

$H^+ + OH + H_2O \rightarrow$ also becomes important. It is possible that the mobility of HO is greatly increased at high acid, because of the opportunity a complex of formula H_2O^+ affords for the radical to move by electron transfer in the water lattice.

The most interesting observation made in the experiments in alkaline solution is that X in these solutions can exceed unity. This means that not only the oxygen formed by the ozone decomposed, but also additional oxygen is brought into isotopic equilibrium with the solution. The means by which the exchange occurs is not known. The qualitative kinetic observations: that the extent of exchange diminishes both at high alkali and low alkali, that it increases as the pressure of oxygen increases, and that the turnover of oxygen per molecule of ozone increases as the ozone concentration decreases are compatible with a mechanism in which an intermediate formed on the decomposition of O_3 catalyzes the exchange of OH^- and O_2 . A possibility is that the hydroxyl radical ion is the intermediate in question. In alkaline solution, HO, which can be expected to lose a proton in approximately the same range of acidity as H_2O_2 , will be present at least in part as O^- . The exchange of hydroxyl with water (and therefore of O^-) already has been demonstrated. The exchange of O^- and oxygen may occur *via* the reaction $O^- + O_2 = O_3^-$. The ion O_3^- is known to be formed on the reaction of O_3 and solid KOH, and has been characterized in the solid state.⁸ A distinct mechanism for the exchange, in which O_3 engages in a reversible reaction with OH^- , analogous for example to the reaction of SO_2 and OH^- , also fits the observations made thus far, except possibly the dependence of exchange on (O_2). A simple means of distinguishing the two modes of action would be that followed in acid solu-

(8) I. A. Karzarnovskii, B. P. Nikolski and T. A. Abletsova, *Doklady Akad. Nauk. S.S.S.R.*, **64**, 69 (1949).

tion, to study inhibition of the exchange. Experiments of this type performed thus far lead to no definite conclusion. The failure of Cl^- to inhibit the exchange does not rule out the O^- mechanism.⁹ The couple $OH^- = HO + e^-$, $E^0 = -1.9$, is not sufficiently powerful to oxidize Cl^- to Cl . If HO is further stabilized by the change $HO + OH^- = H_2O + O^-$, the oxidation becomes even less favorable. If a value of 10^{-10} is assumed as the dissociation constant of HO, E^0 for the principal couple in alkaline solution: $2OH^- + H_2O + e^-$ is -1.6 volt. Neither equilibrium nor mechanism favor a rapid reaction of O^- and Cl^- . The single experiment with H_2O_2 and O_3 merely confirms an observation which can be made more directly, that H_2O_2 and O_3 react rapidly in alkaline solution. An O^- mechanism has been proposed for the γ -ray induced chain exchange of O_2 and water in alkaline solution.¹⁰ It is likely that the intermediate causing the catalysis in this system and that studied by us is the same. But also for the radiation induced reaction, no observations are published that definitely rule out catalysis by O_3 which may be produced at low concentration, as the cause of the exchange.

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(9) The report (Paper 126, Division of Physical and Inorganic Chemistry, 123rd meeting, ACS, Los Angeles, March, 1953) that Cl^- does inhibit was wrong.

(10) E. J. Hart, S. Gordon and D. A. Hutchison, *THIS JOURNAL*, **74**, 5548 (1952).

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Evidence for a Bridged Activated Complex for Electron Transfer Reactions

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The reaction of Cr^{++} with a variety of ions of the type $Co(NH_3)_5X^{++}$ as oxidizing agent takes place with quantitative transfer of X to the reducing agents. For the system with $X^- = Cl^-$, it has been shown that the transfer takes place without there being any exchange with chloride ion in solution. These observations lead to the conclusion that the activated complexes for the electron transfer reactions in question have configurations in which X makes a bond simultaneously to Cr and to Co. Any group which has unpaired electrons available for interaction with Cr^{++} is found to provide a more accessible pass for electron transfer than does the proton coordination shell of $Co(NH_3)_5^{+++}$. A bridged activated complex also explains observations made on reactions of Cr(III) complexes catalyzed by Cr^{++} . Results obtained with other oxidizing agents which are substitution-inert show that although formation of a bridged activated complex does take place, *net* transfer of the bridging group from oxidizing agent to reducing agent is not an essential feature of the electron transfer process. Strong evidence is presented in support of the view that a bridged activated complex is involved also in the action of substitution-labile oxidizing agents containing Fe(III) on Cr^{++} (or in the "catalysis" of the reaction of Cr^{++} and Fe^{+++} by anions), and in the exchange of electrons between Fe^{++} and Fe(III) species.

The formulas of most aquo ions in water are not known, and therefore the problem of the mechanism of oxidation-reduction reactions involving them goes particularly deep. Furthermore, nothing is known about the changes in the coordination spheres which may accompany electron transfer, although such information is essential to the

description of the electron transfer process. Information of this kind is difficult to obtain for all but a few aquo ions, the few comprising those which yield substitution-inert products on undergoing electron transfer. The reducing agent Cr^{++} qualifies for an investigation of the kind implied. The results of a study of the products formed when it is

oxidized by various agents forms the subject of the present report.¹ Although Cr(II) is labile to substitution, most of the product complexes containing Cr(III) in acid solution preserve their identity for periods of time long compared to the rate of oxidation of Cr⁺⁺. Thus it can often be shown that a group in question found combined with Cr(III) did not combine with it after the act of oxidation of Cr(II). In such cases the conclusion follows that the group was attached in the activated complex, and some features of the structure and composition of the activated complex are therefore given a definite description. The entry of all the groups F⁻, Cl⁻, Br⁻, I⁻, SO₄⁻ into the coordination sphere of Cr(H₂O)₆⁺⁺⁺ is so slow under the conditions of our experiments that this route is negligible in accounting for the complex ion products observed. In fact, at the concentration of halide present in most of the experiments, the ions² CrCl⁺⁺, CrBr⁺⁺ and CrI⁺⁺ are unstable with respect to Cr(H₂O)₆⁺⁺⁺ and X⁻, and if the systems are left to reach equilibrium, the concentrations of CrX⁺⁺ remaining are negligible in comparison to those generated by oxidation of Cr⁺⁺.

The conclusions drawn from the results obtained on the oxidation of Cr⁺⁺ have this general significance. As a minimum they serve to show what kind of process can take place when an aquo cation is oxidized. By comparing kinetic properties of paths for the oxidation of Cr⁺⁺ with those for reactions in which only substitution-labile ions are involved, the extension of the model processes to them can be justified.

Experimental Method

The apparatus for storing and dispensing the solution of Cr⁺⁺ was similar to that described by Lingane and Pecsok.³ The reaction flask, 500 ml. in capacity, was fitted with four ground glass entries, one to accommodate the delivery tube of the pipet, one for the mercury seal stirrer, one providing entrance and exit for gas, one for introducing reagents, and a stopcock at the bottom to serve as a drain.

The solution containing Cr⁺⁺ was prepared by reducing chromium(III) perchlorate in 1 M HClO₄ with amalgamated Zn, and was protected from the atmosphere by passing a stream of CO₂ through the storage vessel. Solutions properly prepared developed only a trace of chloride ion even after a week at room temperature. The conditions contributing to favorable behavior were not studied thoroughly, but these are believed to be important: the zinc must be pure; it should be amalgamated lightly and should be used immediately; anions other than ClO₄⁻ should be avoided. The solutions of chromium(III) perchlorate were prepared by reducing K₂Cr₂O₇ with H₂O₂, and removing the KClO₄ formed. These solutions were used at 0.10 and 0.25 M, with equal success in generating and preserving Cr⁺⁺.

Most of the cobaltamine compounds were prepared by Mr. Franz A. Posey. Any modifications of standard procedures found helpful in their preparation will be described in a future publication bearing his name. (NH₄)₂IrCl₆ was prepared from commercial iridium chloride, by oxidation with Cl₂ in the presence of NH₄Cl in solution. Ferric perchlorate was prepared from FeCl₃, heating the salt with perchloric acid, and crystallizing it from this medium.

The procedure followed in the experiments was this. The solution for reaction was made up, omitting Cr⁺⁺, in-

troducted into the reaction flask, and then left for periods of one-half to one hour. During this time the solution was stirred and a stream of carbon dioxide was passed through the reaction vessel. For experiments at the controlled temperature of 2.1 ± 0.2°, the vessel was surrounded by an ice-bath. The reaction was initiated by adding the solution containing Cr⁺⁺. Any Cr⁺⁺ left at the end of the reaction was oxidized using H₂O₂ or K₂Cr₂O₇. Finally, the product solution was removed and analyzed.

Free chloride is readily separated from chloride in CrCl⁺⁺ by using Ag⁺. No measurable loss of bound chloride takes place, even at room temperature, when the operation is carried out in acid solution. Chloride bound in CrCl₂⁺ is more labile, and some loss from this complex ion takes place when excess Ag⁺ is added. The presence of CrCl₂⁺ is demonstrated by the fairly rapid postclouthing which takes place after Ag⁺ is added and AgCl removed by filtration. Both CrCl⁺⁺ and CrCl₂⁺ yield Cl⁻ rapidly to Ag⁺ at 95–100°. Loss to Ag⁺ of Br⁻ and of I⁻ from chromic complexes is too rapid for a quantitative separation of free and bound halide by using this reagent. In the single experiment involving the distinction between free SO₄⁻ and SO₄⁻ associated with Cr⁺⁺, the free SO₄⁻ was removed as BaSO₄.

The extinction of Cr⁺⁺⁺ differs sufficiently from that of Cr^{III}, Cr^{II}, Cr^I species so that fairly accurate spectrophotometric analyses can be made. This method was the only one used for determining CrI⁺⁺ and CrBr⁺⁺ in the presence of Cr⁺⁺⁺. The color of any Fe(III) species present was suppressed by adding concentrated phosphoric acid to the solutions for analysis. The wave length region from 750 to 600 mμ was found to be most useful in analyses, since contributions to the optical density by other colored species are relatively least here. The absorption coefficients of chromium(III) species in this wave length region are rather insensitive to fairly drastic changes in the environment, as for example changing from 2 M HClO₄ to 2 M HCl, which occasions at most a 2% change in the values.

The notation adopted in this paper is as follows: M^{zn} specifies an aquo ion of indicated charge; the symbol followed by a Roman numeral is used when only the oxidation state is specified; the symbol with a Roman numeral superscript, and a symbol subscript, specifies the oxidation state, and the identity but not the number of the associated ions.

The extinction coefficients tabulated are defined by the equation

$$\alpha = \frac{1}{cd} \log \frac{I_0}{I}, \text{ where } c \text{ is in moles l.}^{-1} \text{ and } d \text{ in cm.}$$

Results

A. The Reaction of Cr⁺⁺ with Substitution-Inert Complex Ions. Co(NH₃)₅Cl⁺⁺.—A solution containing Co(NH₃)₅Cl⁺⁺ and ClO₄⁻ was prepared from Co(NH₃)₅Cl₃ by double decomposition with the requisite amount of AgClO₄. The reaction mixture of volume 200 ml. was 0.5 M in HClO₄ and contained 2.98 millimoles of Co(NH₃)₅Cl⁺⁺. Even at 2° the reaction with Cr⁺⁺ takes place rapidly (the half-life is only a fraction of a minute under the conditions described), and on reaction the mixture changes from the violet-pink color of Co(NH₃)₅Cl⁺⁺ to green. Chromous ion was used in slight excess to ensure complete consumption of the reactant species containing complex-bound chloride. A negligible amount of free chloride was found at the end of the reaction, and for each mole of Co(NH₃)₅Cl⁺⁺ reduced, 0.98 mole of Cl⁻ was found associated with Cr(III). The complete transfer of Cl⁻ from Co(NH₃)₅Cl⁺⁺ to Cr⁺⁺ was also demonstrated spectrophotometrically. The spectrum of the Cr(III) product obtained in the reaction agrees quantitatively with that of CrCl⁺⁺ prepared by an independent method (*vide infra*).

In another experiment, free chloride containing the radioactive isotope Cl³⁶ was present in the reaction mixture, in molar amount twice that of Co(NH₃)₅Cl⁺⁺ and at a concentration of 0.03 M. The radioactivity of the chloride attached to Cr(III) after reaction was found to be 10 counts per minute above background; on complete mixing of the chloride in the system a counting rate of 2,250 per minute would have been observed.

Co(NH₃)₅Br⁺⁺.—The conditions of the reaction were the same as those described for the chloro complex. The reaction is again very rapid, seemingly more rapid than with Co(NH₃)₅Cl⁺⁺ because no delay in the consumption of Cr⁺⁺ can be detected. In this system also, the transfer of halide

(1) Earlier communication, H. Taube, H. Myers and R. I. Rich, *THIS JOURNAL*, **75**, 4118 (1953).

(2) Of these ions, the most stable is CrCl⁺⁺. The equilibrium quotient (Cr X⁺⁺)/(Cr⁺⁺⁺)(Cl⁻) in a recent careful measurement by H. G. Gates and E. L. King was found to be 0.77 ± 0.06 at 4.9 μ and 74°. At the lower temperature and ionic strength of our experiments, the value of the quotient would be less, perhaps by a factor of 5 or more.

(3) J. J. Lingane and R. I. Pecsok, *Anal. Chem.*, **20**, 425 (1948).

to the reducing agent is essentially quantitative. This conclusion is based on the observations that no immediate precipitate forms when Ag^+ is added to the product solution obtained with $\text{Co}(\text{NH}_3)_5\text{Br}(\text{ClO}_4)_2$ as reactant⁴ (although a general cloudiness begins almost at once and increases gradually) and that the spectrum of the product chromium species using $\text{Co}(\text{NH}_3)_5\text{Br}(\text{ClO}_4)_2$ or $\text{Co}(\text{NH}_3)_5\text{Br}_2$ agrees quantitatively with that of CrBr^{++} prepared by the reaction of Cr^{++} and Br_2 (see Table III). The color change in the reaction of $\text{Co}(\text{NH}_3)_5\text{Br}^{++}$ and Cr^{++} is striking, because the reaction is very rapid and the intense green of the product is in marked contrast to the violet-red color of the cobaltic complex.

$\text{Co}(\text{NH}_3)_5\text{I}^{++}$.—The iodopentamminecobalt(III) was introduced as the perchlorate salt. The molar extinction coefficients of the chromic product obtained on the reaction of $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ in the wave length region 850–650 $\text{m}\mu$ agreed to within 2% with the values obtained for the product of the reaction of Cr^{++} and I_2 (see Table III). Owing to the rapid release of I^- to Ag^+ , the simple precipitation test for completeness of transfer is not successful in this system. However, the agreement of the spectra noted, as well as the observation that the spectra have a reasonable relation to that observed for CrBr^{++} , testify that transfer of iodide is also essentially complete. The reaction is again very rapid. The color of the final solution is an intense green, but the contrast with that of the reactant solution, an olive green, is not as striking as for the systems previously described.

$\text{Co}(\text{NH}_3)_5\text{F}^{++}$.—The reaction of Cr^{++} with this ion is also rapid. Quantitative data are lacking, because the sample of $\text{Co}(\text{NH}_3)_5\text{F}(\text{ClO}_4)_2$ was not very pure. The qualitative observation that the resultant solution is green-gray in color shows that at least some transfer of F^- to Cr takes place.

$\text{Co}(\text{NH}_3)_5\text{SO}_4^+$.—The results of the experiments with this ion are not as quantitative or as satisfying as those cited for the halogeno complex ions. The source of the sulfato ion was the salt $\text{Co}(\text{NH}_3)_5\text{SO}_4\text{HSO}_4 \cdot 2\text{H}_2\text{O}$. Barium perchlorate in excess of that required to precipitate the free SO_4^{--} was added to a solution of the sulfato salt in perchloric acid. The precipitate was too fine to filter at this stage, so the reaction with Cr^{++} was carried out in the presence of BaSO_4 (and Ba^{++}). After reaction, the BaSO_4 was filtered off, though still with difficulty, and the bound SO_4^{--} precipitated by heating and determined as BaSO_4 . The result showed 0.87 mole SO_4^{--} attached per mole $\text{Cr}(\text{III})$ formed. The major errors are in the direction to make this a lower limit for the extent of transfer. The result proves that the bulk of the reaction proceeds by transfer of SO_4^{--} , and it is possible that essentially all of it takes this path.

$\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{+++}$.—The half-life of Cr^{++} in the presence of excess $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{+++}$ at 0.02 M in 0.5 M HClO_4 and at 25° is of the order of a minute. The rate increases as the concentration of acid is lowered, and presumably paths involving both $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{+++}$ and $\text{Co}(\text{NH}_3)_5\text{OH}^{++}$ operate in the acid range studied.

The reaction also was conducted with chloride ion present in the solution, then determining the amount attached in the product $\text{Cr}(\text{III})$. The experimental conditions were the same as those described above, except that the reactant solution was made 0.1 M in NaCl . The mole ratio of bound chloride to $\text{Cr}(\text{III})$ formed was found to be less than 0.05. Attachment of chloride to $\text{Cr}(\text{III})$ is not an efficient process with $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{+++}$ as oxidizing agent nor does there appear to be a striking catalysis of the reaction by chloride ion.

$\text{Co}(\text{NH}_3)_6^{+++}$.—The salt $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ was used for this experiment, dissolved in 0.3 M HCl . The solubility is strongly suppressed as chloride concentration is increased so that it was necessary to work at a lower concentration level of acid. The reaction took place at room temperature, about 28°. The initial concentration of the luteo salt was 0.01 M and of Cr^{++} , 0.02 M . After 50 minutes the excess Cr^{++} was oxidized with H_2O_2 and an estimate made of the residual $\text{Co}(\text{NH}_3)_6^{+++}$ by precipitating it as the perchlorate, drying and weighing. The result showed that $\text{Co}(\text{NH}_3)_6^{+++}$ had decreased to 45% of its initial value. A rough value for the 2nd order specific rate based on this experiment is 0.7 l. mole⁻¹ min.⁻¹.

cis- $\text{Coen}_2\text{Cl}_2^+$.—The purpose of examining the reaction of Cr^{++} with this ion was to learn whether more than one

chlorine is transferred by an oxidizing agent with chlorine atoms in *cis* positions. The rate of the reaction with *cis*- $\text{Coen}_2\text{Cl}_2^+$ proved to be rapid. Only one atom was found associated with $\text{Cr}(\text{III})$ per equivalent of reaction. Although enough $\text{Coen}_2\text{Cl}_2^+$ was added to be in excess of the Cr^{++} (by 30%) so as to reduce the opportunity for catalysis of dissociation of CrCl_2^+ by Cr^{++} , the experiment must be regarded as inconclusive on the point of interest. A direct study of the relative rates in question is required, and if necessary a compound must be used which offers a more favorable relation of these rates.

$\text{CrCl}_3(\text{s})$.—Catalysis of the dissolution of CrCl_3 by reducing agents has been referred to frequently.⁵ In an experiment we performed, 1.610 millimoles of CrCl_3 was left in contact with 100 ml. of solution 0.001 M in Cr^{++} and 1 M in HClO_4 at room temperature for 10 minutes. During this time the dissolution of the solid was essentially complete. After quenching the reaction, the chloride associated with $\text{Cr}(\text{III})$ was determined and found to be 1.537 millimoles. This amount in comparison to the amount of CrCl_3 used shows that the net change proceeds largely to form CrCl^{++} as the product. The reaction was repeated with radioactive chloride added to the solution initially. The radioactivity of the chloride found attached to $\text{Cr}(\text{III})$ was measured as 90 counts per minute above background; for complete exchange, 1630 counts per minute would have been observed.

CrCl_2^+ .—The source of the dichloro complex ion was commercial green chromic chloride. Experiments on solutions of the salt using ion exchange resins⁶ have shown that at least 98% of the $\text{Cr}(\text{III})$ is initially in the form CrCl_2^+ . The solution used was 0.0225 M in the chromium (III) salt and 1 M in HClO_4 . Two samples of known volume were removed at intervals, the Cr^{++} was then added, and additional samples were taken. The results of this experiment, performed at room temperature, are recorded in Table I.

TABLE I
THE REACTION OF CrCl_2^+ AND Cr^{++}

Sample no.	1	2	3 ^a	4	5
Time, b min.	7	32	42	46	57
Fraction Cl^- left on $\text{Cr}(\text{III})$	0.625	0.589	0.331	0.332	0.326

^a Cr^{++} added at time = 41 min.; $(\text{Cr}^{++}) = 2.5 \times 10^{-3} M$. ^b Measured from the time of dissolution.

The experiment was repeated, but at 2° and with (Cr^{++}) at $2.3 \times 10^{-4} M$. The record of this experiment is presented in Table II.

TABLE II
THE REACTION OF CrCl_2^+ AND Cr^{++}

Sample no.	1	2	3
Time after Cr^{++} added, min.	0.4	1.5	10.0
Fraction Cl^- left ^a on $\text{Cr}(\text{III})$	0.436	0.338	0.334

^a The fraction bound to $\text{Cr}(\text{III})$ 5 min. after dissolution was 0.622. The defect from the theoretical value for CrCl_2^+ of 0.667 may be caused by the direct attack of Ag^+ .

Both experiments show that Cr^{++} takes CrCl_2^+ rapidly to the stage CrCl^{++} , and that further change is very much slower. The second experiment permits a rough estimate of the specific rate at 2° as of the order of 10^4 l. mole⁻¹ min.⁻¹.

The reaction of Cr^{++} and CrCl_2^+ was also carried out with radioactive chloride added to the solution. A small but definite fraction of the associated chloride reaches radioactive equilibrium during the reaction. The counting rate of the associated chloride was found to be 73 per minute above background; for complete exchange 2180 per minute would have been expected. Separate experiments showed that the pick-up of radioactivity was not caused by exchange of CrCl_2^+ or CrCl^{++} with Cl^{*-} , nor by the quenching procedure. The latter process involving slight addition of Cl^- to Cr^{++} on oxidation by H_2O_2 accounts for only a counting rate of 10 per minute above background. In an

(4) The compound $\text{Co}(\text{NH}_3)_5\text{Br}(\text{ClO}_4)_2$ was prepared by Mr. Paul E. Nessman.

(5) R. Abegg and Fr. Auerbach, "Handbuch der anorganischen Chemie," Vol. 4, Verlag von S. Hirzel, Leipzig, 1921, p. 78.

(6) E. L. King, private communication.

additional experiment, in which the concentration of chloride was doubled, the fraction exchanged was little altered.

Because CrCl^{++} appears as a well defined stage in the reaction of Cr^{++} and CrCl_2^+ , and because only a relatively small amount of Cr^{++} is needed, the reaction is a good one for developing CrCl^{++} almost free from other Cr(III) species. Figure 2 shows the values of the molar extinction coefficients of CrCl^{++} prepared by this method. Those obtained for CrCl^{++} prepared by the reaction of $\text{Co(NH}_3)_5\text{Cl}^{++}$ and Cr^{++} differ by less than 1% in the wave length region 700 to 625 $\text{m}\mu$.

$\text{CrI}_3(\text{s})$.—This compound, as anhydrous salt, was furnished through courtesy of Dr. Maurice Griffel, Iowa State University. The rate of dissolution by water is very slow but with a trace of Cr^{++} present, the reaction is much more rapid and produces an intense green color in the solution. This color is undoubtedly caused by a chromium(III)-iodide complex ion, and the behavior of the system is presumably like that of CrCl_3 with Cr^{++} . The complex is rapidly aquotized when the solution is warmed.

AuCl_4^- .—The work of Rich and Taube⁷ shows that tetrachloroaurate ion undergoes substitution by H_2O and Cl^- measurably slowly. The reaction with Cr^{++} was conducted at 2° in a solution 0.5 *M* in HClO_4 , and containing AuCl_4^- in excess of that required for the oxidation of Cr^{++} . The product solution was green, but discolored by what was apparently colloidal gold. Excess Fe^{++} was added to reduce Au complexes to Au, and the free chloride was removed as AgCl . Analysis of the resulting solution showed 1.00 mole of bound Cl^- for each mole of Cr^{++} oxidized.

Fe(CN)_6^{--} .—No quantitative observations were made on the reaction, but the qualitative observations are sufficiently striking to be worthy of record. On adding an exactly equivalent amount of Cr^{++} to a solution 0.005 *M* in $\text{K}_3\text{Fe(CN)}_6$ (and 0.01 *M* in HClO_4), an olive-brown precipitate formed at once and then persisted for days without apparent change. The system of the same stoichiometry arrived at by mixing $\text{Cr(H}_2\text{O)}_6^{+++}$ and Fe(CN)_6^{--} is entirely different. No obvious change takes place on mixing the two ions, and the only changes noted after a time are those resulting from the gradual decomposition and discoloration of the Fe(CN)_6^{--} in the air-saturated, faintly acid solution.

IrCl_6^- .—The reduction of IrCl_6^- by Cr^{++} takes place extremely rapidly, and the end-point is easily recognizable because IrCl_6^- has an intense reddish-brown color, very much more intense than that of the products. If the reaction takes place at 2°, and if Cr^{++} is added rapidly, the initial product is observed to be green in color. This color is quickly lost, and the solution then changes to a drab olive-brown shade. An attempt was made to follow the second color change spectrophotometrically. By the time of the first reading, 2 minutes after mixing, the change was almost complete, but the residual change registered suggests a half-time of ca. 0.5 min. for the second color change. The constitution of the final solution appears to be settled by the following observations. The extinction is the same as that of a solution made by mixing $\text{Cr(H}_2\text{O)}_6^{+++}$ and IrCl_6^- (this ion was generated by reducing IrCl_6^- with Sn^{++}). It is certain that little formation of inner sphere complex ions takes place when $\text{Cr(H}_2\text{O)}_6^{+++}$ and IrCl_6^- are mixed, because the color adjusts to the final shade immediately on mixing, and, more convincingly, because the extinction in the range 650 $\text{m}\mu$ to 400 $\text{m}\mu$ is, except for minor variations, that calculated by adding the contributions for $\text{Cr(H}_2\text{O)}_6^{+++}$ and IrCl_6^- . Some association of the oppositely charged species does take place, for $\text{Cr(H}_2\text{O)}_6^{+++}$ is extracted somewhat less efficiently by a resin when IrCl_6^- is present in the solution, but the product of the association is presumably an outer sphere complex ion.

B. Reactions with Halogens.—The results of the experiments on oxidation of Cr^{++} with halogens are related to the work reported here, because in the cases of Br_2 and I_2 , the direct reactions are convenient ways of generating 1:1 chromic-halide complexes. The conditions provided for the reactions were: temperature 2°, (HClO_4) 1 *M*, no halide present initially (except in the case of I_2), Cr^{++} added to a solution containing the halogen in excess. Excess Cl_2 or Br_2 was removed by a stream of air, and excess I_2 in preparation for spectrophotometric measurements was reduced with SO_2 .

With Cl_2 as reactant, free Cl^- is found in the solution at

the end of the reaction, and only 75% of the chloride is left in association with Cr(III) . The product solution obtained with Br_2 as the oxidizing agent contains practically no free bromide when tested immediately after the reaction. Evidently transfer of bromine to chromium is complete on reaction. The direct test for complete transfer fails in the $\text{Cr}^{++}\text{-I}_2$ reaction, but the less direct evidence tending to this conclusion already mentioned seems sufficient to establish it.

The rates of aquotization of CrCl^{++} and CrBr^{++} in strong acid are slow enough so that the extinctions can be measured without difficulty in a cell compartment at room temperature. With CrI^{++} , a correction must be applied for the change of extinction with time.

The ions CrBr^{++} and CrI^{++} have not been prepared previously, substantially free from other Cr(III) ion species. Their extinction coefficients are recorded in Table III. CrBr^{++} shows two distinct peaks in the visible region, as is characteristic of most simple complex ions of Co(III) and Cr(III) .⁸ The strong absorption in the ultraviolet shown by $\text{Cr(H}_2\text{O)}_6^{+++}$ moves progressively toward longer wave lengths in the series $\text{Cr(H}_2\text{O)}_5\text{H}_2\text{O}^{+++}$, $\text{Cr(H}_2\text{O)}_5\text{Cl}^{++}$, . . . , $\text{Cr(H}_2\text{O)}_5\text{I}^{++}$, and for the last named ion obscures the second peak in the visible region.

TABLE III

EXTINCTION COEFFICIENTS OF CrBr^{++} AND CrI^{++}
Medium, 0.5 *M* HClO_4 , temp. 25°

	CrBr^{++} from		CrI^{++} from	
	$\text{Cr}^{++} + \text{Br}_2$	$\text{Cr}^{++} + \text{Co(NH}_3)_5\text{Br}^{++}$	$\text{Cr}^{++} + \text{I}_2$	$\text{Cr}^{++} + \text{Co(NH}_3)_5\text{I}^{++}$
750	0.8	0.9	3.7	3.7
700	6.2	6.2	19.9	19.8
675	11.3	11.3	30.6	30.1
650	17.1	17.2	35.7	35.4
625	19.9 ^a	20.1	34.1 ^c	
600	18.2		21.7	
580	14.0		16.5	
560	9.8		10.3	
540	6.0		6.4	
520	4.2		5.9	
500	4.8		9.9	
480	9.6		28.5	
460	16.6		32.1 ^d	
440	22.2 ^b		44.5	
420	20.6		75	
400	13.4			
380	5.7			
360	2.4			
340	5.3			
320	25.4			

^a Max. at 622, $\alpha = 19.9$. ^b Max. at 432, $\alpha = 22.4$.
^c Max. at 644, $\alpha = 40.0$. ^d Max. at 475, $\alpha = 32.3$.

C. Results with Labile Complex Ions as Oxidizing Agents.—Table IV contains most of the data obtained on the formation of Cr(III)-Cl^- complexes in the oxidation of Cr^{++} by Fe(III) in the presence of chloride ion.

For a system in which paths described by the rate laws: $k_1(\text{Fe}^{+++})(\text{Cr}^{++})$, $k_H(\text{Fe}^{+++})(\text{Cr}^{++})/(\text{H}^+)$, $k_{\text{Cl}^-}(\text{Fe}^{+++})(\text{Cr}^{++})(\text{Cl}^-)$ compete, in which only the k_{Cl^-} term contributes to the formation of CrCl^{++} , and all the Cr^{++} reacting by this activated complex does form CrCl^{++} , the relation

$$\frac{\text{Cr}^{+++}}{\text{CrCl}^{++}}(\text{Cl}^-) = \frac{k_1}{k_{\text{Cl}^-}} + \frac{k_H}{k_{\text{Cl}^-}(\text{H}^+)}$$

must hold. In this relation, $(\text{Cr}^{+++})/(\text{CrCl}^{++})$ is the ratio of Cr(III) not converted to CrCl^{++} , compared to that which is, and (Cl^-) represents the free chloride concentration. The data in Table IV show that the function on the left is almost constant over an eightfold range in (Cl^-) , but does

(8) M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **266**, 49 (1951).

(7) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 1 (1954).

TABLE IV
THE FORMATION OF CrCl^{++} IN THE OXIDATION OF Cr^{++} BY
 Fe(III) IN THE PRESENCE OF Cl^-

Temp. 2°; $\mu = 2.2$					
(H ⁺)	(Cl ⁻) ₀	Av. (Cl ⁻) ^a	$\frac{\text{Cr}^{+++}}{\text{CrCl}^{++}}$	$\frac{\text{Cr}^{+++}(\text{Cl}^-)}{\text{CrCl}^{++}}$	Method
0.565	0.0250	0.0233	3.90	0.091	Spec.
.565	.0500	.0467	1.90	.089	Spec.
.565	.1000	.0947	0.91	.086	Spec.
.568	.1000	.0929	0.93	.085	Grav.
2.06	.0125	.0115	4.00	.0460	Spec.
2.06	.0500	.0455	1.06	.0483	Spec.
2.06	.1000	.094	0.50	.0472	Spec.
2.06	.0250	.0222	2.28	.0484	Grav.
2.06	.0500	.0449	1.04	.0467	Grav.
2.06	.1000	.0927	0.49	.0455	Grav.

^a Corrected for change in volume on addition of Cr^{++} (2% in the spectrophotometric experiments, 4% in the gravimetric), for the consumption of Cl^- by formation of CrCl^{++} , and for consumption by association with Fe^{+++} . The value of the equilibrium quotient $(\text{FeCl}^{++})/(\text{Fe}^{+++})(\text{Cl}^-) = K_{\text{FeCl}^{++}}$ under the present conditions was estimated as 1.7 by reference to the work of Rabinowitch and Stockmayer.⁹

change slightly, in the direction that at high (Cl^-) , somewhat too much bound Cl^- is formed. Figure 1, which includes also data at intermediate (H^+) not reported in Table IV, shows that the variation of the function $(\text{Cr}^{+++})(\text{Cl}^-)/(\text{CrCl}^{++})$ with (H^+) follows the requirements of equation 1.

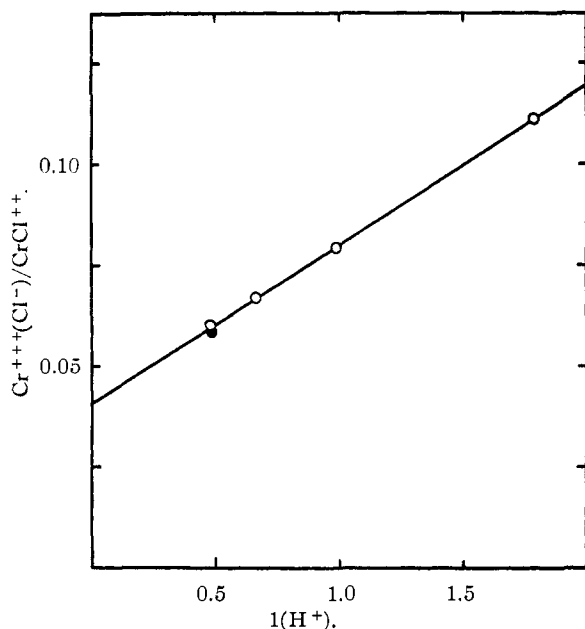


Fig. 1.—The efficiency of addition of chloride to chromium as a function of acidity: open circles, spectrophotometric data; solid circles, gravimetric data.

Experiments were also performed in media at higher concentrations of chloride ion, made up by replacing HClO_4 by HCl . Only the spectrophotometric method of analysis was used because the separation of free chloride from bound chloride with Ag^+ becomes inconvenient at high chloride concentration. Figure 2 shows the molar extinction coefficients for the product of the oxidation at the highest chloride concentration studied, 2 M, compared to the molar extinctions for CrCl_2^+ and CrCl^{++} . Applying the law for the variation of $\text{Cr}^{+++}/\text{CrCl}^{++}$ with (Cl^-) established at lower chloride concentration, it follows that less than 2% of the Cr^{++} is converted to $\text{Cr}(\text{H}_2\text{O})_6^{+++}$ in 2 M Cl^- , so

(9) E. Rabinowitch and W. H. Stockmayer, *THIS JOURNAL*, **64**, 335 (1942).

that only the distribution of Cr(III) between CrCl^{++} and CrCl_2^+ need be considered. From the relation of the extinctions for the product compared to that for CrCl^{++} , it is evident that some species besides this ion is formed. However, the extinctions observed cannot be accounted for quantitatively by combining the CrCl^{++} and CrCl_2^+ curves, and apparently the additional species differs from the CrCl_2^+ obtained from ordinary solid green chromic chloride.

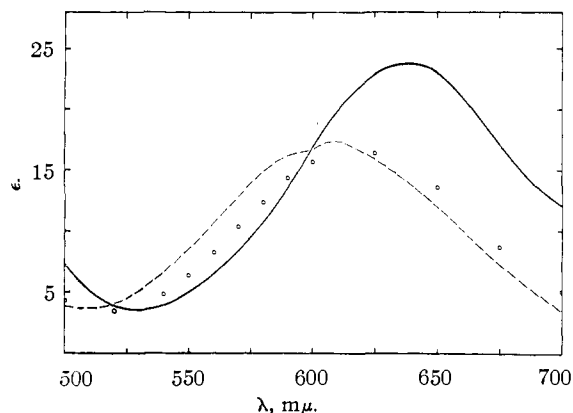


Fig. 2.—Comparison of the spectrum of the species $\text{Cr}_{\text{Cl}}^{\text{III}}$ produced in 2 M HCl with that of CrCl^{++} (broken line) and CrCl_2^+ (solid line).

In another experiment Cr^{++} (0.25 millimole) was added to 200 ml. of solution 0.0040 M in CrCl_2^+ , 0.01 M in Fe(III) and 1 M in HCl , at 2°. The extinction of the final solution was slightly less than that obtained by adding the extinctions of the product obtained in the absence of CrCl_2^+ to that of CrCl_2^+ , and could be accounted for by assuming a slight net dissociation of CrCl_2^+ to the extent of 3.9%. The experiment proves that under the usual experimental conditions (higher Fe(III) and relatively much less CrCl_2^+ than in the test experiment), the consumption of Cr^{++} by Fe(III) is rapid enough so that any CrCl_2^+ would be largely preserved. This conclusion may not apply, however, to CrCl_2^+ of the kind developed by the reaction with $\text{Fe}^{+++} + \text{Cl}^-$, although a large difference in the rate of reaction with Cr^{++} would not be expected for the two forms. The present experiment further leads to the conclusion that the specific rate for the reaction of Cr^{++} with $\text{Fe}_{\text{Cl}}^{\text{III}}$ in 1 M HCl is four times that with CrCl_2^+ .

The account of experiments performed on the reaction of Cr^{++} and Fe^{+++} with Br^- present appears in Table V.

TABLE V
THE FORMATION OF CrBr^{++} BY THE REACTION OF Fe^{+++} AND
 Cr^{++} IN THE PRESENCE OF Br^-

Temp. 2.1°; $\mu = 2.2$; $(\text{Fe(III)})_0, 0.020 \text{ M}$			
(H ⁺)	(Br ⁻)	$\frac{\text{Cr}^{+++}}{\text{CrBr}^{++}}$	$\frac{\text{Cr}^{+++}}{\text{CrBr}^{++}}$
0.563	0.0736	3.92	0.289
0.563	.221	1.31	.289
1.055	.221	0.805	.182
2.07	.0242	4.10	.099
2.07	.0730	1.455	.106
2.07	.221	0.484	.107

A feature of interest is that $(\text{Cr}^{+++})(\text{Br}^-)/(\text{CrBr}^{++})$ is constant as (Br^-) varies, thus a relation of the type of equation 1 describes the dependence of the yield of complex halide on halide concentration in this system also. The general form of the variation of the yield of CrBr^{++} with (H^+) is that required by equation 1. However, an important requirement of equation 1 is not satisfied by the data for Br^- and Cl^- taken together. The ratio of slope to intercept in graphs of the type of Fig. 1 should be the same for both. While the data for Br^- are not very extensive, they are sufficient to show that this condition is not fulfilled. The data in the chloride system are complete enough to establish equation 1 as a description of them, and evidently in the

bromide system some additional factor enters. The qualitative behavior of the bromide system is that the path $\text{Fe}^{+++} + \text{Cr}^{++}$ is suppressed relative to $\text{Fe}^{+++} + \text{Cr}^{++} + \text{OH}^-$. A deviation of this type would be observed if a rate term $k_{\text{HBr}}(\text{Fe}^{+++})(\text{Cr}^{++})(\text{H}^+)(\text{Br}^-)$ contributes to the formation of CrBr^{++} . Equation 1 then becomes

$$\frac{\text{Cr}^{+++}}{\text{CrBr}^{++}} (\text{Br}^-) = \frac{k_1 + k_{\text{H}^+}}{k_{\text{Br}^-} + k_{\text{HBr}}(\text{H}^+)} = \frac{1}{(\text{H}^+)} \left[\frac{k_1(\text{H}^+) + k_{\text{H}}}{k_{\text{HBr}}(\text{H}^+) + k_{\text{Br}^-}} \right]$$

If, by coincidence, the ratio $k_1/k_{\text{H}} = k_{(\text{HBr})}/k_{\text{Br}^-}$, the intercept in a plot such as Fig. 1 would disappear. The *ad hoc* interpretation advanced does not seem particularly attractive in the chemistry it implies, and a more detailed study of the system is required to make it convincing, or to reveal the true cause of the discrepancy.

A study of the type described for Cl^- and Br^- as "catalysts" was not made with F^- , for lack of a simple means of analyzing the products. A series of experiments was performed with F^- and Cl^- present together, observing the success of F^- in winning chromium from the path $k_{\text{Cl}^-}(\text{Cr}^{++})(\text{Fe}^{+++})(\text{Cl}^-)$. A decrease in the yield of CrCl^{++} when F^- is present does not prove that the competing path produces CrF^{++} , but this conclusion may be inferred by analogy with the Cl^- and Br^- systems, and with the behavior of the $(\text{NH}_3)_5\text{CoX}^{++}$ ions. It can be inferred more directly from the observation that the product chromium solution has a marked green color, even when as at high concentration of HF the formation of CrCl^{++} is slight.

The results of the experiments with Cl^- and F^- present simultaneously are shown in Table VI.

TABLE VI

EFFECT OF F^- ON THE FORMATION OF CrCl^{++}

Temp. 2.1°, $\mu = 2.2$; $(\text{NaCl})_0 = 0.100 M$, $(\text{Fe}(\text{ClO}_4)_3)_0 = 0.0215 M$, $(\text{HClO}_4)_0 = 2.06 M$; added 2.02 meq. Cr^{++} ; volume 200 ml.

HF added	$\frac{(\text{Cr}^{+++} + \text{CrF}^{++})}{(\text{CrCl}^{++})}$	$\frac{(\text{Cr}^{+++} + \text{CrF}^{++})}{(\text{CrCl}^{++})}$	(HF) ^a
0.00760	1.09	0.105	0.00295
.0152	1.75	.169	.00683
.0304	3.30	.332	.01695

^a Calculated assuming $(\text{FeF}^{++})(\text{H}^+)/(\text{Fe}^{+++})(\text{HF}) \equiv K_{\text{H}^+ \cdot \text{FeF}^{++}} = 175$, $(\text{FeCl}^{++})/(\text{Fe}^{+++})(\text{Cl}^-) = 1.7$ under the experimental conditions. In the absence of data on the variation of $K_{\text{H}^+ \cdot \text{FeF}^{++}}$ with μ , the value at $\mu = 0.5$ was used¹⁰; a correction was applied for the change in temperature, following Hudis and Wahl.¹¹

For a reaction in which the formation of CrCl^{++} competes with the formation of the aquo ion and of the fluoro ion,¹² the relation expressed by equation 2 follows

$$\frac{(\text{Cr}^{+++} + \text{CrF}^{++})(\text{Cl}^-)}{(\text{CrCl}^{++})} = \frac{k_a}{k_{\text{Cl}^-}} + \frac{k_{\text{HF}}(\text{HF})}{k_{\text{Cl}^-}} \quad (2)$$

In equation 2, k_a describes the combined Fe^{+++} and FeOH^{++} paths, and k_{HF} refers to the path expressed by the rate law $k_{\text{HF}}(\text{Fe}^{+++})(\text{Cr}^{++})(\text{HF})$. When the function on the left is plotted against (HF), the data are observed to conform fairly well to a straight line plot. There seems to be no reason to question the validity of equation 2, but the choice of the values for the equilibrium quotients used in calculating the free HF concentration may be in considerable error. A smaller value for the quotient $K_{\text{H}^+ \cdot \text{FeF}^{++}}$ would improve the agreement of the data.

D. Other Systems.—The reaction of Fe^{+++} and I^- is so rapid that a study of the formation of CrI^{++} by the reaction of Fe^{+++} with Cr^{++} in the presence of I^- is made very difficult. Ceric ion in excess oxidizes Cr^{++} to $\text{Cr}_2\text{O}_7^{2-}$.

The reaction of Cr^{++} with oxidizing agents which offer a $2e^-$ oxidation as the initial attack on Cr^{++} have an interest

(10) H. W. Dodgen and G. K. Rollefson, *THIS JOURNAL*, **71**, 2600 (1949).

(11) J. Hudis and A. C. Wahl, *ibid.*, **75**, 4153 (1953).

(12) If fluoride ion does not add, but merely catalyzes the reaction to form Cr^{+++} , the relation is left unaltered on the right and on the left $\text{Cr}(\text{III})$ is shown distributed between Cr^{+++} and CrCl^{++} .

separate from that which guided the work reported here, and will be reported separately.

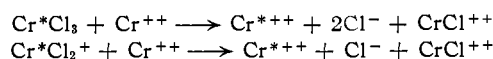
Discussion

The observations on the reaction of $\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$ with Cr^{++} yield the most definite formulation of the activated complex. It must have an arrangement of the reactant molecules that permits the transfer of chlorine from cobalt to chromium without allowing it to exchange with the solution. In effect, therefore, chlorine must make a bond both with cobalt and chromium in the activated complex, as

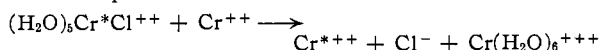


The efficient transfer of electronegative groups which is observed with the other substitution-inert oxidizing agents makes it likely that a similar type of activated complex provides the reaction path in these systems also.

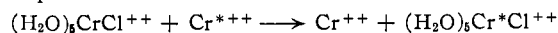
Direct atom transfer, involving again an atom bridge activated complex, is the most reasonable explanation of the observations on the catalysis by Cr^{++} of the dissociation of CrCl_3 , CrI_3 and CrCl_2^+ . The reactions for the two types of species may be represented as



From this formulation it is immediately clear why the systems persist in the well defined stage CrCl^{++} (CrI^{++}), and why little exchange with Cl^- in solution is observed during the reactions. Although reaction may continue involving chlorine transfer between Cr^{++} and CrCl^{++} , this process does not affect the stoichiometry and can only be detected by using radioactive chromium as a tracer. The results obtained with the complex cobalt cations showing that attack on Cl is more rapid than on H_2O are preparation for the conclusion that the process



will prove to be much slower than



The description of the activated complex has stressed the feature of the transfer of an electronegative group in the reactions which were investigated. This emphasis is made only because the observation of the transfer provides the basis for the conclusions about the activated complex which were reached, and is not meant to imply that net atom transfer is an essential part of the electron transfer process. The essential feature is rather that an appropriate bridge provides a more accessible pass for the flow of electrons than does the proton coordination sphere of an ammonated or aquated cation. Whether net transfer of an electronegative group from oxidizing agent to reducing agent takes place depends on the relative substitution lability of the two reactants, and also on the relative substitution lability of the ions left sharing the bridge atom after electron transfer. There is no simple relation between net atom transfer and electron transfer for reactions involving net chemical change. When cobalt(III) complexes react with Cr^{++} , they bring the bridging group

into the activated complex because they accept substitution less readily than does Cr^{++} . After electron transfer, Co(II) and Cr(III) are left sharing the bridging group. The shared group is then expected to leave with Cr(III) when the bridge complex is dissociated because Co(II) complexes are known to be more substitution-labile than those of Cr(III) . Similarly, when $\text{Fe}^{\text{II}}\text{H}_2\text{O}$ and Cr(III) share a bridging group, this is expected to remain associated with Cr(III) on dissociation of the complex. The reaction of Cr^{++} and $\text{Fe(CN)}_6^{\text{=}}$ is apparently one in which there is no net transfer, but the bridge with CN^- persists in the insoluble product. Fe(II) forms inner orbital complexes with CN^- which are substitution-inert hence the system containing the insoluble product, and the one of the same stoichiometry arrived at by mixing $\text{Cr(H}_2\text{O)}_6^{+++}$ and $\text{Fe(CN)}_6^{\text{=}}$ are slow to reach the common equilibrium state. The behavior of the system $\text{Cr}^{++} + \text{Fe(CN)}_6^{\text{=}}$ is intermediate between $\text{Co(NH}_3)_6\text{X}^{+++}\text{-Cr}^{++}$ and $\text{Cr}^{++}\text{-IrCl}_6^-$. In the one mentioned last, there is no net transfer of chlorine to the reducing agent. It is likely, however, that the intermediate green substance which is observed is the bridge complex $(\text{H}_2\text{O})_3\text{CrClIrCl}_5$. Complexes of Ir(III) are relatively inert to substitution, and when the complex is disrupted, the bridging Cl remains with Ir(III) rather than with Cr(III) . These considerations suggest that a system could be selected in which an electronegative atom is transferred from reductant to oxidant on reaction. They furthermore suggest that when a bridged activated complex provides the path for electron exchange in a system in which there is no net chemical change (as for example in electron exchange between Fe^{++} and Fe^{+++}), some transfer of the shared group will always accompany electron transfer. The ion with the charge and electron structure which confers the lower lability will, in the majority of events, take the bridging group into the activated complex, and later out of it. When the electron is transferred, the relative substitution labilities of the ions sharing the bridge are reversed. This point of view makes no prescription as to the direction of atom transfer compared to that of electron transfer. The relation depends on the substitution lability of the reduced form compared to the oxidized form; the lability to substitution of the oxidized form is not necessarily less than that of the reduced form.

The process of electron transfer through bridging atoms in crystalline solids has been discussed by Zener.^{13,14} Presumably the role of the bridging atoms for the complexes in solution under discussion is the same, their role being to absorb and deliver the electron transferred. The rates of reaction with Cr^{++} increase in the order $\text{Co(NH}_3)_6^{+++}$, $\text{Co(NH}_3)_5\text{H}_2\text{O}^{+++}$, $\text{Co(NH}_3)_5\text{Cl}^{++}$, $\text{Co(NH}_3)_5\text{Br}^{++}$. It should be noted that in each of the ions except $\text{Co(NH}_3)_6^{+++}$ a pair of electrons is available on the bridging group for interaction with Cr^{++} . The mechanism of reaction with

(13) C. Zener, *Phys. Rev.*, **82**, 403 (1951).

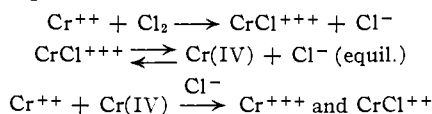
(14) The author (H.T.) is grateful to Dr. Sol. Weller for bringing the paper of ref. 13 to his attention.

$\text{Co(NH}_3)_6^{+++}$ is not known, whether by electron transfer through the proton coordination shell,¹⁵ or by interaction of Cr^{++} with a pair of electrons left unshared when the ion loses a proton. There is also a question about the "bridge" mechanism with $\text{Co(NH}_3)_5\text{H}_2\text{O}^{+++}$ as oxidizing agent, but this will be resolved by oxygen tracer experiments in progress.

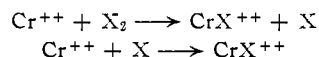
The experiment with $\text{Co(NH}_3)_5\text{H}_2\text{O}^{+++}$ oxidizing Cr^{++} in the presence of chloride ion suggests that specific catalysis of electron transfer by negative ions depends largely on their ability to serve as bridges. An activated complex involving Cl^- as a bridge between Co(III) and Cr^{++} is not readily accessible in this system, owing to the reluctance of the Co(III) complex ion to undergo substitution. A slight addition of Cl^- to chromium was observed, however, so that some mode of action besides serving as a bridge must be open for the negative ion. A possibility is a path in which electron transfer in

a complex such as $\left[\begin{array}{c} \text{H} \\ (\text{NH}_3)_5\text{CoOOCr(H}_2\text{O)}_n \\ \text{H} \end{array} \right]^{+5}$ is consummated by Cl^- substitution on chromium.

In the foregoing it has been assumed that the reactions discussed involve $1e^-$ changes. There is no direct evidence supporting this assumption, but there is a powerful argument against the assumption of a $2e^-$ change. A $2e^-$ change would form the highly unstable intermediate products Cr(IV) and Co(I) with Co(III) as oxidizing agent and Cr(IV) and Fe(I) with Fe(III) , and is highly unlikely energetically. Some additional evidence supporting $1e^-$ transfer is comparison with the behavior of systems in which the oxidizing agent is capable of producing a $2e^-$ change. The difference between the reaction of Cr^{++} with Cl_2 on the one hand and Cr^{++} with Br_2 or I_2 on the other may be that with Cl_2 the reaction proceeds at least in part by a primary $2e^-$ change in Cr^{++}



while with the less powerful oxidizing agents Br_2^{16} and I_2 only the $1e^-$ path, which adds halide efficiently, takes place



A primary $2e^-$ attack on Cr^{++} does not necessarily result in complete transfer; the stage Cr(IV) is probably substitution-labile, and, furthermore, mixed products are to be expected in the reaction of Cr^{++} and Cr(IV) . In view of experiments⁷ on the exchange between AuCl_4^- and Cl^- induced by Fe^{++} , it is likely that the primary attack of Cr^{++} on AuCl_4^- is also a $1e^-$ change.

The results obtained with the labile oxidizing systems $\text{Fe}^{+++} + \text{X}^-$ show that with F^- , Cl^- or Br^- present paths involving these ions compete

(15) The analogous system $\text{Co(en)}_3^{+++}\text{-Co(en)}_3^{+++}$ studied by W. B. Lewis, C. D. Coryell and J. W. Irvine, *J. Chem. Soc.*, 386 (1949), appears to be a clear-cut example of electron transfer not involving direct atom bridges.

(16) P. R. Carter and N. Davidson (*J. Phys. Chem.*, **58**, 877 (1952)) have proven a $1e^-$ primary process for the reaction of Fe^{++} and Br_2 .

efficiently with the aquo and hydroxy paths. They have also shown, at least with Br^- and Cl^- , that participation of the halide ion leads to formation of CrX^{++} . One structural feature of the activated complex is therefore made definite; this is that X⁻ makes bonds to chromium in it. The question of whether the halide also makes a bond to Fe^{+++} is not so definitely settled. We can infer with some confidence that it does, from the observations with the substitution-inert complex ions and from the observation that Cl^- does not catalyze the reaction of $\text{Co}(\text{NH}_3)_6\text{H}_2\text{O}^{+++} + \text{Cr}^{++}$ appreciably but does have a strong effect on $\text{Fe}^{+++} + \text{Cr}^{++}$. The essential difference between the two oxidizing agents is that Fe^{+++} accepts substitution in the first sphere much more readily, and therefore can make use of Cl^- as a bridging group.

The data also lead to the conclusion that there is no important path for catalysis by Cl^- or Br^- which does not involve the formation of a halide-chromium bond in the activated complex. A plausible activated complex for such a path would be one in which Cr^{++} attacks $\text{FeX}_{\text{aq}}^{++}$ at a water molecule rather than at X. If such a path did contribute, $\text{Cr}(\text{II})$ would not be converted completely to CrX^{++} even at high halide but would be distributed between Cr^{+++} and CrX^{++} in the ratio of the halide-catalyzed, non-addition and halide-catalyzed, halide-addition rates. The effect on rate law 1 would be to add a halide-dependent term in the numerator on the right-hand side. In the case of Br^- , the relation is particularly free from the influence of terms in the denominator higher than first power in halide, which might obscure the point at issue, and show that the halide-dependent non-addition path can be at most 5% of the halide addition path. Although terms of higher order do appear in describing the dependence of yield of CrCl^{++} on chloride concentration, thus making it more difficult to assess the importance of an halide-dependent, non-addition path, in this system the path in question must also be a minor one. The results with the substitution-inert oxidizing agents also suggest the conclusion that an oxidizing agent offering both Cl^- and H_2O as point of attack for Cr^{++} is much more vulnerable at the halide group.

It is not clear from the data what products result from the processes corresponding to the higher order terms mentioned for Cl^- , whether, for example, a term $k_{2\text{Cl}}(\text{Fe}^{+++})(\text{Cl}^-)^2(\text{Cr}^{++})$ corresponds to the formation of CrCl_2^+ alone or of both CrCl^{++} and CrCl_2^+ . A four-membered ring with two bridging atoms would seem to be a favorable arrangement for an activated complex containing two chlorides, and on this basis any CrCl_2^+ formed would have the *cis* arrangement. It is possible that the difference between CrCl_2^+ formed by oxidizing Cr^{++} in strong Cl^- medium and that obtained by dissolving green chromic chloride is that one is the *cis* isomer and the other the *trans*.

In Table VII are entered the relative rates at which Cr^{++} reacts with various $\text{Fe}(\text{III})$ species. These relative rates have been calculated as implied by equations 1 and 2 from the data of Fig. 1 and Tables V and VI, and depend on the values for

equilibrium quotients $K_{\text{FeCl}^{++}}$ and $K_{\text{H}^+, \text{Fe}^{++}}$ cited earlier, as well as the quotients $K_{\text{FeBr}^{++}} = (\text{FeBr}^{++})/(\text{Fe}^{+++})(\text{Br}^-) < 0.03$, $K_{\text{FeOH}^{++}, \text{H}^+} = 0.45 \times 10^{-3}$. The estimate of the upper limit for $K_{\text{FeBr}^{++}}$ is based on unpublished work¹⁷ which places an upper limit of 0.1 at $\mu = 2$ and 25° , and on the temperature dependence established by Rabinowitch and Stockmayer.⁹ The hydrolysis quotient¹⁸ of Fe^{+++} is calculated from the value of 2.5×10^{-3} for $\mu = 2$ and 25° , using the temperature coefficient measured by Rabinowitch and Stockmayer. Table VII also contains the relative rates of electron exchange between Fe^{++} and various $\text{Fe}(\text{III})$ species calculated from a compilation of Hudis and Wahl¹¹, based on their work, that of Silverman and Dodson¹⁹ and Gryder and Dodson.²⁰

TABLE VII

RELATIVE RATES OF REACTION OF Cr^{++} WITH $\text{Fe}(\text{III})$ SPECIES, AND OF ELECTRON EXCHANGE BETWEEN Fe^{++} AND $\text{Fe}(\text{III})$ SPECIES

	Relative rates	
	For Cr^{++} (at 2° , $\mu = 2.2$)	For Fe^{++} (at 0° , $\mu = 0.5$)
Fe^{+++}	1	1
FeF^{++}	3	11.1
FeCl^{++}	18	11.1
FeBr^{++}	>100	..
FeOH^{++}	2.8×10^3	1.16×10^3

^a Estimated from the "slope" when the data of Table V are plotted as in Fig. 1.

Accepting the conclusion that the activated complexes involve bridging atoms, the results show the rate of electron transfer from Cr^{++} to $\text{Fe}(\text{III})$ complexes to decrease in order with the groups OH^- , Br^- , Cl^- , F^- , H_2O in the bridges. Thus, as for the complexes of $\text{Co}(\text{III})$, it appears that a factor other than the distance of approach permitted by the bridge atoms is important in determining the relative rates.

Care must be exercised in drawing conclusions from an array of relative rates such as that shown in Table VII. Since for the systems referred to, equilibrium with respect to complex ion formation is established rapidly, the experimental results yield only the composition of the activated complex, and contain no implication as to the way the activated complex is formed. Table VII shows what the relative specific rates are when we choose to express the rates in terms of the species represented. The choice $\text{Cr}^{++} + \text{Fe}^{+++}$, $\text{CrF}^+ + \text{Fe}^{+++}$, ..., $\text{CrOH}^+ + \text{Fe}^{+++}$, equally consistent with the rate law, might yield a quite different order for the efficiency of the bridging groups. When the reactants $\text{Cr}^{++} + \text{F}^- + \text{Fe}^{+++}$, $\text{Cr}^{++} + \text{Cl}^- + \text{Fe}^{+++}$, etc., are chosen as the basis for comparison, fluoride appears as the most efficient of the halide ions. If the object is to eliminate from consideration the different tendencies of the ions to associate with the cations and to limit the discussion to the relative rates of electron transfer in the com-

(17) A. S. Wilson, Ph.D. Dissertation, Univ. of Chicago, 1950.

(18) A. S. Wilson and H. Taube, *THIS JOURNAL*, **74**, 3509 (1952).

(19) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

(20) J. W. Gryder and R. W. Dodson, *THIS JOURNAL*, **73**, 2890 (1951).

plexes $[\text{CrXFe}]^{+4}$, it is necessary to compare the rates at unit concentration of these species. The data on stabilities to make this comparison possible do not exist. It might be supposed, however, that the complexes would be enough more stable with F^- than Cl^- to reveal a higher specific rate of electron transfer in the chloride bridge complex.

The relative rates shown in Table VII are useful in making comparisons without inquiring into their meaning. The similarity of the relative rates in the two columns suggests that the activated complex involved when Fe^{++} and Fe(III) complexes exchange electrons is of the same type as that for the reaction of Cr^{++} with Fe(III) complexes. Comparison of the activation energies observed for electron exchange between Fe^{++} and Fe(III) complexes with that of substitution on Fe^{++} or Fe^{+++} ,²¹ shows that the rate-determining act is not the substitution to form the bridged activated complex. The energy values are compatible with the assumption that a bridged chemical complex formed as an equilibrium process having ΔH° lower than the activation energy for substitution. If, as seems likely, ΔH° is positive the activation energy for electron transfer in the bridged complex must be small. The low rate for electron transfer in the bridged complex as compared to dissociation of the complex must then be a matter of a much lower temperature-independent factor, *i.e.*, a relatively specific relation of the positions of a large number of atoms is required to make the electron transfer possible.

A condition for a bridged activated complex to provide a more favorable pass for electron transfer

(21) J. Bjerrum and K. R. Poulson, *Nature*, **169**, 463 (1952), have measured ~ 13 kcal. as the activation energy for substitution by CNS of solvent on Fe^{+++} . If the activation energy for substitution on Fe^{++} is similar to that on Ni^{++} and Co^{++} , it is even higher than 13 kcal.

than some other process is that at least one of the partners be able to undergo a substitution process readily. Thus although $(\text{NH}_3)_5\text{CoH}_2\text{O}^{+++}$ is inert to substitution, Cr^{++} is labile so that the bridge

complex $\left[\begin{array}{c} \text{H} \\ (\text{NH}_3)_5\text{CoOCr} \\ \text{H} \end{array} \right]^{+5}$ can still provide a

path for electron exchange. A bridge other than that involving H_2O or OH^- is not readily accessible, however, because this would require substitution on Co(III) . On the basis of present information, one cannot be certain that such a substitution may not take place under some labilizing influence of the other reactant, but neither are there any observations which suggest such an influence. Common cations which are fairly labile to substitution²² and for which bridged activated complexes must be considered for oxidation-reduction or electron exchange reactions in water involving them are: Ti^{++} , Ti^{+++} , Ti(IV) , V^{++} , V^{+++} , V(IV) , V(V) , Cr^{++} , Cr(IV) (?), Mn^{++} , Mn^{+++} , Fe^{++} , Fe^{+++} , Co^{++} , (Co^{+4} possibly), Cu^+ , Cu^{++} , Ag^+ , Ag^{++} , Eu^{++} , Eu^{+++} , Ce^{+++} , Ce(IV) , Tl^+ , Tl^{+++} . It is admitted that not all electron transfer reactions involve such direct atom bridges. When both partners are substitution-inert and have the coordination spheres blocked, other types of activated complexes are almost certainly involved.

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(22) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF UTAH]

Citrate Complexes with Iron(II) and Iron(III)¹

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The results of *pH* titrations of iron(II) perchlorate and citric acid in 1:1 mixture, at ionic strength 1.0, showed that the iron(II) complexes with citrate may be formulated as FeHCit , FeCit^- and FeOHCit^- . The formation constants of these complexes have been calculated. The results of *pH* titrations of iron(III) perchlorate and citric acid in 1:1 mixture, at ionic strength 1.0, showed that the iron(III) complexes with citrate may be formulated as FeHCit^+ , FeCit , FeOHCit^- and $\text{Fe(OH)}_2\text{Cit}^-$. The formation constants of these complexes have been calculated. Polarographic measurements on iron(II)-iron(III) mixtures in excess citrate, at ionic strength 1.0, demonstrated that two separate reduction processes are involved. The formation constants previously calculated were shown to be consistent with the data obtained polarographically, and the reversible polarographic processes were related to definite reactions.

Many different investigators have studied the citrate complexes of iron(III) with results which differ considerably. Bobtelsky and Jordan² have attempted to relate the breaks in the conductivity titration of iron(III) with citrate to the complex ion composition, but Bertin³ has recognized that the change in the hydrogen ion concentration and

the number of acid hydrogens in the complex were the important factors in causing the breaks in the conductance titration. A line of reasoning starting from *pH* titration curves led Bertin to conclude that the iron(III) citrate complexes were 1:1 complexes containing different numbers of acid hydrogens. A spectrophotometric study of iron(III) and citrate in acid solution, by the method of constant variations, permitted Lanford and Quinan⁴ to identify FeHCit^+ as the form of the complex existing when the solution was 0.08 to 0.15 *M* in HNO_3 . Lin-

(1) The work on this investigation was supported by National Science Foundation Research Grant NSF-G62.

(2) M. Bobtelsky and J. Jordan, *THIS JOURNAL*, **67**, 1824 (1945); **69**, 2286 (1947).

(3) C. Bertin, *Bull. soc. chim. France*, 489 (1949).

(4) O. E. Lanford and J. R. Quinan, *THIS JOURNAL*, **70**, 2900 (1948).