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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

# The Formation of a Dinuclear Cr(III) Species by Oxidation of Chromous Solutions[1]

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The dissolved chromic species formed when chromous perchlorate is oxidized in aqueous solution by molecular oxygen is shown by visible spectrum and behavior toward a cation-exchange resin to be the same as the hydrolytic polymer which forms first when chromic solutions are refluxed. Analysis of the solution for chromium, perchlorate and free acid shows the species to have a charge of +2 per Cr atom. Ion-exchange experiments indicate that +4 is the most likely charge for the entire species, which is consistent with its being dinuclear Cr(III) species with the two Cr atoms bound by either an O or two OH bridges. This same product can be formed by oxidation of $Cr^{++}$ with $Tl^{+3}$ and in lower yield by $ClO_3^-$, HClO, $Cr_2O_7^=$ and $H_2O_2$. It is absent when the oxidation is performed with $Fe^{+3}$, $Cu^{++}$, $Cl_2$ or $Br_2$. It is believed that the dimer results from reaction of the intermediate Cr(IV) with $Cr^{++}$.

Products formed when acidified chromous perchlorate solutions are oxidized have been investigated previously. Taube and Myers[2] found that the oxidation product depends on the nature of the oxidizing agent. Reagents such as $Fe^{+3}$ or $H_2O_2$ produce hexaquo chromic ion, $Cr(H_2O)_6^{+3}$, but reagents such as $Co(NH_3)_5Cl^{++}$, $I_2$ or $Br_2$ produce the complex $Cr(H_2O)_5X^{++}$ (X being Cl, I, Br, respectively). They showed that the halogen atom in the final complex originated in the oxidizing agent, thereby indicating that the reaction proceeds with halogen atom transfer rather than by electron transfer alone. A third type of product of the oxidation of chromous perchlorate solutions was reported by Ardon and Stein.[3] It is obtained by oxidation of acidic chromous perchlorate solution with molecular oxygen. The blue-green solution so obtained was shown to contain chromium only in the +3 oxidation state which, however, was neither $Cr(H_2O)_6^{+3}$ nor one of its mononuclear substitution products. It was concluded that this product must be a hydrolytic polymer of $Cr^{+3}$.

Polynuclear hydrolysis products of $Cr^{+3}$ are known to exist in aged or boiled solutions of chromic salts.[4] A characteristic property of these products is the slow rate of their formation and decomposition. In contrast to mononuclear hydrolysis products, such as $Cr(H_2O)_5OH^{++}$ which are in rapid equilibrium with the hexaquo chromic ion and are immediately converted to it by increasing acidity, the hydrolytic polymers react only very slowly with acid and persist for long periods in highly acid solution. It is generally agreed that these polynuclear compounds consist of a number of chromic ions, with water molecules of hydration, connected by "ol" bridges, $Cr{-}\overset{H}{O}{-}Cr{-}\overset{H}{O}{-}$, or "oxo" bridges, Cr–O–Cr–O–. Various structural formulas have been proposed for these products,[4] but none of them ever was proved. Neither crystallization, nor identification of individual compounds has been reported. The main difficulty in investigating these compounds is their extreme solubility and the fact that the solutions usually contain more than one component.

Laswick and Plane[5] succeeded in separating the boiled solutions of chromic perchlorate by means of ion-exchange chromatography into three main components: (1) unchanged hexaquo chromic ion $Cr(H_2O)_6^{+3}$ which constituted the main soluble component at all times and could be eluted from cation-exchange resin (Dowex 50) by 1 *M* $HClO_4$; (2) a polynuclear blue-green species which was formed quickly upon boiling the solution and attained a steady concentration after a few minutes of boiling, and could not be eluted with 1 *M* $HClO_4$, but was eluted with a solution of 0.02 *M* $La(ClO_4)_3$ at *p*H 2; (3) a second, green, polynuclear species which formed in the boiling solution at a much slower rate and was not eluted by 0.02 *M* $La(ClO_4)_3$ but could be eluted by 0.2 *M* $La(ClO_4)_3$ at *p*H 2. The visible absorption spectrum of each compound was measured and the various concentrations in the boiling solutions were determined.

A study of the formation of polynuclear Cr(III) by the reaction between oxygen and chromous ion is important for an understanding of the mechanism of this and possibly other oxidations by molecular oxygen. The purpose of the present work is to identify the reaction product, making use of the chromatographic method employed by Laswick and Plane,[5] to learn whether this product is identical with one of those obtained in boiled chromic

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(2) H. Taube and H. Myers, THIS JOURNAL, **76**, 2103 (1954).

(3) M. Ardon and G. Stein, *J. Chem. Soc.*, 2095 (1956).

(4) Subject reviewed by C. L. Rollinson in "Chemistry of the Coordination Compounds," Edited by J. C. Bailar, Jr., and D. H. Busch, Reinhold Publ. Corp., New York, N. Y., 1956. Chapter 13.

(5) J. A. Laswick and R. A. Plane, Paper presented at 133rd National Meeting of the American Chemical Society, San Francisco. 1958.

solutions and to find out whether it is formed from chromous by any oxidizing agents other than $O_2$.

## Experimental

**Materials.**—Chromous perchlorate was prepared by electrolytic reduction of chromic perchlorate under nitrogen. The cell consisted of two compartments divided by sintered glass, a mercury cathode, a cathode solution of *ca.* 0.07 *M* $Cr(ClO_4)_3$ and an anode solution of *ca.* 0.1 *M* $HClO_4$. This method was developed by L. B. Anderson. Preparation of chromic perchlorate has been described previously.[6] HClO (*ca.* 0.1 *M*) was prepared by the method of Taylor and Bostock.[7] $La(ClO_4)_3$ was prepared from A. R. $La_2O_3$ and $HClO_4$; $Tl(ClO_4)_3$, from $TlCl_3$ and $HClO_4$ *via* $Tl(OH)_3$; $Fe(ClO_4)_3$ and $Th(ClO_4)_4$, by fuming the chloride with $HClO_4$. All other materials were A. R. grade. Dowex 50 cation-exchange resin (pretreated with acetone, HCl and NaOH) smaller than 200 mesh (fines removed by flotation) was used for the batch experiments, and 140 to 200 mesh was used in the column experiments after brief bleaching with warm alkaline $H_2O_2$.

The ion-exchange batch experiments were conducted in 50- and 100-ml. volumetric flasks containing 1 and 2 g. of resin, respectively, and slowly rotated end over end. The column experiments were conducted in columns 1 cm.$^2$ in cross section and several cm. high using flow rates of *ca.* 0.1 cm. per min.

A Beckman D.U. spectrophotometer was used for spectral measurements. An a.c. bridge with Campbell–Shackelton ratio box was used for the conductometric titrations.

Chromous concentrations were determined by reaction with concentrated $Fe_2(SO_4)_3$ under nitrogen and back titration of the resulting ferrous with standard dichromate. Total chromium concentrations were determined either by titration with standardized $FeSO_4$ after oxidation to dichromate with ammonium persulfate or spectrophotometrically as $CrO_4^=$ after oxidation with alkaline $H_2O_2$. Thorium and lanthanum were precipitated as oxalates, ignited and weighed as oxides. Sulfate was precipitated and weighed as $BaSO_4$.

## Results and Discussion

**Structure of the Product.**—The first step toward elucidation of the structure of the product of air oxidation of $Cr^{++}$ was to determine whether it was a single species or a mixture of several species such as that found in boiled chromic solutions. Chromous perchlorate in $HClO_4$ solution was shaken with oxygen for *ca.* 10 minutes and the resulting blue-green solution added to an acid form cation-exchange column. It formed a sharp band at the top of the column and could not be eluted with 1 *M* $HClO_4$. An eluting solution of 0.02 *M* $La(ClO_4)_3$ and 0.01 *M* $HClO_4$ caused a slow displacement, leaving no chromium species behind. This behavior is identical with that of the blue-green fraction separated from boiled chromic solutions.[5]

The absorption spectrum of the original solution of air oxidized chromous perchlorate became constant about 15 minutes after oxidation and was found to match the spectrum of the blue-green fraction from boiled chromic solutions (peaks at 418 m$\mu$, $\epsilon$ 22, and 580 m$\mu$, $\epsilon$ 19).

Attempts to crystallize a product directly from oxidized chromous perchlorate solutions were not successful. On vacuum evaporation, the solutions changed to thick oils, which contained small green crystals that could not be separated and were extremely hygroscopic. After a few days, hexaquo chromic perchlorate began to separate from the solution.

By addition of 9 *M* $H_2SO_4$ to an equal volume of the air oxidized chromous perchlorate solution (*ca.* 2 *M* in Cr) and half that volume of concentrated $HClO_4$ (70%), a green crystalline sulfate precipitated which could be separated by quickly filtering off the solution and air-drying on the filter. The crystals were not hygroscopic. A solution made by dissolving the crystals in 1 *M* $HClO_4$ had the same absorption spectrum as the original solution. When absorbed on an ion-exchange column, it behaved like the starting material (unaffected by 1 *M* $HClO_4$; eluted by a 0.02 *M* $La(ClO_4)_3$ solution). The crystals apparently contained the same chromic species as the original solution.

Analysis of the crystals gave a ratio of $Cr/SO_4^=$ equal to 2:3. As the positive charge per chromium is necessarily less than 3, the crystals probably represent an acid sulfate salt, which is not surprising considering the extreme acidity of the solution. This conclusion is further supported by the reaction of the crystals with ethanol. Without dissolving any of the chromium, ethanol removes $H_2SO_4$ from the crystals, thereby reducing the $Cr/SO_4^=$ ratio to nearly 1:1. This behavior is analogous to that of bisulfates of alkali metals.[8]

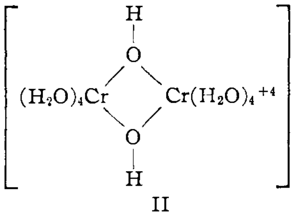
The preceding results obtained from spectral, ion exchange and crystallization experiments indicate that the product of $Cr^{++} + O_2$ consists of only one chromic species, which is identical with the first polynuclear ion formed in boiling chromic perchlorate solutions.

The next step was the determination of the electrical charge per chromium atom of the polynuclear ion, which was done as follows. A solution of chromous perchlorate containing perchloric acid was air oxidized, analyzed for chromium (0.851 formal, of which 99.9% had been reduced to $Cr^{++}$) and perchlorate, (2.328 *M*) and then 10.00 ml. was titrated conductometrically, with 1.031 *M* NaOH. The resulting curve, given in Fig. 1, is typical for a strong acid plus a weak acid and shows a definite break at the point (6.30 ml. of NaOH) where all the free $HClO_4$ has been neutralized. From the condition of electrical neutrality, a value of +1.97 ± 0.04 for the charge per chromium atom can be calculated. A repeat titration gave an identical result. A potentiometric titration of the free acid showed a potential jump in the same region, but this method was much less reliable.

A charge of +2 per chromium atom can fit several polynuclear structures consistent with the usual octahedral coördination of Cr(III): a dinuclear species of either of the forms

$$[(H_2O)_5Cr{-}O{-}Cr(H_2O)_5]^{+4}$$

I



II

or a chain of the type $-\overset{H}{O}-Cr(H_2O)_4-\overset{H}{O}-Cr(H_2O)_4-\overset{H}{O}-Cr(H_2O)_4-$ which could be either joined at the ends

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(6) A. L. Phipps and R. A. Plane, THIS JOURNAL, **79**, 2458 (1957).

(7) R. L. Taylor and C. Bostock, *J. Chem. Soc.*, **101**, 451 (1912).

(8) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, Green and Co., New York, N. Y., 1922, p. 685.

to form a ring of three or more chromic nuclei or could be terminated by a group similar to I or II. Very large chains can very likely be ruled out because such large ions would probably not be held strongly by an ion-exchange resin.

The knowledge of the total charge $X$ of the polynuclear ion and of the charge $+2$ per chromium atom is sufficient for the determination of the number $n$ of chromic nuclei in the ion ($n = X/2$). Unfortunately, no accurate method was available for the determination of $X$, but the fact that $X$ is a whole and even number and $X > 2$, *i.e.*, 4, 6, 8, etc., permits the use of a somewhat crude method for finding the most likely value of $X$. In a series of ion-exchange batch experiments, of the type suggested by Cady and Connick,[9] solutions of initial concentrations of chromium and $La(ClO_4)_3$ were shaken with known amounts of acid resin. After equilibrating for 3.5 hr. the solutions were analyzed (Table I). (Experiments equilibrated for longer periods gave similar results but were probably less accurate due to measurable decomposition of the chromic species.) Conditions were chosen to give a constant molar fraction of each component in the resin. By assuming activity coefficients ratios of the components in solution are constant the charge, $X$, can be derived from any pair of experiments using the mass action expression

$$K = \frac{[La_1]^{1/3}[Cr_{R_1}]^{1/x}}{[La_{R_1}]^{1/3}[Cr_1]^{1/x}} = \frac{[La_2]^{1/3}[Cr_{R_2}]^{1/x}}{[La_{R_2}]^{1/3}[Cr_2]^{1/x}}$$

TABLE I

ION-EXCHANGE RESULTS

| | [Cr] | [$Cr_R$] | [La] | [$La_R$] | |
|---|---|---|---|---|---|
| 1 | 0.0106 | 0.470 | 0.0156 | 0.720 | $X_{1,2} = 2.96$ |
| 2 | .0206 | .470 | .0306 | .720 | $X_{2,3} = 2.79$ |
| 3 | .0305 | .475 | .0457 | .713 | $X_{1,3} = 2.90$ |

R designates concentrations in the resin phase, given in units of millimoles per gram. Solution concentrations are in moles per liter.

The results of the three experiments calculated in pairs gave an average value of $X = 2.88$. Although the resin concentrations were constant and the solution activity changes may cancel out to some extent, $K$ is probably not constant. If $K$ varied by not more than ± 10% between the two extreme experiments, calculations based on this pair would indicate that the true value of $X$ must lie in the range 2.3 to 4.1. Another series of experiments using $Th(ClO_4)_4$ in place of $La(ClO_4)_3$ gave values of $X$ lying in the same range. Taken at face value, the results might suggest that the most probable charge for the species is $+3$. Such a value would be possible, for example, by the ion pairing of a species such as I or II with perchlorate ion. However, in view of the lack of activity coefficient corrections, such a detailed interpretation does not seem warranted and rather the results are taken merely to rule out species of charge greater than $+4$. Thus, a dinuclear species is indicated. The further observation that the chromium species is held by the resin more strongly than $La^{+3}$, but less strongly than $Th^{+4}$, and the fact that this chromic species is the first formed in boiling chromic solutions[5] support its being dinuclear.

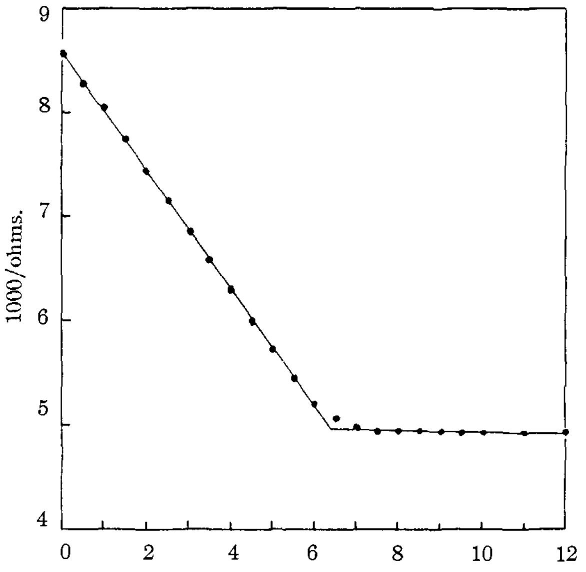

Fig. 1.—Conductometric titration with 1 $M$ NaOH of free acid in 10 ml. of 0.851 formal Cr(III) solution; perchlorate concentration 2.328 $M$; readings corrected for volume change during titration.

There are two alternative structures for the dinuclear species, I and II mentioned earlier, having an oxo bridge and a diol bridge, respectively. No decision between them was attempted in the present work. A distinction could be made by measuring the number of non-exchangeable oxygen atoms bound to each chromium atom. This number should be 5.5 for I and 5.0 for II. An isotope study with $O^{18}$ is now in progress in this Laboratory for determining this number and for detecting the origin of the bridging oxygen atoms.

**Mechanism of Formation.**—From the point of view of reaction mechanism it seemed of interest to find out whether the dinuclear species could be formed from chromous perchlorate only by means of molecular oxygen or whether other oxidizing agents could produce it as well. To clarify this point, a number of oxidation reactions were investigated and it was established that formation of the dimer is not limited to $O_2$ oxidation but that it is a hitherto unnoticed product of many oxidations of $Cr^{++}$.

The procedure used in this phase of the investigation was to oxidize a solution of *ca.* 0.3 $M$ chromous perchlorate (under nitrogen) with an excess of oxidizing agent all in 1 $M$ $HClO_4$, separate and identify the resulting chromic species by ion-exchange chromatography. (In the case of $Tl^{+3}$ as oxidizing agent, a slight excess of $Cr^{++}$ was used; the residue was oxidized by $O_2$.)

$Br_2$ and $Cl_2$ were found to produce $CrBr^{++}$ and $CrCl^{++}$, respectively, along with smaller amounts of $Cr(H_2O)_6^{+3}$, but no detectable amount of the dinuclear species. $Fe^{+3}$ produced only $Cr(H_2O)_6^{+3}$. These results are in agreement with those of Taube and Myers.[2] $Cu^{+2}$ likewise produced pure $Cr(H_2O)_6^{+3}$.

$H_2O_2$ was found to form $Cr(H_2O)_6^{+3}$ as the main

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[9] H. W. Cady and R. E. Connick, THIS JOURNAL, **80**, 2646 (1958).

product together with an appreciable amount of the dinuclear species. Some 14% of the total chromium was found in this latter form in a typical experiment. HClO likewise yielded mixed products. In a typical experiment, the distribution was 40% $CrCl^{++}$, 29% $Cr(H_2O)_6{}^{+3}$ and 31% dinuclear ion. An acid dichromate solution gave equal amounts of $Cr(H_2O)_6{}^{+3}$ and dinuclear chromic. On oxidation with $HClO_3$, the dinuclear species is the main product (some $^2/_3$ of the total Cr) with the rest equally divided between $CrCl^{++}$ and $Cr(H_2O)_6{}^{+3}$. $Tl^{+3}$ produced almost pure dinuclear chromic with but traces of $Cr(H_2O)_6{}^{+3}$. Finally, arsenic acid was tried as oxidizing agent, but it did not react quickly with $Cr^{++}$.

The oxidizing agents examined can be classified according to the nature of the chromic species they produce: (1) reagents which produce mononuclear chromic species—hexaquo chromic ion or its substitution products: $Fe^{+3}$, $Cu^{++}$, $Cl_2$ $Br_2$; (2) reagents which produce the dinuclear chromic species: $O_2$, $Tl^{+3}$. Reagents belonging to both groups are $H_2O_2$, HClO, $HClO_3$ and $Cr_2O_7{}^{=}$.

The results can be interpreted by assuming a one electron transfer oxidation for group I and a two electron transfer oxidation for group II. (These terms are meant to include also the possibility of mono or divalent atom transfer.) The scheme shown is proposed

$$\text{(a)}\quad Cr^{++} + \text{one electron oxidizing agent} \longrightarrow Cr^{+3}\ \text{(mononuclear)}$$

$$\text{(b)}\quad Cr^{++} + \text{two electron oxidizing agent} \longrightarrow Cr(IV)$$

$$Cr^{++} + Cr(IV) \longrightarrow \text{dinuclear species}$$

This scheme is in agreement with the findings of J. Picard who demonstrated that chromium species of a higher oxidation number than 3 can be detected in air oxidized chromous solutions when $Cr^{++}$ is extremely dilute and $O_2$ is in excess.[10] Concerning the other oxidizing agents, previous investigators record some information. $Tl^{+3}$ seems to act as a two electron oxidizing agent in its fast reactions.[11,12] $HClO_3$ has been shown to oxidize sulfites by two successive oxygen atom transfers (each step equivalent to a two electron transfer) followed by a different mechanism for the last two electrons.[13] If $HClO_3$ reacts similarly with $Cr^{++}$, the reaction should lead to the observed mixed product with dimer predominating. $Fe^{+3}$ and $Br_2$ are believed to be one electron oxidizing agents,[2,14] in agreement with the above interpretation. The mechanism of $H_2O_2$ oxidation reactions is a controversial issue.[15-17] While not attempting to settle the issue, we think it noteworthy that the scheme proposed here suggests that there are competing one and two electron-transfer reaction paths in the chromous perchlorate oxidation by $H_2O_2$.

The results with dichromate can be interpreted by the reactions

$$Cr(VI) + Cr^{++} \longrightarrow Cr(V) + Cr(H_2O)_6{}^{+3}$$

$$Cr(V) + Cr^{++} \longrightarrow Cr(IV) + Cr(H_2O)_6{}^{+3}$$

$$Cr(IV) + Cr^{++} \longrightarrow \text{dimer}$$

If $Cr^{++}$ reacts faster with both Cr(V) and Cr(IV) than with Cr(VI), this scheme would account for the 1:1 distribution of the product chromium atoms between hexaquo chromic ion and the dinuclear ion. It is noteworthy that the proposed mechanism consists of a series of one electron transfer reactions. Dinuclear chromium is, nevertheless, produced in this case because the Cr(IV) can be formed from Cr(VI) rather than by a two electron oxidation of $Cr^{++}$.

The fact that arsenic acid with a potential of $-0.56$ v., more than enough to oxidize $Cr^{++}$ to $Cr^{+3}$ ($+0.44$ v.) does not react with $Cr^{++}$ suggests that this two electron oxidizing agent[17] is too weak to produce sufficient Cr(IV) concentration for a fast over-all reaction. Westheimer has shown that the $Cr^{+3}$/Cr(IV) potential must be more negative than $-1.5$ v.[18] If it is much more negative than this limit, arsenate would not be expected to form the dinuclear species rapidly by the mechanism proposed.

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[15] J. H. Baxendale, "Advances in Catalysis," Vol. IV, Academic Press, Inc., New York, N. Y., 1952, p. 31.

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[17] F. H. Westheimer, "A Symposium on the Mechanism of Enzyme Action," Johns Hopkins Press, Baltimore, Md., 1954, pp. 337, 338.

[18] F. W. Westheimer, *Chem. Revs.*, **45**, 449 (1949).