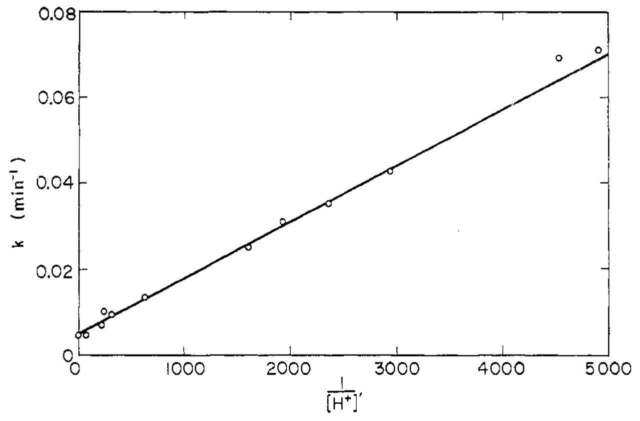

Fig. 2.—The dependence of k on acidity at 25° and $\mu = 0.5$ (NaCl added).

that the chromous ion formed at the electrode rapidly converts $CrCl_2^+$ to $CrCl^{+2}$ according to the fast reaction

$$*CrCl_2^+ + Cr(II) \longrightarrow *Cr(II) + CrCl^{+2} + Cl^- \quad (5)$$

which has a rate constant[10] of roughly $10^4\ M^{-1}\ \text{min.}^{-1}$.

Mechanism.—The first term in eq. 4 may be taken as the rate of aquation of the *trans*-$CrCl_2^+$ species, as is shown in the recent work of Johnson and Reynolds.[6] The second term in eq. 4 represents the dependence of the forward reaction on the concentration of hydrogen ion. In light of the inverse hydrogen dependence the following mechanism is assumed, in agreement with that outlined by Hamm and Shull,[4] to account for this term in the rate law.

$$CrCl_2(H_2O)_4^+ \underset{}{\overset{\text{rapid}}{\rightleftarrows}} CrCl_2(H_2O)_3OH + H^+$$

$$CrCl_2(H_2O)_3OH + H_2O \xrightarrow{\text{slow}} CrCl(H_2O)_4OH^+ \; Cl^-$$

$$H^+ + CrCl(H_2O)_4OH^+ \overset{\text{rapid}}{\rightleftarrows} CrCl(H_2O)_5^{+2}$$

This same type of mechanism is generally accepted in regard to many related reactions.[12]

The rate constant for the aquation of $CrCl_2(H_2O)_3OH$ is 8.15 as compared with 0.0050 for the $CrCl_2(H_2O)_4^+$ species. This ratio of approximately 1630 is in agreement with that found in many analogous systems and is subject to the same general interpretation.[13]

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The Characterization of $[Cr(H_2O)_4OH]_2^{+4}$ and Its Formation by Oxygen Oxidation of Chromous Solutions[1]

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The dinuclear Cr(III) species formed by O_2 oxidation of Cr^{+2} solutions, which is the same species as the early product of boiling Cr^{+3} solutions and of electrochemical reduction of $Cr_2O_7^{-2}$, was shown by O^{18} exchange studies to be $[Cr(H_2O)_4OH]_2^{+4}$. The fact that but five O atoms per Cr show a measurable exchange rate eliminates the possibility of an oxo bridge. The rate of the oxidation was found to be second order in Cr^{+2} but was directly proportional to the flow rate of O_2 gas. Isotope labeling showed that all of the O atoms of the oxidizing agent, O_2, are transferred to the product. These results are understood in terms of a mechanism which involves a peroxide-bridged intermediate.

When chromous perchlorate solutions are oxidized by air or O_2, a dinuclear product of total charge +4 results.[3] The same product is formed as the first step in hydrolytic polymerization of heated chromic perchlorate solutions,[4] or by electrolytic reduction of $Cr_2O_7^{-2}$.[5] The charge found for the species[3] is consistent with its being either $[(H_2O)_5CrOCr(H_2O)_5]^{+4}$ or $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{+4}$. Because of the importance of this species in a wide variety of different processes, and because of the general difficulty in deciding between oxo and hydroxo bridging in Cr(III) polymers, the present experiments were undertaken.

If to a solution of the dinuclear species, H_2O^{18} is added, thoroughly mixed, and the solvent is promptly sampled, the amount of exchangeable O atoms is found. By difference, the number of O atoms "held back" in the dinuclear species is obtained as was done in establishing coordination number six for the simple Cr^{+3} ion.[6] In this way, decision can be made between the oxo-bridged structure, O/Cr = 5.5, and the hydroxy-bridged one, O/Cr = 5.0.

Once the structure of the dinuclear Cr(III) has been established, further experiments could indicate its mechanism of formation by the O_2 oxidation of Cr^{+2}.

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(1) Supported by the United States Air Force through the Air Force Office of Scientific Research and Development Command.

(2) Based on a thesis presented in partial fulfillment of the degree of Doctor of Philosophy.

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TABLE I

EXCHANGE BETWEEN DIMER AND H_2O^{18}

Cr, g.	H_2O_T, g.	$N^0 \times 10^3$	$N^\infty \times 10^3$	O exch. per Cr
0.3096	4.4506	5.8546	5.3866	5.14
0.3097	4.4518	5.8316	5.3757	5.06
0.3097	4.4554	5.8231	5.3765	4.95
0.2349	4.6053	5.5722	5.2584	5.09
0.2352	4.6168	5.5564	5.2505	4.99
0.2356	4.6066	5.5793	5.2686	5.02

This mechanism is important since little is known about the details of molecular oxygen oxidation, and the kinetically inert Cr(III) product can prove helpful in giving such information. The experiments in the present study performed for this purpose are the establishment of the stoichiometry, the kinetics of the reaction, and O^{18} tracer experiments.

Experimental

Chromous perchlorate solutions were prepared electrolytically as described previously.[3] Other reagents, used in various analyses, were A.R. grade. Chromous concentrations were measured under nitrogen by reaction with excess ferric ion and titration of the resulting ferrous ion with standard dichromate. Total chromium concentrations were determined by titration with standardized ferrous solution after persulfate oxidation to dichromate. In order to find total H_2O concentration, perchlorate was determined by precipitation as the tetraphenylarsonium salt.

For the O^{18} exchange experiments, chromous solution (*ca.* 1 *M*) was shaken with air for 20 min. to ensure complete oxidation to the dimer. After cooling, 5 ml. was thoroughly mixed with 1 ml. of O^{18}-enriched water and 5 ml. of the mixture pipetted into a distillation flask filled with dry nitrogen and attached to a vacuum line. About 1 g. of water was distilled under vacuum while the solution was stirred with a magnetic stirrer. The water was then transferred to a weighed sample tube, reweighed, and a measured amount (*ca.* 50 mg.) of CO_2 added. The sample was kept at 25° for 1 week or more to allow isotope equilibration. Finally, the CO_2 was distilled at $-78°$ and analyzed in an isotope ratio mass spectrometer, which was standardized by means of known mixtures. For determination of isotopic composition in the dimer solution after complete exchange, the solutions were allowed to stand for 35–40 days at room temperature and then sampled as before.

For the O^{18} tracer experiments, a 15-ml. solution of Cr^{+2} was prepared, mixed with 5 ml. of O^{18}-enriched water, and sampled isotopically as before. Normal O_2 was bubbled for 15–20 min. through the solution to oxidize the Cr^{+2} to dimer and the solvent again sampled by distillation.

Stoichiometry of the O_2–Cr^{+2} reaction was determined by mixing chromous perchlorate solutions and O_2 gas in a closed flask fitted with a manometer. The solution was stirred magnetically and the entire vessel thermostated. The pressure change after reaction was complete, as shown by both steady pressure and the lack of reducing power in the final solution, coupled with the calibrated flask volume and initial amount of Cr^{+2} present gave the stoichiometry.

Kinetic measurements were made in a reactor at whose bottom was a sintered glass plate. Air, or O_2 gas, was passed through a flow meter, through a scrubber containing $Cr(ClO_4)_3$ of concentration comparable to the reacting solution, and finally through the sintered plate into the chromous solution. The entire reactor and scrubber were immersed in a bath at 0°. Prior to an experiment, dilute perchloric acid was pipetted into the reactor and saturated with the gas; chromous solution was then pipetted into this. At predetermined time intervals, the reaction was quenched by addition of a known volume of standardized ceric ammonium sulfate solution. The unreacted ceric was titrated with ferrous solution to determine by difference the extent of Cr^{+2}–O_2 reaction to that time.

TABLE II

O_2 PRESSURE CHANGE ON COMPLETE REACTION OF 1.633 MMOLES OF Cr^{+2}[a]

ΔP, mm.	O_2, mmole	Cr^{+2}/O_2
155	0.409	4.00
151	0.398	4.10
154	0.405	4.03
156	0.411	3.97
153	0.403	4.05

[a] Volume, 49 cc.; temperature, 25°.

Results

Formula of Dimer.—Table I gives the mole fraction of H_2O^{18} in the distillate at zero and infinite times and the number of H_2O molecules/Cr atom which exchanged during the experiments. The experimental error for the final result is ±1%, and so the data indicate that the species initially holds back 5 oxygen atoms/Cr atom. This result means either that the species is $[Cr(H_2O)_4OH]_2^{+4}$ with all O atoms exchanging during the experiment or else that it is $[(H_2O)_5CrOCr(H_2O)_5]^{+4}$ with the oxo bridge not exchanging even after 1 month. To decide between the two possibilities, it is necessary only to calculate the expected infinite-time mole fraction of O^{18} from the isotopic enrichment of the water added. However, the calculated result will not exactly equal the experimental value due to isotope fractionation on distillation, which selectively removes the lighter isotope. If it is assumed that all O atoms bound to Cr exchange during the experiments, the ratio of calculated to observed *N* at infinite time is 1.011 ± 0.001 for all experiments. This value compares favorably with the corresponding value found by Hunt and Taube for simple chromic solutions.[6] On the other hand, if it assumed that there is a bridge O which does not exchange, the ratio of calculated to observed N^∞ is 0.984, which, being less than unity, is unreasonable. Thus, the experiments show conclusively that the dimer is $[Cr(H_2O)_4OH]_2^{+4}$.

Data obtained for the determination of the stoichiometry of the Cr^{+2}–O_2 reaction are given in Table II. The figures show that four Cr^{+2} per O_2 react. Since this is just the amount of O_2 needed to oxidize the Cr^{+2} to the +3 oxidation state, there is no appreciable side reaction, such as the net production of peroxide.

Data obtained for the rate studies are given in Table III. Plots of $-\log (\Delta C/\Delta t)$ *vs.* $-\log C$ gave slopes ranging between 1.95 and 2.06 and plots of $1/C$ *vs.* *t* were straight lines as can be seen from the apparent second-order rate constant (slope) calculated for each point in the last column of the table. For this purpose, initial Cr^{+2} concentrations were obtained by extrapolation. In addition to showing that the reaction is second order in Cr^{+2}, the results show (note especially the third, fourth, and fifth series which are identical except in acidity) that within the range of H^+ concen-

TABLE III

RATE OF O_2 OXIDATION OF Cr^{+2} AT 0°

Initial M	Sec.	M	$1/M$	$(M\ \text{sec.})^{-1}$
Cr^{+2} 0.589	15	0.392	2.55	5.7
H^+ 0.10	30	0.306	3.26	5.2
	45	0.245	4.08	5.3
	60	0.208	4.80	5.2
Cr^{+2} 0.455	15	0.330	3.03	5.5
H^+ 0.22	30	0.259	3.86	5.5
	45	0.213	4.69	5.5
Cr^{+2} 0.416	15	0.296	3.38	6.5
H^+ 0.10	30	0.222	4.50	7.0
	45	0.178	6.63	7.1
Cr^{+2} 0.416	15	0.294	3.41	6.6
H^+ 0.21	30	0.222	4.50	7.0
	45	0.179	6.59	7.0
Cr^{+2} 0.416	15	0.292	3.42	6.8
H^+ 0.40	30	0.221	4.52	7.1
	45	0.183	6.47	6.8
Cr^{+2} 0.645[a]	15	0.317	3.15	10.7[a]
H^+ 0.10	30	0.209	4.78	10.8
	45	0.157	6.35	10.7
Cr^{+2} 0.589[b]	15	0.178	5.62	26.1[b]
H^+ 0.10				

[a] Flow rate of air twice that of first set. [b] O_2 used in place of air at flow rate of first set.

tration 0.1 to 0.4 M, there is no dependence on H^+ concentration. Finally, comparison of the first set of experiments with the last two shows that if the flow rate of air is doubled, the rate doubles, of if O_2 is substituted for air, the rate is increased by about a factor of five. Thus, the over-all rate is apparently first order in O_2, but the interpretation of this result is not obvious. The fact that the rate of oxidation depends on the flow rate of the oxygen indicates that the oxygen does not reach solubility equilibrium prior to reacting with the chromous ion. However, the apparent second-order dependence on chromous concentration seems to mean that it is not a simple diffusion-controlled process that is being measured.

In order to obtain information concerning the reaction mechanism, duplicate experiments were run in which Cr^{+2} in O^{18}-enriched solvent was oxidized by O_2 of normal O^{18} content. In one experiment, the mole fraction of O^{18} in the distilled solvent was 6.571×10^{-3} prior to oxidation and 6.564×10^{-3} following oxidation. For the duplicate, the mole fractions O^{18} were 6.499×10^{-3} prior and 6.503×10^{-3} following. If one O atom/two Cr^{+2} atoms exchanged with the solvent, the mole fraction should have decreased by 0.04×10^{-3}. Apparently, both of the O atoms from O_2 are incorporated into the dimer without exchanging with solvent.

Conclusions

The formation of hydroxo rather than oxo bridges might possibly be dictated by greater thermodynamic stability; however, it is also possible that the product is dictated solely by kinetics since this product is not thermodynamically stable. It very slowly reacts to form, depending on conditions, either hexaaquochromic ion or a higher polymer.[3,4] The kinetic and tracer results give some indication as to the mechanism for the dimer formation from Cr^{+2} and O_2.

The fact that no oxygen exchange occurs during the oxidation rules out a number of possible mechanisms. A likely possibility, which is consistent with this result and also with the empirical second-order dependence on Cr^{+2}, is the formation of a peroxo-bridged dinuclear chromium species like that implied by the work of Joyner and Wilmarth in O_2 oxidation of ammoniacal Cr^{+2} solutions.[7] The only major difference between the mechanisms for the two systems is that in the present case subsequent reaction occurs (oxidation of the remaining half of the Cr^{+2}) without appreciable oxygen exchange. If Cr(IV) should be formed during the subsequent steps, it must be that there is too little time for its exchange prior to its reduction by the remaining Cr^{+2}. It might be noted that the Cr^{+2} concentrations employed here are considerably higher than those used in the ammonia system and the O^{18} sampling procedure necessitated in the present work is less precise. Therefore, it can be stated only that our results indicate that a peroxo-bridged intermediate is formed, and there is no indication that Cr(IV) is involved in following steps.

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