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The Effect of Chloride Ions on the Kinetics of the Oxidation of Chromium(II) by Iron(III)¹

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The kinetics of the oxidation of chromium(II) by iron(III) in the presence of chloride ions have been investigated by the use of flow techniques. Since the formation of FeCl^{2+} from Fe^{3+} and Cl^- proceeds relatively slowly, it proved possible to estimate the rate constants for the various chloride-catalyzed paths by adding chloride to only the chromium(II) solution on the one hand, and to both the chromium(II) and iron(III) solutions on the other. The results are consistent with the rate law: $R = k_1(\text{Cr}^{2+})(\text{Fe}^{3+}) + k_2(\text{Cr}^{2+})(\text{FeOH}^{2+}) + k_3(\text{Cr}^{2+})(\text{FeCl}^{2+}) + k_4(\text{Cr}^{2+})(\text{Fe}^{3+})(\text{Cl}^-)$ where R is the rate of the oxidation-reduction reaction and $k_1 = 2.3 \times 10^3 \text{ } F^{-1} \text{ sec.}^{-1}$, $k_2 = 3.3 \times 10^6 \text{ } F^{-1} \text{ sec.}^{-1}$, $k_3 = 2 \times 10^7 \text{ } F^{-1} \text{ sec.}^{-1}$, and $k_4 = 2 \times 10^4 \text{ } F^{-2} \text{ sec.}^{-1}$ at 25.0° and ionic strength 1.00 F . It was found that CrCl^{2+} is produced in both chloride-catalyzed paths. The natures of these two paths are discussed.

The chloride-catalyzed oxidation of chromium(II) by iron(III) has been studied by Taube and Myers² and by Ardon, Levitan, and Taube.³ Taube and Myers found that both $(\text{H}_2\text{O})_5\text{CrCl}^{2+}$ and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ were produced in the oxidation and that their relative amounts depended upon the chloride and hydrogen ion concentrations of the solutions. They proposed that the $(\text{H}_2\text{O})_5\text{CrCl}^{2+}$ arose from the reaction of $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ and that this reaction proceeds *via* an inner-sphere activated complex containing a Fe-Cl-Cr bond. This interpretation has been questioned by Zwickel and Taube.⁴ By studying the chloride-catalyzed oxidation of $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ by $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ at -50° , where the formation of $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ from $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and Cl^- proceeds relatively slowly, Ardon, Levitan, and Taube have shown recently that $(\text{H}_2\text{O})_5\text{CrCl}^{2+}$ is produced even when $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ is not present prior to the reaction. However, they did not study the oxidation of $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ by $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ or identify the products of this reaction. We have studied the kinetics of the oxidation of chromium(II) by iron(III) in the presence of chloride ions at 25.0° and find that the chloride-catalyzed reaction proceeds *via* two paths at this temperature; one of these paths involves $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ as a reactant and the other does not. The former reaction is very rapid and both paths produce $(\text{H}_2\text{O})_5\text{CrCl}^{2+}$.

Experimental

Chemicals.—Thallos perchlorate and sodium perchlorate were prepared as described elsewhere.⁵ Iron(III) perchlorate (G. Frederick Smith Chemical Co.) and chromium(III) perchlorate (Amend Drug and Chemical Co.) were purified by recrystallization from perchloric acid. Solutions of chromium(II) in perchloric acid were prepared by electroreduction of the chromium(III) at a lead cathode.⁶ Perchloric acid (70%, Baker Analyzed Reagent) and hydrochloric acid (38%, Baker and Adamson) were used without further purification. The reactant solutions were prepared with triple distilled water in an argon atmosphere (General Dynamics, N. Y.). The argon was purified by passing it through an activated copper column at 120° (BTS catalyst, Badische Anilin-und Soda-Fabrik AG, Ludwigshafen am Rhein, Germany). The chromium(II) solutions were standardized by adding aliquots to excess thallium(III) in 2 F hydrochloric acid and determining the thallium(I) produced by a coulometric method.⁷

Procedure.—The kinetics were studied by the use of the flow apparatus which has been described previously.⁸ The disappearance of iron(III) was followed spectrophotometrically; wave lengths of 336 $m\mu$ and of 260 to 300 $m\mu$ were used to observe the FeCl^{2+} and Fe^{3+} , respectively.

The products of the reaction were separated chromatographically.⁹ Aliquots of the reaction mixture were withdrawn from the stopping syringe and added to a Dowex 50W-X8 cation-exchange column. The $(\text{H}_2\text{O})_5\text{CrCl}^{2+}$ and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ were eluted with 1 F and 3 F perchloric acid, respectively, and the chromium(III) in the fractions was determined as described elsewhere.⁸

Results

Order of the Reaction.—The chromium(II)-iron(III) reaction was found to be first order with respect to each of the reactants. Plots of $\log [b(a-x)/a(b-x)]$ vs. t , where a and b are the initial concentrations of the reactants and x is the concentration of product at time t , gave straight lines. The values of the second-order rate constants in 1.00 F HClO_4 at 25.0° , calculated from the slopes of these lines, are presented in Table I. Individual determinations of the rate constants differed from the mean by less than 5%. The average of the values presented in Table I is $(7.7 \pm 0.1) \times 10^3 \text{ } F^{-1} \text{ sec.}^{-1}$.

TABLE I
THE ORDER OF THE CHROMIUM(II)-IRON(III) REACTION IN
1.00 F PERCHLORIC ACID AT 25.0°

$[\text{Cr(II)}] \times 10^4,$ F	$[\text{Fe(III)}] \times 10^3,$ F	$k \times 10^{-4},$ $F^{-1} \text{ sec.}^{-1}$
1.78	6.51	7.8
1.94	6.51	7.8
3.73	6.51	7.7
3.93	6.51	7.9
9.27	6.51	7.3
9.27	13.0	7.6
9.27	26.0	8.2
9.27	52.0	7.9
9.40	6.51	7.7
9.43	26.0	7.6
9.75	3.25	7.6
18.9	6.51	7.4
19.0	6.51	7.7
19.0	6.51	7.5
19.1	3.25	7.6
28.4	3.25	7.4
37.3	3.25	7.7
38.8	7.51	7.5
38.9	6.51	7.5

The Effect of Acid.—The effect of acid on the reaction was studied in mixtures of sodium perchlorate and perchloric acid at a total ionic strength of 1.00 F . The results are consistent with the rate law

$$R = k_1(\text{Cr}^{2+})(\text{Fe}^{3+}) + k_2(\text{Cr}^{2+})(\text{FeOH}^{2+}) \quad (1)$$

Since K_h , the equilibrium constant for the hydrolysis

(9) J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

(3) M. Ardon, J. Levitan, and H. Taube, *ibid.*, **84**, 872 (1962).

(4) A. M. Zwickel and H. Taube, *ibid.*, **83**, 793 (1961).

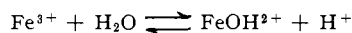
(5) G. Dulz, Ph.D. Thesis, Columbia University, New York, N. Y., 1962.

(6) R. Flatt and F. Sommer, *Helv. Chim. Acta*, **25**, 684 (1942).

(7) R. P. Buck, P. S. Farrington, and E. H. Swift, *Anal. Chem.*, **24**, 1195 (1962).

(8) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

reaction



is $\ll (\text{H}^+)$, we obtain

$$k = k_1 + k_2 K_h / (\text{H}^+) \quad (2)$$

where $k = R / (\text{Cr}^{2+}) [\text{Fe}(\text{III})]$. The value of K_h is 1.69×10^{-3} at 25.0° and ionic strength 1.00 F .¹⁰ We have plotted k as a function of $1/(\text{H}^+)$ in Fig. 1.

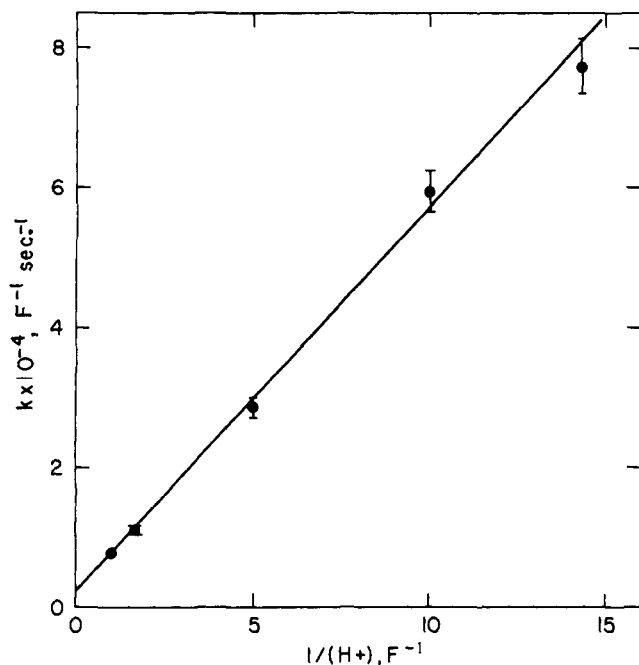
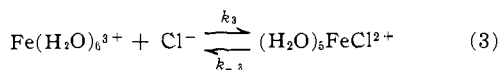


Fig. 1.—Effect of acid on the rate of the chromium(II)–iron(III) reaction at 25.0° .

From the slope and intercept of Fig. 1 we calculate that $k_1 = (2.3 \pm 0.2) \times 10^3 F^{-1} \text{ sec}^{-1}$ and $k_2 = (3.3 \pm 0.3) \times 10^6 F^{-1} \text{ sec}^{-1}$ at 25.0° and ionic strength 1.00 F .

The Effect of Chloride.—In order to determine the effect of chloride on the kinetics of the chromium(II)–iron(III) reaction, it is necessary first to consider the rate of formation and dissociation of $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$. Connick and Coppel¹¹ have studied these reactions and have calculated values of k_3 and k_{-3} defined by the equation



using a value of K_3 determined by Rabinowitch and Stockmayer.¹² We have reanalyzed their data using the value of K_3 determined recently by Woods, Gallagher, and King¹³ and obtain $k_3 = 19.4 F^{-1} \text{ sec}^{-1}$ and $k_{-3} = 6.7 \text{ sec}^{-1}$ at 25.0° and an ionic strength of 1.00 F .¹⁴ It should be noted that k_3 and k_{-3} are overall rate constants and include the contributions of the acid-dependent paths.

In the presence of chromium(II) the rate of disappearance of $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ is given by the expression

(10) R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955).

(11) R. E. Connick and C. P. Coppel, *ibid.*, **81**, 6389 (1959).

(12) E. Rabinowitch and W. H. Stockmayer, *ibid.*, **64**, 335 (1942).

(13) Sr. M. J. M. Woods, P. K. Gallagher, and E. L. King, *Inorg. Chem.*, **1**, 55 (1962).

(14) The values of k_3 which we determined in the course of these studies are in excellent agreement with those obtained by Connick and Coppel.

$$-\frac{d(\text{FeCl}^{2+})}{dt} = -k_3(\text{Fe}^{3+})(\text{Cl}^-) + k_{-3}(\text{FeCl}^{2+}) + k_4(\text{FeCl}^{2+})(\text{Cr}^{2+}) \quad (4)$$

where k_4 is the rate constant for the reaction of $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ with Cr^{2+} . Preliminary experiments in which chloride was added to both the chromium(II) and iron(III) solutions on the one hand [$(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ present at its equilibrium concentration prior to the oxidation–reduction reaction], and to only the chromium(II) solution on the other [no $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ present initially], established that the reaction of Cr^{2+} with $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ proceeded much more rapidly than any other oxidation–reduction reaction in the system and that it also proceeded much more rapidly than the formation and dissociation of $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$. Under these conditions eq. 4 reduces to

$$-\frac{d(\text{FeCl}^{2+})}{dt} = k_4(\text{FeCl}^{2+})(\text{Cr}^{2+}) \quad (5)$$

Consequently, the reaction of Cr^{2+} with $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ could be followed directly at $336 \text{ m}\mu$, where $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ is the only absorbing species. The concentrations used in these studies were: $[\text{Fe}(\text{III})] = 2.79 \times 10^{-5} F$, $[\text{Cr}(\text{II})] = 5.20 \times 10^{-5} F$ and $3.52 \times 10^{-5} F$, $(\text{HCl}) = 0.10 F$, and $(\text{HClO}_4) = 0.90 F$. The value of k_4 was found to be $2 \times 10^7 F^{-1} \text{ sec}^{-1}$ at 25.0° and ionic strength 1.00 F . It is readily seen that under the above conditions $k_4(\text{FeCl}^{2+})(\text{Cr}^{2+}) \gg k_{-3}(\text{FeCl}^{2+})$ and $k_4(\text{FeCl}^{2+})(\text{Cr}^{2+}) \approx 10k_3(\text{Fe}^{3+})(\text{Cl}^-)$ even after 90% of the FeCl^{2+} has reacted, as is required for eq. 5 to be valid.

If the chloride is added to only the chromium(II) solution and if there is a chloride-catalyzed path which does not involve $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ as a reactant, the rate of disappearance of Fe(III) is given by the expression

$$-\frac{d[\text{Fe}(\text{III})]}{dt} = k_1(\text{Cr}^{2+})(\text{Fe}^{3+}) + k_2(\text{Cr}^{2+})(\text{FeOH}^{2+}) + k_3(\text{Fe}^{3+})(\text{Cl}^-) + k_5(\text{Fe}^{3+})(\text{Cl}^-)(\text{Cr}^{2+}) \quad (6)$$

where the steady-state approximation for the concentration of $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ has been made. Provided $[\text{Cr}(\text{II})] \gg [\text{Fe}(\text{III})]$ and $(\text{Cl}^-) \gg [\text{Fe}(\text{III})]$, a pseudo-first-order rate constant for the reaction can be defined as

$$k = [k_1 + k_2 K_h / (\text{H}^+) + k_5(\text{Cl}^-)](\text{Cr}^{2+}) + k_3(\text{Cl}^-) \quad (7)$$

The disappearance of iron(III) was followed using wave lengths in the range 260 to 300 $\text{m}\mu$ and values of k were calculated from these measurements. These values are plotted in Fig. 2 as a function of the chromium(II) concentration at chloride concentrations of 0.05 and 0.10 F . It is seen that the data satisfy eq. 7 reasonably well. From the slopes of these lines we calculate that $k_5 = (2.2 \pm 0.4) \times 10^4 F^{-2} \text{ sec}^{-1}$ at 25.0° and ionic strength 1.00 F . These measurements thus provide evidence for a chloride-catalyzed oxidation–reduction path which does not involve $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ as a reactant. Evidence for such a path at -50° has been obtained previously by Ardon, Levitan, and Taube.³

In order to determine the chemical form of the chromium(III) produced in the following reaction mixtures were investigated: (a) $[\text{Cr}(\text{II})] = 2.0 \times 10^{-4} F$, $[\text{Fe}(\text{III})] = 1.04 \times 10^{-2} F$, $(\text{HCl}) = 0.075 F$, $(\text{HClO}_4) = 0.925 F$; chloride initially in both the chromium(II) and iron(III) solutions. (b) $[\text{Cr}(\text{II})] = 4.7 \times 10^{-3} F$, $[\text{Fe}(\text{III})] = 1.04 \times 10^{-2} F$, $(\text{HCl}) = 0.075 F$, $(\text{HClO}_4) = 0.925 F$; chloride initially in only

the chromium(II) solution. It was found that the chromium(III) species produced in reaction a consisted of 99% CrCl^{2+} and 1% Cr^{3+} while those produced in reaction b consisted of 31% CrCl^{2+} and 69% Cr^{3+} .

Since $(\text{FeCl}^{2+}) \gg (\text{Cr}^{2+})$ in reaction a, and if it is assumed that the reaction of FeCl^{2+} with Cr^{2+} produces only CrCl^{2+} , it follows that

$$\frac{(\text{Cr}^{3+})}{(\text{CrCl}^{2+})} = \frac{[k_1 + k_2 K_h / (\text{H}^+)]}{k_4 K_3 (\text{Cl}^-)} \quad (8)$$

Substitution in eq. 8 of the rate constants determined above gives $(\text{CrCl}^{2+})/[\text{Cr(III)}] = 0.998$, which is in excellent agreement with the observed value of 0.99.

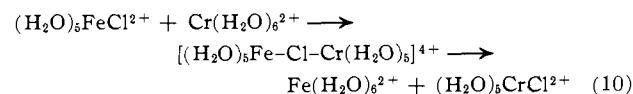
If it is assumed that the reaction path involving Cr^{2+} , Fe^{3+} , and Cl^- (but not FeCl^{2+}) also produces only CrCl^{2+} , and if a steady-state assumption for the concentration of FeCl^{2+} is made, the yield of Cr^{3+} in reaction b is given by

$$\frac{(\text{Cr}^{3+})}{[\text{Cr(III)}]} = \frac{k_1 + k_2 K_h / (\text{H}^+)}{k_1 + k_2 K_h / (\text{H}^+) + k_3 (\text{Cl}^-)} - \frac{[k_1 + k_2 K_h / (\text{H}^+)] k_3 (\text{Cl}^-)}{[k_1 + k_2 K_h / (\text{H}^+) + k_3 (\text{Cl}^-)]^2 (\text{Cr}^{2+})_0} \ln \frac{[k_3 (\text{Cl}^-) + \{k_1 + k_2 K_h / (\text{H}^+) + k_3 (\text{Cl}^-)\} (\text{Cr}^{2+})_0]}{k_3 (\text{Cl}^-)} \quad (9)$$

where $(\text{Cr}^{2+})_0$ is the initial concentration of chromium(II). Equation 9 predicts that the yield of Cr^{3+} should be $73 \pm 3\%$, which is in satisfactory agreement with the observed value of 69%. If it is assumed that the reaction path involving Cr^{2+} , Fe^{3+} , and Cl^- does not produce CrCl^{2+} , then the yield of CrCl^{2+} should be 12%, which is much lower than the observed value. The value of $(\text{Cr}^{3+})/[\text{Cr(III)}]$ was also calculated by numerical integration on an IBM 7094 computer without making the steady-state assumption for the FeCl^{2+} concentration. The ratio calculated by this procedure agreed within 0.1% with that given by eq. 9.

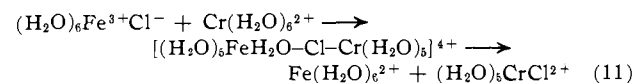
Discussion

It is evident that the chloride-catalyzed reaction proceeds *via* two paths and that $(\text{H}_2\text{O})_5\text{CrCl}^{2+}$ is produced in each of these paths. There does not appear to be much ambiguity concerning the reaction involving $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$; this path very probably proceeds *via* an inner-sphere activated complex as originally proposed by Taube and Myers

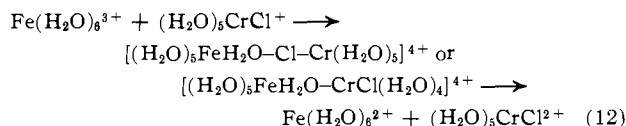


It is of interest that the ratio of CrCl^{2+} to Cr^{3+} produced in this inner-sphere path is much higher than that calculated by Taube and Myers. The reason for this discrepancy lies in the fact that reaction 10 proceeds much faster than the formation of $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ from $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and Cl^- under the conditions used by Taube and Myers.¹⁵

The nature of the second chloride-catalyzed path is less certain. Two formulations which are consistent with the rate law are



(15) H. Taube, personal communication. It should be noted that the value of k_3 did not become available until 1959.



It is not possible to distinguish between these two formulations on the basis of the evidence available at present. In order to account for the formation of $(\text{H}_2\text{O})_5\text{CrCl}^{2+}$, reaction 11 would have to proceed *via* an (outer-sphere) activated complex in which the chloride was bonded directly to the chromium. Since $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ does not undergo substitution readily, it is likely that reaction 12 also proceeds *via* an outer-sphere complex, although the possibility of a water-bridged inner-sphere activated complex, with chloride acting as a nonbridging ligand, cannot be ruled out.

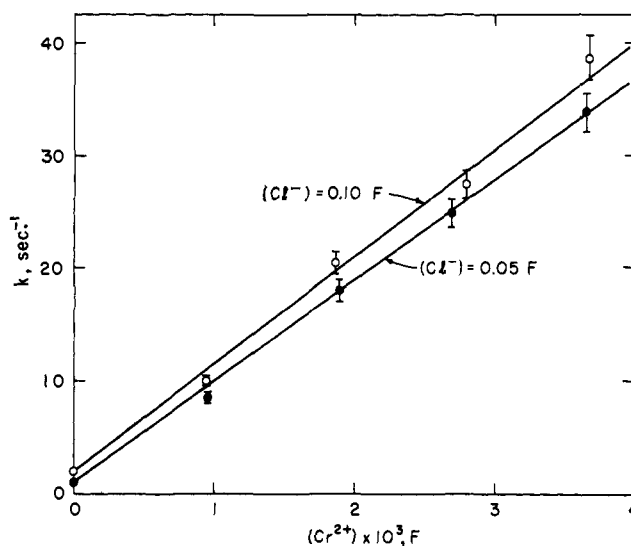


Fig. 2.—Effect of chloride on the rate of the chromium(II)–iron(III) reaction at 25.0°; $[\text{Fe(III)}] = 3.25 \times 10^{-5} F$.

For purposes of comparing the rates of the two chloride-catalyzed oxidations, k_4 may be converted to a third-order rate constant by multiplying it by K_3 . We then obtain

$$R_3 = 6 \times 10^7 (\text{Fe}^{3+}) (\text{Cl}^-) (\text{Cr}^{2+}) F \text{ sec.}^{-1}$$

for the rate of the chloride-catalyzed oxidation involving $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ as a reactant (provided the equilibrium

TABLE II
COMPARISON OF THE RELATIVE RATE CONSTANTS FOR THE CHROMIUM(II)–CHROMIUM(III), CHROMIUM(II)–IRON(III), AND IRON(II)–IRON(III) REACTIONS AT 25.0°

X	Relative rate constants		
	Cr^{2+} – $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_6\text{X}$	Cr^{2+} – $\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6\text{X}$	Fe^{2+} – $\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6\text{X}$
H_2O	1	1	1
OH^-	$> 8 \times 10^4$ ^a	1.4×10^3	1.1×10^{3c}
Cl^-	$> 2 \times 10^{6b}$	1×10^4	6.2^d

^a A. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954). ^b D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958). ^c J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952). ^d N. Sutin, J. K. Rowley, and R. W. Dodson, *ibid.*, **65**, 1248 (1961).

between $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and Cl^- is maintained). The rate of the chloride-catalyzed oxidation which does not involve $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ is given by

$$R_3 = 2 \times 10^6 (\text{Fe}^{3+}) (\text{Cl}^-) (\text{Cr}^{2+}) F \text{ sec.}^{-1}$$

The path involving $(\text{H}_2\text{O})_5\text{FeCl}^{2+}$ as a reactant thus proceeds about 3000 times faster than the chloride-catalyzed path which does not. These results provide additional support for Taube's conclusion that substitution in the inner coordination shell of the iron(III) is a requirement for marked chloride catalysis.¹⁶

The relative rate constants for the Cr(II)-Fe(III), Cr(II)-Cr(III), and Fe(II)-Fe(III) reactions are com-

pared in Table II. It will be seen that chloride has a larger effect than hydroxide on the rates of the Cr^{2+} -Cr(III) and Cr^{2+} -Fe(III) reactions but not on the rate of the Fe²⁺-Fe(III) reaction. It is of interest that the relative rate constants for the Cr^{2+} -Fe(III) reactions lie between those for the two electron exchange reactions.

Acknowledgment.—It is a pleasure to acknowledge helpful discussions of this problem with Drs. R. W. Dodson and H. Taube.

(16) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 34. (1959).