite–chlorite reaction. Preliminary data for the iron(II)–chlorite reaction indicates that chlorate ion is indeed produced.[2] Even in the vanadium(II)–chlorite reaction, small amounts of chlorate ion are produced.[3] The present study of the chromium(II)–chlorite reaction shows no evidence of chlorate production even up to 95% reaction. This does not rule out other reactions of the type

$$2HClO_2 + HOCl = 2ClO_2 + Cl^- + H_2O + H^+ \quad (22)$$

$$Cl_2 + 2HClO_2 = 2ClO_2 + 2Cl^- + 2H^+ \quad (23)$$

In the uranium(IV)–chlorite reaction, these reactions were shown to be absent since the corresponding uranium(IV)–chlorine dioxide reaction is considerably slower

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(32) R. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, **11**, 1419 (1957).

(33) Since the extinction coefficient of the most absorbing chromium(III) species is ≈21 M^{-1} cm^{-1} at the most favorable wavelength in the visible region, a solution 2.4×10^{-3} N in each reactant would be necessary for an optical density change of 0.1 absorbance unit. Thus, at 5°, with a 2-cm path length, a mixing time as short as 4 msec would be required if the mixing were to be 0.1 of the first half-life of these reactions, or mixing times of 1 and 0.2 msec would be necessary if respective path lengths of 5 and 1 mm were used.

(34) S. Glasstone, K. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 199.

(35) The rate constants given in Table VI are in terms of the equation

$$6H^+ + 6Cr(II) + ClO_3^- = 6Cr(III) + Cl^- + 3H_2O.$$

and apply to the total rate of disappearance of chromium(II) and therefore are six times larger than the rate constants for the rate-determining reaction. Therefore, the activation parameters were calculated with the apparent second-order rate constants given in Table VI after correcting them by a factor of $^1/_6$.

and no chloride dioxide was detected even in 0.5 *M* $HClO_4$. The chromium(II)–chlorine dioxide reaction (see Table VII) is probably slightly faster than the chromium(II)–chlorite reaction. The data of Emmenegger and Gordon[36] indicate that the reaction between 10^{-3} *M* chlorine and 10^{-3} *M* chlorine(III) in 0.5 *M* perchloric acid to produce chlorine dioxide has a half-life greater than 6×10^{-2} sec. The corresponding second-order reaction between similar concentrations of chromium(II) and chlorine(III) is at least 10 times faster. The maximum chlorine concentration in the chromium(II)–chlorite reaction is surely several orders of magnitude less than the above estimate. Therefore, no significant production of chlorate ion or chlorine dioxide would be expected in the presence of such a potent reducing agent as chromium(II).

A similar calculation for the apparent half-lives in the hypochlorite–chromium(II) and the hypochlorite–chloride reaction[37] (to form chlorine) indicates that the former is at least 10 times faster than the latter in the absence of initial chloride ion. These considerations also rule out the possibility of chlorine(I)–chloride ion reaction in any of the other reactions studied. In the absence of chlorine–chlorine interactions, a comparison of the stoichiometry of the various chlorine oxidant–chromium(II) reactions is justified.

In light of this interpretation, a mechanism which consists of step-by-step reductions of chlorate ion with the other chlorine species as intermediates can probably be discarded on the basis of marked inconsistencies with the stoichiometric data. Conversely, a mechanism which involves chromium(II)–chlorine oxidant intermediates is consistent with the stoichiometric data if it is assumed that the stoichiometry of subsequent chromium(II) reductions with these intermediates yields different ratios of products than those resulting from the reaction of the uncomplexed oxidizing agent and chromium(II). Further, there does seem to be direct evidence of a complex of this type in the chlorine dioxide–chromium(II) reaction.

In conclusion, the observed rates for the ClO_2, ClO_2^-, OCl^-, and Cl_2 reactions with chromium(II) are several orders of magnitude greater than the corresponding chlorate reaction. However, all seem to occur *via* an inner-sphere mechanism since considerable chlorine and oxygen[38] from the oxidizing agent is transferred to the chromium(III) products. The mechanism of these reactions probably involves the formation of chromium(II)–oxidizing agent intermediates which are unstable with respect to further reduction by the excess chromium(II) present. The reactions do not seem to be complicated by other chlorine reactions or interactions.

Acknowledgments.—The authors wish to express their appreciation to the Atomic Energy Commission for its generous support of this research through Grant No. AT-(40-1)-2858 and to Mr. Bassam Z. Shakhashiri for his help and suggestions on the tracer experiments.

[36] G. Gordon and F. Emmenegger, to be published.

[37] M. Eigen and K. Kustin, *J. Am. Chem. Soc.*, **84**, 1355 (1962).

[38] At least in the chlorate–chromium(II) reaction.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING,
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Thermodynamics of Proton Dissociation in Dilute Aqueous Solution. IV. p*K*, Δ*H*°, and Δ*S*° Values for Proton Ionization from $[1,12\text{-}B_{12}H_{10}(COOH)_2]^{2-}$ [1a]

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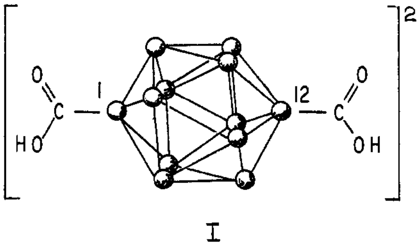
Consecutive p*K*, Δ*H*°, and Δ*S*° values valid at 25° and $\mu = 0$ are reported for proton ionization from the $[1,12\text{-}B_{12}H_{10}(COOH)_2]^{2-}$ ion in aqueous solution. The Δ*H*° values were determined calorimetrically. The thermodynamic data indicate that the ionic charges on the B_{12} cage are localized in the vicinity of the carboxyl groups and that the second proton ionization is largely unaffected by the increased negative charge resulting from ionization of the first proton.

Introduction

Values of Δ*H*° and Δ*S*° for proton ionization from several carboxylic acids of general type (RR′R″)C-COOH have been reported.[2] A major conclusion in both studies was that for the acids involved p*K* was a linear function of Δ*S*°; Δ*H*° being approximately constant at -0.4 ± 1.0 kcal/mole. A recently reported acid,[3] $[1,12\text{-}B_{12}H_{10}(COOH)_2]^{2-}$ (H_2A^{2-}, I), provides an example of a carboxylic acid in which boron



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[1] (a) Supported by National Institutes of Health Grant No. RG-9430-04. (b) National Defense Education Act Pre-doctoral Fellow, 1962–1965.

[2] (a) L. D. Hansen, Ph.D. Dissertation, Brigham Young University; (b) L. Eberson and I. Wadsö, *Acta Chem. Scand.*, **17**, 1552 (1963).

[3] W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Am Chem. Soc.*, **86**, 115 (1964).