tural types for polymers would probably show the observed steric sensitivity to substituents.

A final point worthy of note concerns the explanation of a rather striking observation previously reported.[43] It was found that the ultraviolet absorption spectrum of Ni(AA)₂ in chloroform was very different from that in methanol, as shown here in Fig. 7. In methanol there is no doubt that the solute is present entirely as the solvated species Ni(AA)₂·2CH₃OH, and it thus shows an ultraviolet band quite typical of those found[43] in other acetylacetone complexes containing ordinary chelate rings. The anomalous spectrum found in chloroform can now be explained by the presence of both normal, nonbridging rings and bridging rings in the trimer. The former presumably give rise to the band at ∼ 300 mμ while the bridging rings cause the absorption at lower wave lengths.

Acknowledgments.—We are grateful to the United States Atomic Energy Commission (Contract At(30-1)-1965) and The Research Corporation for financial support. JPF expresses his

(42) Because of the small size of Ni compared to Pt, such a structure would not permit the placing of Ni atoms directly over the unique ring carbon atoms as in the Pt compounds. Instead, the nickel atoms would be above points near the centers of gravity of the OCCCO portions of the rings, and the bonding would have to be regarded as delocalized (sandwich-like). This may be fanciful, but it is not impossible, since the highest filled pi orbital of the ring would be a totally symmetric one according to a simple l.c.a.o. analysis, and the nickel atom possesses an empty orbital of the same symmetry (mainly p_z in character) in its valence shell.

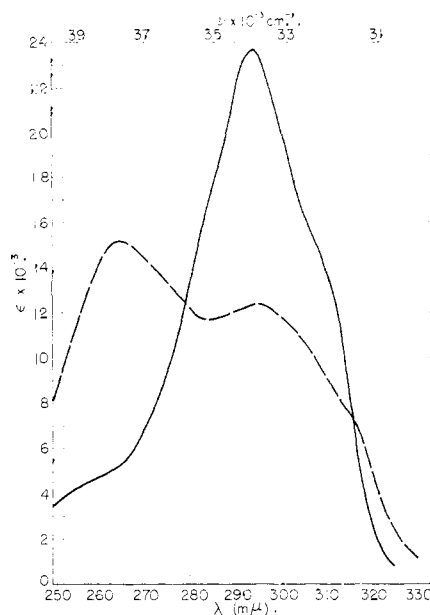(43) R. H. Holm and F. A. Cotton, J. Am. Chem. Soc., **80**, 5658 (1958).

Fig. 7.—The ultraviolet spectrum of bis-(acetylacetonato)-nickel(II) in methanol (solid line) and in chloroform (broken line).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

The Mechanism of the Exchange of Chromium(III) and Chromium(VI) in Acidic Solution[1-3]

By CARL ALTMAN AND EDWARD L. KING

The rate of exchange of chromium(III) and chromium(VI) in acidic aqueous solution at 94.8° is governed by the rate law: Rate = $[Cr(OH_2)_6^{+3}]^{1/3} [H_2CrO_4]^{2/3} \{k[H^+]^{-2} + k'\}$. On the basis of this rate law one concludes that the rate-determining step in the exchange is a reaction of chromium(III) and chromium(V), chromium(V) being in chemical equilibrium with chromium(III) and chromium(VI). The chromium-(III)-chromium(VI) exchange is completed by the relatively rapid exchange of chromium(V) and chromium(VI). The values of k and k' for solutions of ionic strength = 0.92 M are 6.6 × 10⁻⁷ moles l.⁻¹ sec.⁻¹ and 1.4 × 10⁻⁵ mole⁻¹ l. sec.⁻¹, respectively. (In arriving at the conclusions stated in this summary, the probable presence of appreciable amounts of dimeric chromium(VI) in the reaction solutions was neglected and a relatively uncertain value of the first dissociation constant of monomeric chromic acid was used.)

The rate of exchange of chromium(III) and chromium(VI) in acidic aqueous solution is very low. At 45° and a total chromium concentration of 0.02 gram atoms per liter, 43% exchange is observed in 1200 hours.[4] The slowness of this process is expected; the chromium species differ by three units in oxidation state and the coördination number of chromium differs in the two species,

(1) Taken in part from the Ph.D. thesis of Carl Altman, University of Wisconsin, 1957.

(2) Supported in part by grants from the United States Atomic Energy Commission (Contract AT(11-1)-64, Project No. 3) and the Research Committee of the Graduate School, University of Wisconsin.

(3) Presented at the 133rd National Meeting of the American Chemical Society, San Francisco, California, April 13–18, 1958.

(4) H. E. Menker and C. S. Garner, J. Am. Chem. Soc., **71**, 371 (1949).

chromium(III) exhibiting coördination number 6 in aquochromium(III) ion and chromium(VI) exhibiting coördination number 4 in chromate ion and dichromate ion. These factors suggest not only that the exchange rate may be low but also that the rate law may be more complicated than the usual second order rate laws exhibited by many exchange reaction systems. The objective of the present study was the elucidation of those features of the exchange reaction mechanism which are discernible from the form of the rate law.

Experimental Methods and Results

Reagents.—All solutions used in this work were prepared with doubly distilled water, the second distillation being from an alkaline permanganate solution using a Barnstead still.

Chromium(III) perchlorate was prepared by the reaction of chromium trioxide with a barely insufficient amount of formic acid in the presence of excess perchloric acid. The product which crystallized from the reaction mixture was washed with perchloric acid and twice recrystallized from 0.5-1 N perchloric acid. The product was free of chromium(VI) as determined by diphenylcarbazide reagent.[5] Solutions prepared from this reagent were judged to be relatively free of polymeric chromium(III) species.[6]

Sodium dichromate solutions were prepared using reagent grade material which was recrystallized for some of the experiments.

Solutions containing both sodium perchlorate and perchloric acid were prepared by treating reagent grade sodium carbonate with excess reagent grade perchloric acid.

The Cr^{51} tracer was obtained from the Oak Ridge National Laboratory in the form of a solution of chromium(III) chloride in hydrochloric acid. The tracer was converted to chromium trioxide by fuming in nitric acid followed by fuming in perchloric acid, in which chromium trioxide is insoluble. The chromium trioxide was washed with 72% perchloric acid and was then dissolved in water. Such solutions served as chromium(VI) tracer. Portions of the solution of chromic acid were reduced to chromium(III) with hydrogen peroxide, the excess of which was decomposed by the insertion of a small piece of platinized platinum into the solution. Such solutions served as chromium(III) tracer. The decay of the radioactivity of six different samples was followed for periods up to 8 half-lives in duration. The average of the observed values of the half-life was 28.0 ± 0.3 days. A value of 27.8 ± 0.3 days has been reported for the half-life of this nuclear species.[7]

Analytical Methods.—The total chromium content of solutions was obtained from the absorbancy of an alkaline solution at 375 mμ where chromate ion has a molar absorbancy index of 4815.[8] Oxidation of chromium(III) prior to this measurement was accomplished by peroxide.

The perchloric acid content of the chromium(III) perchlorate solutions was determined by a method already described.[9]

The sodium perchlorate content of the sodium perchlorate–perchloric acid solutions was obtained from the amount of sodium carbonate used, and the acidity was determined by titration with strong base.

Analyses of the acidic reaction mixtures for chromium(VI) were performed by the measurement of the absorbancy at 351 mμ, where the molar absorbancy indices of chromium(III) and chromium(VI) are 2.3 and 1600, respectively. Such analyses were performed upon each reaction mixture after the pre-heating period and in many cases also after the exchange period.

(5) B. E. Saltzman, *Anal. Chem.*, **24**, 1016 (1952); T. L. Allen, *ibid.*, **30**, 447 (1958).

(6) The polymerization of chromium(III) has been studied by a number of workers, *e.g.*, N. Bjerrum and C. Faurholt, *Z. physik. Chem.*, **130**, 584 (1927), H. T. Hall and H. Eyring, *J. Am. Chem. Soc.*, **72**, 782 (1950), M. Ardon and G. Stein, *J. Chem. Soc.*, 2095 (1956), and J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959). In the last of these papers, an ion-exchange procedure was developed for the separation of monomeric and polymeric chromium(III) species. One can, therefore, unambiguously establish values of the absorbancy indices of the polymeric species. In our work, done before the publication of this paper, qualitative use of absorbancy data allowed some information regarding the polymer content of chromium(III) perchlorate solutions. The absorbancy in the ultraviolet region is particularly sensitive to the presence of polymeric species. The more polymer-free a solution is, the lower will be the minimum in the absorbancy in the region of 230 mμ. In the present study a value of ~1.0 for the absorbancy index for hexaaquochromium(III) ion at 230 mμ was found; this is only slightly higher than the value observed by H. S. Gates and E. L. King (*J. Am. Chem. Soc.*, **80**, 5011 (1958)). The low maximum in the absorbancy curve for hexaaquochromium(III) ion at ~260 mμ is a convenient reference point. The chromium(III) perchlorate stock solution prepared for this work showed a value of 0.22 for A_{230}/A_{260} ($A = \log I_0/I$). This value is lower than values for this ratio calculated from spectral data reported by others for hexaaquochromium(III) ion (P. J. Elving and B. Zemel, *J. Am. Chem. Soc.*, **79**, 1281 (1957); R. A. Plane and J. P. Hunt, *ibid.*, **79**, 3343 (1957)). It cannot be asserted, of course, that the figure 0.22 represents the true value for polymer-free solution; the true value may be lower than this.

(7) W. S. Lyons, *Phys. Rev.*, **87**, 1126 (1952).

(8) G. W. Haupt, *J. Research Natl. Bur. Standards*, **48**, 414 (1952).

(9) E. L. King and J. A. Neptune, *J. Am. Chem. Soc.*, **77**, 3187 (1955).

The Exchange Experiments.—The low rate of this exchange reaction has imposed certain experimental difficulties. At the elevated temperatures required to make the rate conveniently measurable, a portion of the chromium-(VI) was reduced by trace impurities, a process which appeared to induce exchange. Such difficulties were largely eliminated by preheating the reaction solution containing all reagents except the tracer at the reaction temperature for 16 to 25 days. In this time interval as much as a few per cent of the chromium(VI) was reduced in most of the solutions.[10] The chromium content of the tracer solutions added after this preheating period was, at most, a few per cent of the amount of chromium in the same oxidation state in the reaction solution.[11] In some experiments, individual reaction aliquots were sealed in tubes to be immersed in the thermostat; in others, a particular solution was sampled at various times. The temperature of the thermostat was 94.8 ± 0.1°. The samples were kept in the dark; no attempt was made to investigate the influence of light upon the reaction rate. At most 2-3% of the chromium(VI) was reduced during the exchange period.

Although the chromium(III) perchlorate stock solution was relatively free of polymeric species, it cannot be asserted that polymeric species did not grow into the reaction solutions during the exchange experiments. There was no kinetic manifestation of the presence of such species, and it has been shown in earlier work[12] that such species are not present at significant concentrations in solutions in which the formation of polymers is more likely than it is in the present work; the solutions studied earlier were, however, heated at 94.6° for a shorter time interval.

Determination of the Extent of Exchange.—Portions of reaction mixture were analyzed for Cr^{51} activity in the two oxidation states by the following procedure. After cooling the reaction mixture to room temperature, amounts of inactive chromium(III) perchlorate and/or sodium chromate were added to bring the concentration of chromium in each oxidation state to a standard level. The pH value of the solution was adjusted to 2-2.5 and excess lead nitrate was added. The final concentration of lead ion in solution after the precipitation of lead chromate was 10^{-2} molar. The precipitated lead chromate was separated from the mother liquor by centrifugation, washed and mounted as a sample of constant thickness over a standard area on filter paper by the conventional "chimney" arrangement. The chromium(III) in the decantate plus washings was converted to chromium(VI) by peroxide after the solution was made alkaline. The solution was reacidified to a pH-value of 2-2.5 after the excess peroxide was first decomposed. Additional lead nitrate was added and the lead chromate was separated and mounted as before. Under the conditions employed, the procedure was effective in separating chromium(III) and chromium(VI), each state being recovered to an extent greater than 98%.

The extent of exchange was calculated on the basis of the activity of the chromium(III) and chromium(VI), the known composition of the solution, and the total activity present in the sample as established by the values of the sum of the chromium(III) and chromium(VI) activities in all samples containing the same amount of tracer. In arriving at the average value of the extent of exchange at a particular time, the values obtained from each of the two fractions were weighted inversely proportional to the square of the activity in the fraction. In general, the activity of a sample was established by the observation of 10^4 counts or more.

The Rate of Exchange.—The fraction of exchange, f, as a function of time was fitted, by the method of averages, to the equation

$$\log (1 - f_t) = \log (1 - f_0) + \frac{R}{2.303} \times \left\{ \frac{[Cr^{III}] + [Cr^{VI}]}{[Cr^{III}] \times [Cr^{VI}]} \right\} t \quad (1)$$

(10) The exchange rate observed in one solution in which ~50% of the chromium(VI) was reduced will not be reported. Two other solutions in which ~20% of the chromium(VI) was reduced in the preheating period will be considered.

(11) In the runs at the lowest concentration of chromium(VI) (exp. 1 and 6), approximately two-thirds of the chromium(VI) was added as tracer; reducing impurities are not, however, likely to be added with the chromium(VI) tracer.

(12) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

in which R is the rate of exchange (in gram atoms of chromium per liter per second), $[Cr^{III}]$ and $[Cr^{VI}]$ stand for the stoichiometric concentrations of chromium(III) and chromium(VI), in gram atoms per liter, and f_t and f_0 are the values of the fraction of exchange at times t and zero, respectively. The line was not restricted to go through the origin, and the values of f_0 so obtained were in the range 0.00 to 0.13 with the average value being 0.05. In general, the experimental points were reasonably close to the straight line (equation 1); the average difference of the individual values of f/f_{calcd} from unity was 0.04 if the 4.4% of the points with $|(f/f_{calcd}) - 1| > 0.2$ were omitted. The number of points per experiment was in the range 3 to 10, with the average being 7. The number of "half-lives" which elapsed between the first and last experimental point was in the range 0.4 to 3.3, with the average being 1.9. The magnitude of the "half-life" in the thirty-three experiments being reported was between 9 and 700 hr. In Table I the results of these experiments are summarized.

TABLE I

THE RATE OF EXCHANGE OF CHROMIUM(III) AND CHROMIUM(VI) IN ACIDIC SOLUTION AT 94.8°[a]

	Concentrations (at 94.8°) (in gram atoms per liter)			R
	$[Cr^{III}]$	$[Cr^{VI}]$	$[H^+]$	(g. atom l. $^{-1}$ sec. $^{-1}$)
1	0.0422	0.00023	0.098	4.55×10^{-9}
2	.0422	.00123	.098	1.20×10^{-8}
3	.0422	.0109	.098	3.89×10^{-8}
4	.0424	.0282	.098	9.9×10^{-8}
5	.0422	.0845	.099	2.57×10^{-7}
6	.0422	.00024	.098	$5.1_1 \times 10^{-9}$
7	.0422	.00123	.098	1.62×10^{-8}
8	.0444	.0845	.100	2.97×10^{-7}
9	.0107	.0844	.100	2.08×10^{-8}
10	.0423	.0844	.099	1.83×10^{-7}
11	.0845	.0844	.099	4.94×10^{-7}
12	.169	.0845	.099	1.15×10^{-6}
13	.00429	.0437	.0397	1.46×10^{-8}
14	.00429	.0437	.0643	6.05×10^{-9}
15	.00429	.0437	.1292	2.65×10^{-9}
16	.00429	.0437	.265	1.54×10^{-9}
17	.00429	.0437	.4045	1.24×10^{-9}
18	.00429	.0437	.545	1.18×10^{-9}
19	.00429	.0437	.687	1.11×10^{-9}
20	.00429	.0437	.829	1.21×10^{-9}
21	.00176	.0437	.127	7.05×10^{-10}
22	.00297	.0437	.129	1.51×10^{-9}
23	.00587	.0437	.131	4.96×10^{-9}
24	.00851	.0437	.132	6.57×10^{-9}
25	.0146	.0437	.138	1.56×10^{-8}
26	.0291	.0437	.150	4.46×10^{-8}
27	.0422	.0437	.157	6.40×10^{-8}
28	.0843	.0438	.188	1.23×10^{-7}
29	.1266	.0438	.216	1.99×10^{-7}
30	.0843	.0760	.103	4.33×10^{-7}
31	.0845	.0758	.150	3.25×10^{-7}
32	.0845	.0758	.199	2.34×10^{-7}
33	.0845	.0758	.246	1.98×10^{-7}

[a] In each series the ionic strength was held approximately constant with sodium perchlorate. The values of the ionic strength were: exp. 1–5, $I = 0.7 \pm 0.02\ M$; exp. 6–8, $I = 0.47\ M$; exp. 9–12, $I = 1.16\ M$; exp. 13–20, $I = 0.91 \pm 0.03\ M$; exp. 21–29, $I = 0.93 \pm 0.02\ M$; exp. 30–33, $I = 0.79\ M$.

The Equilibria Existing in the Reaction Solutions.—An empirical rate law from which conclusions regarding mechanism are to be drawn must involve the concentrations of species and not stoichiometric concentrations. It is necessary, therefore, to take into account all equilibria which appreciably influence the concentration of any species upon which the rate depends, but not those which do not alter appreciably the concentration of such species.

The reaction

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^- + H_2O$$
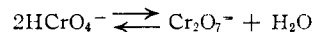
occurs to an appreciable extent at 25° in the chromium(VI) concentration range studied in this work.[13] The equilibrium quotient for this reaction at 94.8° is not known with certainty. The value of ΔH^0 determined by La Mer and Read,[14] which leads to the result that no more than 14% of chromium(VI) exists as dimers at the highest concentrations studied in this work, was considered to be correct in the original interpretation of the present work.[1] The recent study by Hepler[15] suggests, however, a much smaller value of ΔH^0 ($= -4.7 \pm 0.3$ kcal./mole dichromate ion); this value leads to the conclusion that as much as ~60% of chromium(VI) is present as dimers at the highest concentration studied. Although ignoring the presence of ~14% dimers might be justifiable, the same cannot be said of ignoring the existence of 60% of the chromium(VI) in the form of dimers.

To discuss the consequences of the presence of a significant amount of dichromate ion in the reaction solutions, one must anticipate the interpretation of this study. The rate-determining step in the exchange appears to be a reaction of chromium(III) and chromium(V), which is in chemical equilibrium with chromium(III) and chromium(VI). The possible existence of a dimeric species containing one atom of chromium(V) and one atom of chromium(VI) has been suggested by Westheimer[16] on the basis of observations on the rate of the iron(II)–chromium(VI) reaction. If the extent to which this chromium(V)–(VI) species forms is comparable to the extent of formation of dimeric chromium(VI) at the same concentration of chromium(VI), the dependence of the equilibrium concentration of chromium(V) upon the concentrations of chromium(III) and chromium(VI) is not greatly altered by the dimerization of chromium(VI). At low concentrations of chromium(VI), with both chromium(V) and chromium(VI) being monomeric, the equilibrium concentration of chromium(V) is dependent upon $[Cr^{III}]^{1/3}[Cr^{VI}]^{2/3}$. At high concentrations of the chromium(VI), with both chromium(V) and chromium(VI) being present as dimeric species containing chromium(VI), the equilibrium concentration of chromium(V) is dependent upon $[Cr^{III}]^{1/3}[Cr_2^{VI}]^{5/6}$, the chemical equation for equilibrium in these solutions being

$$2Cr^{III} + 5Cr_2^{VI} \rightleftharpoons 6Cr^V \cdot Cr^{VI}$$
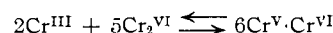
Because the dimerization of chromium(VI) need not, therefore, necessarily manifest itself in a dramatic way in the reaction orders, the interpretation of the exchange to be presented in this paper will not take into account the uncertain extent of dimerization of chromium(VI) in the reaction solutions at 94.8°.

The value of the first acid dissociation quotient for monomeric chromic acid H_2CrO_4 is relatively uncertain. Tong and King[13b] have interpreted an approximately 10% variation in the average absorbancy index of chromium(VI) (extrapolated to low concentrations of chromium(VI)) with acidity in solutions of ionic strength equal to 1.0 M to give a value of $Q_{11} = [H^+][HCrO_4^-]/[H_2CrO_4] = 1.2$. In obtaining this value, it was assumed that the activity coefficient quotient $f_{H^+} \times f_{HCrO_4^-}/f_{H_2CrO_4}$ remained constant as the medium changed from 1 M lithium perchlorate to 1 M perchloric acid. The uncertainty in this assumption probably could contribute an uncertainty of 20–30% in the value of Q_{11}. In addition to the uncertainty regarding the constancy of the relevant quotient of activity coefficients, it cannot be considered certain that the absorbancy indices of the species $HCrO_4^-$ and H_2CrO_4 at wave lengths rather distant from the wave length of maximum absorption are independent of the composition of the medium at constant ionic strength. This relatively uncertain value of Q_{11} has been corrected to 94.8° and the appropriate value of ionic

(13) (a) J. D. Neuss and W. Rieman, *J. Am. Chem. Soc.*, **56**, 2238 (1934); (b) J. Y.-P. Tong and E. L. King, *ibid.*, **75**, 6180 (1953); (c) W. G. Davies and J. E. Prue, *Trans. Faraday Soc.*, **51**, 1045 (1955).

(14) V. K. La Mer and C. L. Read, *J. Am. Chem. Soc.*, **52**, 3098 (1930); these authors report a value of -13.6 kcal./mole for ΔH^0 for $2HCrO_4^- = Cr_2O_7^- + H_2O$, in the calculation of which a value of $Q = 52.6$ was used. If the value $Q = 35.5^{13b}$ is used, the calculated value of ΔH^0 is -14.6 kcal./mole.

(15) L. G. Hepler, *J. Am. Chem. Soc.*, **80**, 6181 (1958).

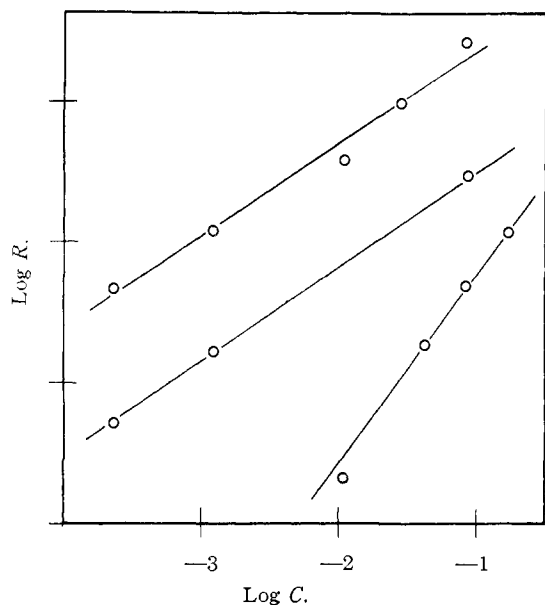(16) F. H. Westheimer, *Chem. Revs.*, **45**, 419 (1949).

Fig. 1.—The rate of exchange as a function of the concentration of chromium(III) and chromium(VI): upper line, chromium(VI) dependence, exp. 1–5; middle line, chromium(VI) dependence, exp. 6–8; lower line, chromium(III) dependence; exp. 9–12 (The straight lines have slopes 2/3 and 4/3.)

strength by assuming the values of $\Delta S^0 = -22$ e.u. at 25° and $\Delta C_p^0 = -40$ e.u.[17] The ionic strength dependence of the value of Q_{11} at each of the two relevant temperatures has been assumed to be similar to that exhibited by acetic acid.[18]

The acid dissociation constant value for hexaaquochromium(III) ion at 95° obtained by Postmus and King[12] has been used in calculating the hydrogen ion contributed to the solution by this weak acid.

Chromium(III) and chromium(VI) are known to interact to form complexes which are quite unstable at 25°.[9] It has been assumed that such species do not tie up a significant fraction of the chromium(III) or chromium(VI) in the reaction solutions at 94.8°, and the kinetic data do not refute this assumption.
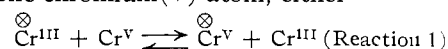
Discussion of Results

Consideration of the results of experiments 1–12 leads to the conclusion that the rate of exchange is proportional to the product $[Cr^{III}]^{4/3}[Cr^{VI}]^{2/3}$. These reaction orders are consistent with a reasonable mechanism. Reaction orders for chromium(III) and chromium(VI) which differ from these by only one-sixth of a unit, an order of $3/2$ with respect to chromium(III) and an order of $1/2$ with respect to chromium(VI), are also consistent with a reasonable mechanism, and the basis of our choice should, therefore, be specified. The values of R in experiments 6–8, in which the concentration of chromium(VI) varies by a factor of $\sim$350, are nicely consistent with the $2/3$ order in chromium(VI) as is shown by the plot in Fig. 1. The chromium(VI) dependence of R obtained in experiments 1–5, with the same range of chromium(VI) concentrations, is also more nearly $2/3$-order than

(17) K. S. Pitzer, *J. Am. Chem. Soc.*, **59**, 2365 (1937).

(18) H. S. Harned and F. C. Hickey, *ibid.*, **59**, 1284 (1937). Since the maximum temperature studied by these authors was 40°, our approximation involves a considerable extrapolation. The assumed values of Q_{11} at 94.8° at the several values of I were: $I = 0.47\ M$, $Q_{11} = 0.136$; $I = 0.7{-}0.8\ M$, $Q_{11} = 0.14$; $I = 0.9\ M$, $Q_{11} = 0.139$; $I = 1.16\ M$, $Q_{11} = 0.136$.

$1/2$-order, although a smooth curve corresponding to varying order would fit the data even better than the straight line. The conclusion being drawn from experiments 1–8 is that the reaction order with respect to chromium(VI) is $2/3$. The reasonable mechanism which leads to a chromium-(VI) order of $2/3$ leads to a chromium(III) order of $4/3$. The values of R obtained in experiments 10–12 are nicely consistent with $R \propto [Cr^{III}]^{4/3}$; the point for experiment 9, the experiment with the lowest concentration of chromium(III), does not fall on this straight line. (A possible rationalization of this will be mentioned later.)

These reaction orders suggest, provisionally, that the transition state for the exchange reaction contains two chromium atoms ($4/3 + 2/3 = 2$) with an average oxidation number of $+4$ per chromium atom ($4/3 \times (+3) + 2/3 \times (+6) = 2 \times (+4)$).[19] Consistent with this is a rate-determining step for exchange involving one chromium(III) atom and one chromium(V) atom, either

$$\overset{\otimes}{Cr}^{III} + Cr^V \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{1cm}{0pt}}} \overset{\otimes}{Cr}^V + Cr^{III} \text{ (Reaction 1)}$$

or

$$\overset{\otimes}{Cr}^{III} + Cr^V \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{1cm}{0pt}}} \overset{\otimes}{Cr}^{IV} + Cr^{IV} \text{ (Reaction 2)}$$

with the chromium(V) being in equilibrium with chromium(III) and chromium(VI), in which case $[Cr^V] \propto [Cr^{III}]^{1/3}[Cr^{VI}]^{2/3}$. To complete the exchange between chromium(III) and chromium(VI), it is necessary only that a relatively rapid process exist for the exchange of chromium(V) and chromium(VI). One such process is the direct "electron-transfer"

$$\overset{\otimes}{Cr}^V + Cr^{VI} \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{1cm}{0pt}}} \overset{\otimes}{Cr}^{VI} + Cr^V \text{ (Reaction 3)}$$

which would be expected to occur relatively rapidly if chromium(V) is, like chromium(VI), an oxygenated species involving four tetrahedrally coordinate oxygen atoms.[20]

One possible mechanism for the establishment of the equilibrium concentration of chromium(V) is

$$\overset{\otimes}{Cr}^{III} + Cr^{VI} \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{1cm}{0pt}}} \overset{\otimes}{Cr}^{IV} + Cr^V \text{ (Reaction 4)}$$

followed by reaction 2. Equilibrium in reaction 4 would be expected to be rapidly established[21] if, in addition to the similarity of the coördination numbers of chromium(V) and chromium(VI) already suggested, chromium(IV) exhibits coördination number six toward oxygen in aqueous solution, thus resembling chromium(III).[22] That

(19) This type of calculation is based upon the assumption that the transition state is in equilibrium with chromium(III) and chromium(VI). It will be shown in footnote 26 that this need not be the case in the present exchange system.

(20) The chromium(V) compound Ba$_3$(CrO$_4$)$_2$ is isomorphous with barium phosphate Ba$_3$(PO$_4$)$_2$ which does contain a tetrahedral anion (R. Scholder, *Angew. Chem.*, **65**, 240 (1953); **66**, 461 (1954)). Manganese(VI) and manganese(VII), which are tetrahedrally coördinated with oxygen atoms in manganate ion and permanganate ion and are isoelectronic with chromium(V) and chromium(VI), exchange very rapidly ($R = 710 \pm 30$ l. moles^{-1} sec.$^{-1} \times$ [MnO$_4$$^-$][MnO$_4$$^-$] at 0°; J. C. Sheppard and A. C. Wahl, *J. Am. Chem. Soc.*, **79**, 1020 (1957); L. Gjersten and A. C. Wahl, *ibid.*, 1572 (1959)).

(21) The analogous equilibria in the plutonium and neptunium systems are rapidly established (R. E. Connick, *J. Am. Chem. Soc.*, **71**, 1528 (1949); J. C. Sullivan, D. Cohen and J. C. Hindman, *ibid.*, **76**, 4275 (1954)).

(22) J. Y.-P. Tong and E. L. King, *J. Am. Chem. Soc.*, **82**, 3805 (1960).

the establishment of chemical equilibrium by reactions 2 and 4 need not simultaneously establish exchange equilibrium is a consequence of the very low equilibrium concentrations of chromium(IV) and chromium(V) under all conditions; a very small amount of net chemical change, during which but very little exchange occurs, establishes chemical equilibrium among the chromium oxidation states.[23]
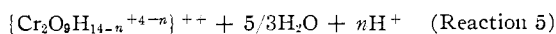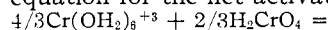
The hydrogen ion concentration dependence of the exchange rate is established by experiments 13–20. Before seeking the functional dependence of R upon [H$^+$], one must take account of the fact that two monomeric chromium(VI) species H$_2$-CrO$_4$ and HCrO$_4^-$ are present at appreciable concentrations. Using the relationship

$$[H_2CrO_4] = [Cr^{VI}] \times \{[H^+]/(Q_{11} + [H^+])\}$$

one obtains

$$F([H^+]) = \frac{R}{[Cr(OH_2)_6^{+3}]^{4/3}[H_2CrO_4]^{2/3}} =$$
$$\frac{R\,(Q_{11} + [H^+])^{2/3}}{[Cr^{III}]^{4/3}[Cr^{VI}]^{2/3}[H^+]^{2/3}} \quad (2)$$

where $F([H^+])$ is expected to be a function of the hydrogen ion concentration alone if the appropriate quotients of activity coefficients are constant at constant ionic strength. The balanced equation for the net activation process[24]
4/3Cr(OH$_2$)$_6^{+3}$ + 2/3H$_2$CrO$_4$ =

$$\{Cr_2O_9H_{14-n}^{+4-n}\}^{++} + 5/3H_2O + nH^+ \quad \text{(Reaction 5)}$$

where n is an integer, indicates that $F([H^+])$ should contain integral powers of [H$^+$].[25] The general shape of the plot of log $F([H^+])$ versus log [H$^+$] and the limiting slopes at high (0.5–0.8 M) and low (0.04–0.06 M) hydrogen ion concentration suggests the dependence

$$F([H^+]) = k[H^+]^{-2} + k' \quad (3)$$

Fitting this equation by the method of averages to the values of $F([H^+])$ from experiments 13 to 20 gives $k = 6.6 \times 10^{-7}$ mole l.$^{-1}$ sec.$^{-1}$ and $k' = 1.4 \times 10^{-5}$ mole^{-1} l. sec.$^{-1}$. The experimental values and the calculated curve are given in Fig. 2. The average difference between observed and calculated values is 5%.

(23) The same situation exists in other exchange reaction systems. In the iodate-iodine system (O. E. Myers and J. W. Kennedy, *J. Am. Chem. Soc.*, **72**, 897 (1950); R. E. Connick and Z. Z. Hugus, Brookhaven National Lab., Report BNL-C-8, 164 (1948)), exchange proceeds by a pathway involving iodate and iodide, the low equilibrium concentration of iodide being established by the reaction

$$3I_2 + 3H_2O \rightleftharpoons 5I^- + IO_3^- + 6H^+$$
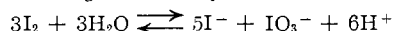
In the silver(I)-silver(II) system (B. M. Gordon and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 273 (1958)), exchange proceeds by a pathway involving silver(I) and silver(III), the low equilibrium concentration of silver(III) being established by the reaction

$$2Ag^{II} \rightleftharpoons Ag^I + Ag^{III}$$

In each of these cases and in the example provided by the present study, the pathway by which chemical equilibrium is established is also a pathway for the exchange reaction. Chemical equilibrium is established with the occurrence of so small an amount of net chemical change, however, that the extent of exchange accomplished during the establishment of equilibrium is negligible.

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

(25) This implication regarding the powers to which [H$^+$] is raised in the expression for $F([H^+])$ is a consequence of balancing the charge in the equation. A feature of the transition-state implied by this formulation, the presence of nine oxygen atoms, is introduced for later discussion.
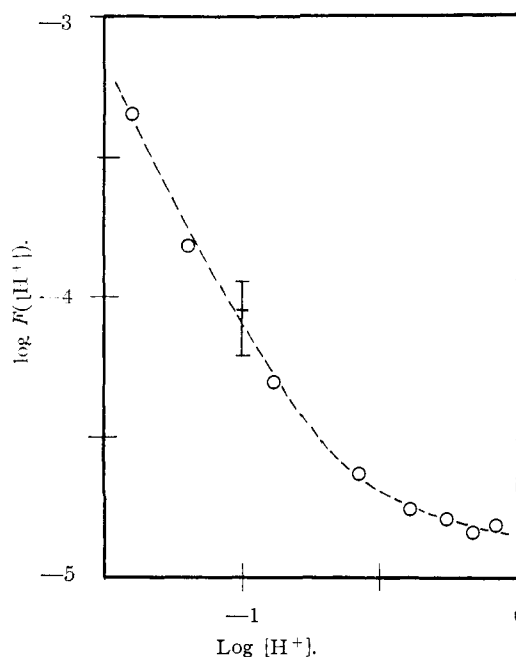

Fig. 2.—The hydrogen ion dependence of the rate of exchange. The vertical line at [H$^+$] = 0.10 M show the range of values given by exp. 21–29, corrected to this value of [H$^+$]. The experimental points are for exp 13–20. (The dashed line is calculated using values of k and k' given in text.)

In experiments 21 to 29, the chromium(III) concentration varies over a 70-fold range and extends to a much lower value than in experiment 9. Before analyzing these data, the mild hydrogen ion concentration variation must be taken into account; this was done with equation 3 using the relative values of k and k' established for this same ionic strength. The values of R, so "normalized" to the same concentration of hydrogen ion, when fit by the method of averages to an equation, log $R = a + b$ log [Cr^{III}], give a value of $b = 1.45$; the average difference between the "normalized" observed values of R and the calculated values is 11%. If the value of b is fixed at 1.33 and values of a calculated from each experiment, the average difference between the individual values of a and the average value is 22%. The superior fit of the 1.45 order may have significance,[26] but, considering

(26) If exchange were occurring by reactions 1 and 3 (or 4) with only reaction 4 at equilibrium, the dependence of R upon the concentrations would be $R \alpha [Cr^{III}]^{3/2}[Cr^{VI}]^{1/2}$. Since the rate of establishment of chemical equilibrium via reaction 2 coupled with reaction 4 can be shown to be governed by the rate law d ln $\{[Cr^V]^3 - [Cr^V]^3_\infty\}/$ d$t = -3\ k_2[Cr^{III}]$, where k_2 is the rate constant for the reaction of Cr^{III} and Cr^V in reaction 2, true equilibrium may not be attained in these experiments with low [Cr^{III}] even though it is attained in experiments 10–12. The consequences of exchange occurring under these non-equilibrium conditions are interesting. In particular, it is to be noted that the mean oxidation number of chromium in the transition state for the exchange under such conditions is not correctly derived from the reaction orders with respect to chromium(III) and chromium(VI); *i.e.* $1/2\{(3/2) \times 2 + (1/2) \times 6\} \neq 4$. The rationalization of the anomaly lies in the fact the reaction (reaction 4) producing chromium(V) also produces chromium(IV) which does not take part in the exchange. Since no net chemical change is occurring in the exchange reaction, a mechanism is acceptable which involves a step producing two unstable intermediates only one of which reacts further; this could not be the case if a net chemical change by a non-chain mechanism were under consideration. (The mechanism proposed for

the scatter of the experimental points and the fact that a significant change in the activity coefficients may accompany the replacement of sodium perchlorate by chromium(III) perchlorate while keeping the ionic strength constant, it does not seem justifiable to assert that the exchange in experiments 9 and 21–29 is governed by a rate law different from equation 2 coupled with equation 3.

The several series of experiments were performed at different values of the ionic strength. A comparison of the results in the several series is made by calculating the value of $F([H^+])$ for $[H^+] = 0.1\ M$. These values are

| I ($\times$ 1. mole^{-1})	0.47	0.70	0.79
Exps.	6–8	1–5	9–12
$10^5 \times F([0.1]) \times$ moles l.$^{-1}$ sec.	17 ± 1	13 ± 2	11 ± 1
I ($\times$ 1. mole^{-1})	0.91	0.93	1.16
Exps.	13–20	21–29	30–33
$10^5 \times F([0.1]) \times$ moles l.$^{-1}$ sec.	8.0 ± 0.4	9.0 ± 1.3	13.0 ± 0.5

That $F([0.1])$ should show the indicated dependence upon I is consistent with the fact that the path with $n = 2$ (see reaction 5), with $(\Delta Z^2)^{\ddagger} = -6$, is dominant at $[H^+] = 0.1\ M$. (The value of $(\Delta Z^2)^{\ddagger}$ is the sum of the squares of the charges on the products minus the sum of the squares of the charges on the reactants in the balanced chemical equation for the net activation process,[24] reaction 5 in the present study.) With this sign for $(\Delta Z^2)^{\ddagger}$, the rate coefficient should decrease with an increase of I at low values of I; the opposite trend at high I is not anomalous.

the exchange of manganese(II) and manganese(VI) by A. W. Adamson (*J. Phys. Chem.*, **55**, 293 (1951)) consisting of the rate-determining exchange of manganese(III) and manganese(IV) also leads to reaction orders 3/2 and 1/2, respectively, which do not suggest the correct mean oxidation number for manganese in the transition state 1/2 ((3/2) $\times$ 2 + (1/2) $\times$ 7) $\pm$ 3.5.)

The rationalization of the fact that the two reaction pathways have transition-states differing in composition by two protons may lie in the symmetry of the transition-state for exchange if such exchange occurs in a single step (*e.g.* reaction 1). If different transition-states for this reaction involve the same bridging atom (or group), the composition of these symmetrical transition states must differ from one another by an even number of atoms. For $n = 0$ and $n = 2$ (see reaction 5), these transition-states could have the geometry
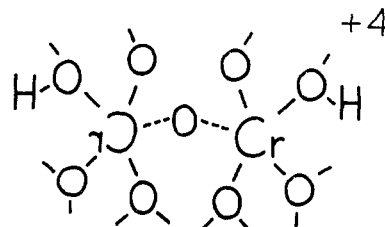
with the indicated H's included for $n = 0$ and omitted for $n = 2$. The necessity of chromium(III) reducing its coördination number to 5 before forming this transition state does not impose upon the reaction

$$Cr(OH_2)_6^{+3} \rightleftharpoons Cr(OH_2)_5^{+3} + H_2O$$
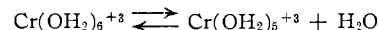
a rate too large to be consistent with the observed rate of O^{18} exchange between water and hexa-aquochromium(III) ion.[27] The shuffling of protons necessary in going from the predominant form of the reactants to a symmetrical transition-state such as this would be accomplished in relatively rapid equilibria and should not be considered a deterrent to the formation of the symmetrical transition-state.

(27) J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951); R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952); J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954).

Alkaline Earth–Tantalum–Oxygen Phases Including the Crystal Structure of an Ordered Perovskite Compound, Ba₃SrTa₂O₉

BY FRANCIS GALASSO,[1] JAMES R. BARRANTE AND LEWIS KATZ

Further investigation of the perovskite-like phases Ba₃CaTa₂O₉ and Ba₃SrTa₂O₉ indicates that an X-ray powder pattern of the first can be indexed on a 4.17 Å. cubic cell, while for the second a hexagonal cell with $a = 5.95$, $c = 7.47$ Å. is required. The structure of the latter can be described as a repetition of three close packed BaO₃ layers with Sr and Ta in an ordered arrangement in octahedral holes. When this phase is heated in the presence of silica it changes to a Ba₅Ta₄O₁₅ type compound. From a plot of cell sizes for solid solutions of Ba₅Ta₄O₁₅ and Sr₅Ta₄O₁₅, it was found that the cell size of the product on heating corresponded to the composition (Ba.₈₅Sr.₁₅)₅Ta₄O₁₅.

Introduction

In previous work compounds of the general formula Ba₃M^{II}Ta₂^{V}O₉ have been reported with M^{II} = Sr, Ca, Zn, Fe, Co, Ni.[2] An inspection of their X-ray powder photographs showed that

(1) United Aircraft Research Laboratories, East Hartford, Connecticut.

(2) Francis Galasso, Lewis Katz and Roland Ward, *J. Am. Chem. Soc.*, **81**, 820 (1959).

these compounds have structures related to that of perovskite. This relationship may be emphasized by writing the formula Ba(M₁/₃^{II}Ta₂/₃^V)O₃ with the parentheses indicating the octahedrally coördinated cations. Further X-ray and preparation studies on the compounds with M^{II} = Ca and Sr were undertaken since it seemed less likely that these large cations would occupy octahedral positions equivalent to those of tantalum.