THE MECHANISMS OF CHROMIC ACID OXIDATIONS

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I. INTRODUCTION

Chromic acid has been long and successfully used as an oxidizing agent, for both preparative and analytical purposes. The procedures underlying the stoichiometric equations 1 and 2

$$HCrO_4^- + 3Fe^{++} + 7H^+ \rightarrow Cr^{+++} + 3Fe^{+++} + 4H_2O \tag{1}$$

$$2HCrO_4^- + 6I^- + 14H^+ \rightarrow 2Cr^{+++} + 3I_2 + 8H_2O \tag{2}$$

are among the classic methods of quantitative analysis. As a preparative reagent (65) chromic acid is customarily used, in aqueous sulfuric acid or in acetic acid solution, to oxidize primary alcohols or aldehydes to acids and to oxidize secondary alcohols to ketones. Chromic acid in acetic acid oxidizes toluene to benzoic acid, ethylbenzene to acetophenone, triphenylmethane to triphenylcarbinol, fluorene to fluorenone, and chrysene to chrysoquinone. Chromic anhydride, dissolved in acetic anhydride and sulfuric acid, oxidizes *o*-xylene to the tetraacetate of *o*-phthalaldehyde; Étard's reagent (chromyl chloride, CrO_2Cl_2) oxidizes substituted toluenes to the corresponding substituted benzaldehydes.

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[1] The views here summarized are conclusions reached by the author largely as the result of a seminar on chromic acid oxidation in which he, Professor T. F. Young, Professor Henry Taube, Dr. Jacob Bigeleisen, and several graduate students participated. The author is especially indebted to one of the students, Dr. Robert Snyder, who contributed greatly to the clarification of this subject, and to Professor James K. Senior, whose help in preparing this manuscript was invaluable.

In all of the preparative reactions just cited, a carbon atom is the one oxidatively attacked; but chromates may also be used in many other reactions (e.g., the conversion of nitroso to nitro compounds or the conversion of sulfides to sulfones), where the oxidative attack is on an atom of an element other than carbon (nitrogen and sulfur, respectively, in the two examples cited). Evidently oxidation by chromates is one of the most versatile of chemical reactions.

It is not the purpose of this paper to attempt an exhaustive review of all the nstances where chromates have been used as oxidizing agents for either analytical or preparative purposes. Instead, attention will here be confined to those reactions which have been investigated with enough detail to throw some light on the mechanisms involved. Such reactions constitute but a small fraction of all those where hexavalent chromium has been used as an oxidizing agent; and even for those which have been more carefully investigated, the information at hand is still far from complete. Nevertheless, from the fragmentary data already available, it is clear that no single mechanism suffices to explain all the reactions of hexavalent chromium, and that intermediate products, in which chromium has the valence of four or five, occur in many (if not all) of the reactions in question.

In assigning a mechanism to the chromic acid oxidation of an organic compound, there are many questions to be answered. Is the reaction a transfer of an oxygen atom (or atoms) from the chromic acid to the organic molecule; is it primarily an electron transfer; or is it a dehydrogenation of the organic molecule? If it is a dehydrogenation, which hydrogen atom in the organic molecule is the one first attacked? What chromium-containing particles (ions or molecules) participate in the reaction? But underlying these and similar questions, there is another even more important one. The conversion of chromic acid to a compound of trivalent chromium is a three-electron change. The oxidation of organic compounds usually occurs in steps, but the final products almost always differ from the reactants by an even number of electrons. Just what is the nature of the electron transfer? Is the organic molecule oxidized in one-electron steps, so that free radicals are formed as intermediates, or is it oxidized directly in two-electron steps? (Three-electron transfers are, for various reasons, so improbable that they are here neglected.) Clearly, either of these alternatives for the first step in the reaction leads to an intermediate in which the chromium atom occurs in an unusual (and unstable) valence state for chromium. A one-electron transfer makes the hexavalent chromium atom temporarily pentavalent; a two-electron transfer makes it temporarily tetravalent.

The first problem here considered is that of the unusual and unstable valence states of chromium. It will be shown below that both pentavalent and tetravalent chromium are needed to account for the available data; divalent chromium may also participate in some of the reactions. The facts now known can be explained on the basis of the following assumptions:

(*1*) The standard oxidizing potential (in acid) of the (Cr^5–Cr^3) couple exceeds 1.75 volts; that of the (Cr^4–Cr^3) couple is probably even greater. (The standard oxidizing potential of the (Cr^6–Cr^3) couple is +1.36 volts.)

(*2*) Those reducing agents which preferentially lose one electron reduce chromic acid first to a molecule or ion containing pentavalent chromium; the subsequent steps of the reaction depend on the other properties of the reducing agent.

(*3*) Those reducing agents which preferentially lose two electrons reduce chromic acid in the following steps:

$$\mathrm{Cr^6 + H_2A \rightarrow Cr^4 + A} \qquad (3)$$

$$\mathrm{Cr^6 + Cr^4 \rightarrow 2Cr^5} \qquad (4)$$

$$\mathrm{Cr^5 + H_2A \rightarrow Cr^3 + A} \qquad (5)$$

Here H_2A and A are the reduced and oxidized forms of the reducing agent; the first is converted to the second by a two-electron change.[2] Equation 4 is only stoichiometrically significant; it is probably the sum of two or more steps.

(*4*) When chromic acid acts upon a mixture of two reducing agents, A and B, of which A preferentially loses one electron, whereas B preferentially loses two, the reaction is a combination of the two schemes just described.

The (partial) reaction mechanisms based on these principles (1 to 4) require two special explanations. It is necessary first to show that some materials are actually oxidized in two-electron steps; and second, to discuss the phenomenon called induced oxidation.

For many years it has been customary to classify reducing agents as (*1*) those which can donate one and only one electron, and (*2*) those which generally if not always donate two electrons. This classification appears justified, despite the efforts of a few chemists to show that all oxidations proceed exclusively by one-electron steps. In this field, the most interesting single experiment is that of Shaffer (61; *cf.* 56), who showed that reaction 6, between ceric ion and thallous ion, although thermodynamically possible, is very slow.

$$\mathrm{2Ce^{++++} + Tl^{+} \rightarrow 2Ce^{+++} + Tl^{+++}} \qquad (6)$$

Shaffer suggested that a triple collision (suggested by the stoichiometry of equation 6) is unlikely, and that, in the absence of such a triple collision, the reaction can not occur without the formation of an unstable and unknown compound of divalent thallium as an intermediate in the reaction. Furthermore he showed that, in conformity with his theory, the reaction between thallous and ceric ions is catalyzed by salts of manganese. Presumably the manganese atom, which can undergo either one- or two-electron changes, functions as a go-between in the transfer of electrons from the thallous to the ceric ion.

It must be admitted, however, that this theory, although reasonable, is not necessarily correct, since the electrostatic repulsion between ceric and thallous

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[2] Designations such as Cr^6 or Cr^5 are used where the nature of the particular ion or molecule containing a chromium atom of the indicated valence cannot be identified (or is immaterial); symbols such as H_2CrO_4, Cr^{+++}, etc., refer to particular molecular or ionic species. Since the formulas for ions containing Cr^5 etc., are unknown, equations in which they appear are balanced only for gross valence change.

ions might in itself be sufficient to prevent reaction. (The slow ferrous–ferric (68) exchange is presumably an example of this sort.)

Browne (40; see 17) made a similar classification of oxidizing agents. He found that, when hydrazine is oxidized, two different sets of products are obtained depending on the oxidizing agent used. According to this scheme, these oxidizing agents fall into two classes: those which easily take up only one electron at a time, and those which easily take up two electrons at a time. These two classes are known respectively as the monodeëlectronators and the dideëlectronators. The statement that an oxidizing agent "easily" takes up one (or two) electrons merely means that such a reaction leads to compounds in which the reduced atom occurs only in known and relatively stable valence states. It is highly improbable that all oxidation–reduction reactions can be explained without taking dideëlectronators into consideration.

II. INDUCED OXIDATIONS

The best evidence for the existence (as unstable intermediates) of pentavalent and tetravalent chromium compounds is the phenomenon known as induced oxidation. A favorite and early example of this phenomenon, discovered by Schönbein (60) in 1858, is the oxidation of iodide to iodine by dichromate, an oxidation which may be induced by ferrous iron. In dilute acid (0.001 *N*) and at low concentrations reaction 2 between chromate and iodide ions is very slow; so also is reaction 7 between ferric and iodide ions. Under these conditions, however, reaction 1 between ferrous and dichromate ions is rapid.

$$2HCrO_4^- + 6I^- + 14H^+ \rightarrow 2Cr^{+++} + 3I_2 + 8H_2O \qquad (2)$$

$$2Fe^{+++} + 2I^- \rightarrow 2Fe^{++} + I_2 \qquad (7)$$

$$HCrO_4^- + 3Fe^{++} + 7H^+ \xrightarrow{\text{rapid}} Cr^{+++} + 3Fe^{+++} + 4H_2O \qquad (1)$$

When a solution containing dilute mineral acid, chromic acid, and iodide is treated with a solution of a ferrous salt, iodine is rapidly liberated; usually the stoichiometry is represented by an equation such as equation 8.

$$HCrO_4^- + Fe^{++} + 2I^- + 7H^+ \xrightarrow{\text{rapid}} Cr^{+++} + Fe^{+++} + I_2 + 4H_2O \qquad (8)$$

It appears that, in the presence of a ferrous salt, iodide ion is rapidly oxidized under experimental conditions where, in the absence of the ferrous salt, that ion is relatively inert. Here the ferrous ion is said to "induce" the oxidation of the iodide.

Another important early example of induced oxidation (also studied by Schönbein (60)) is that (55) of indigo by dichromate; here the inducing agent is oxalic acid. This oxidation was utilized in the industry of the day to produce white designs on blue fabrics. The cloth, dyed with indigo, was printed with a dichromate salt. When the cloth thus printed was treated with oxalic acid, the indigo was bleached only where it was in contact with dichromate. Schönbein showed that sulfuric acid could not be used to replace oxalic; the reaction was therefore a genuine case of induced oxidation. The term "induced oxidation" was introduced by Kessler (39). In an excellent paper published in 1863 he tabulated the then known reactions of this type. Among his examples was the arsenite-induced oxidation of manganous ion by chromic acid, a reaction which he himself had discovered (38) two years previously. He also listed several alleged examples (37; see also 24) of induced oxidation which had been observed before his paper was published; these reactions, however, have never been investigated well enough to be historically important.

Induced oxidations fall into two classes, which may be illustrated by the induced oxidation of iodide and of manganous ions. The induced oxidation of iodide yields two equivalents of iodine for each equivalent of the inductor oxidized. On the other hand, the induced oxidation of manganous salts to manganic salts or to manganese dioxide yields one equivalent of oxidized manganese for each two equivalents of inductor oxidized. In any induced oxidation the "induction factor" is defined as the ratio of the number of equivalents of the reducing agent oxidized to the number of equivalents of the inductor oxidized. In the reactions cited above, the induction factor for the iodide oxidation is 2 and that for the manganous ion oxidations is 0.5.

In all induced chromic acid oxidations (with one possible exception cited below) where the induction factor has been determined, it has been found to be either 2 or 0.5. That is to say, of the three oxidation equivalents supplied by each mole of $HCrO_4^-$, either one or two are used for the induced oxidation; this precise stoichiometry suggests Cr^4 or Cr^5 as the valence state of the chromium atom in the compound which participates as an intermediate in the reaction. How these stoichiometrical considerations indicate the valence of the unstable intermediate may be shown by considering the chromic acid oxidation of iodide ions which is induced by ferrous ions, and the chromic acid oxidation of manganous ions which is induced by arsenite.

The oxidation of iodide by chromic acid may be induced by ferrous ions under conditions where iodide is not oxidized either by chromic acid or by ferric ion alone; hence in such a reaction mixture there must be formed an oxidizing agent more powerful or more rapid (or both) than dichromate. Since the ratio of the number of equivalents of iodide oxidized to the number of equivalents of inductor (ferrous ion) oxidized is 2:1, this more powerful intermediate oxidizer which reacts with the iodide ions probably contains pentavalent chromium. The scheme given in equations 9, 10, and 11 (where hypoiodite is assumed as an intermediate) is one of several which are stoichiometrically correct; it anticipates the results of the kinetic investigations presented later on (see footnote 2).

$$Cr^6 + Fe^{++} \rightleftarrows Cr^5 + Fe^{+++} \tag{9}$$

$$Cr^5 + I^- \rightarrow Cr^3 + IO^- \tag{10}$$

$$2H^+ + I^- + IO^- \rightarrow I_2 + H_2O \tag{11}$$

The oxidation of manganous salts by chromic acid is induced by arsenite under conditions where manganous salts are not oxidized by chromic acid alone. Hence in such a reaction mixture there must be formed some oxidizing agent more powerful or more rapid (or both) than dichromate. Since the ratio of the number of equivalents of manganous salt oxidized to the number of equivalents of inductor (arsenite) oxidized is 1:2, this more powerful intermediate oxidizer which reacts with manganous salt probably contains tetravalent chromium. The scheme given in equations 12, 13, and 14 is a possible one for the reaction in question.

$$Cr^6 + As^3 \rightarrow Cr^4 + As^5 \tag{12}$$

$$Cr^4 + Mn^2 \rightarrow Cr^3 + Mn^3 \tag{13}$$

$$2Mn^3 + 2H_2O \rightarrow MnO_2 + Mn^2 + 4H^+ \tag{14}$$

Summing up these arguments, an induction factor of 2 indicates that the active oxidizing agent is pentavalent chromium, whereas an induction factor of 0.5 indicates that this agent is tetravalent chromium. Since both induction factors have been observed, chromium probably exists in both of these intermediate valence states.

Induced oxidation is in some respects similar to catalysis; but whereas in catalysis the catalyst is recovered unchanged, in induced oxidation the "inductor" is consumed. Moreover, the amount of inductor so consumed usually bears a stoichiometric relation to the amount of product formed. For reaction 2, catalysis by ferrous ion is thermodynamically possible; but the corresponding reaction

$$3Mn^{++} + 2HCrO_4^- + 2H^+ \rightarrow 3MnO_2 + 2Cr^{+++} + 2H_2O \tag{15a}$$

at pH > 0 is thermodynamically impossible (46). Indeed, in the absence of arsenite, reaction 15a proceeds slowly from right to left. Nevertheless, the reaction

$$6H^+ + 2HCrO_4^- + 2H_3AsO_3 + Mn^{++} \rightarrow 2Cr^{+++} + 2H_3AsO_4 + MnO_2 + 4H_2O \tag{15b}$$

is thermodynamically possible, since the standard free-energy change for this induced reaction is negative, owing to the fact that the inductor is consumed in the process.

The above discussion of the stoichiometry of induced oxidations is actually a considerably simplified version of the facts. Clearly, when arsenite is oxidized in the absence of manganous ion, the chromium in either of the intermediate valence states (Cr^4 or Cr^5) is consumed in the oxidation of more arsenite. (The mechanism for this follow-up reaction corresponds to that given in equations 4 and 5; it will be discussed later.) Therefore, when manganous ion and arsenite are both present, they compete for the tetravalent chromium; the higher the concentration of the manganous ion, the more successful will this reagent be in the competition. Since similar considerations apply to all induced oxidations, any stoichiometry corresponding to an induction factor of 2, or of 0.5, is to be regarded as a theoretical limit, which is approached only at high concentrations of the substance the oxidation of which is induced. Every induced oxidation so far investigated has yielded data which support this conclusion.

An asymptotic approach to the induction factor of 2 is shown in table 1A, where the reaction is the chromic acid oxidation of iodide induced by vanadous sulfate; an asymptotic approach to the induction factor of 0.5 is shown in table 1B, where the reaction is the chromic acid oxidation of manganous ion induced by arsenious acid.

TABLE 1A

Asymptotic approach to an induction factor of 2

Oxidation of varying amounts of iodide by 0.009 M $K_2Cr_2O_7$; *reaction induced by 0.00044 M* VSO_4 *in the presence of 0.007 M* H_2SO_4 (*data of Luther and Rutter*)*

RATIO OF MOLES OF I^- TO MOLES OF V^{++}	OBSERVED INDUCTION FACTOR
4.5	1.22
8.7	1.43
19.8	1.47
39.3	1.51
91.2	1.61
182.4	1.68
459.	1.87
903.	1.96
1530.	1.99

* In the last two experiments, the concentration of V^{++} is below that given at the top of the table.

TABLE 1B

Asymptotic approach to an induction factor of 0.5

Oxidation of 0.04 M manganous ion by 0.005 M $K_2Cr_2O_7$; *reaction induced by varying amounts of* H_3AsO_3 *in the presence of 3.5 M* H_2SO_4 (*concentrations approximate*) (*data of Lang and Zwerina*)

RATIO OF MOLES OF Mn^{++} TO MOLES OF As_2O_3	OBSERVED INDUCTION FACTOR
3.2	0.15
3.6	0.30
4.1	0.41
5.6	0.45
7.2	0.46
10.	0.46
14.	0.50
28.	0.51

The induced oxidations involving chromic acid are of two types: (*a*) those where the chromic acid acts as an oxidizing agent and (*b*) those where it acts as an inductor. In reactions of type (*a*) (some of which are listed in table 2) one reducing agent (the inductor, IR) induces the rapid chromic acid oxidation of the acceptor, H_2A, under conditions where, in the absence of IR, H_2A is either not attacked or only very slowly attacked by chromic acid. In reactions of type (*b*) (some of which are listed in table 3) chromic acid, IOx, induces the rapid oxidation of a reducing agent, H_2A, by some oxidizing agent, Ox, under conditions where, in the absence of chromic acid, H_2A is either not attacked or only very slowly attacked by Ox.

TABLE 2

Induced oxidations in which Cr^6 *is the oxidizing agent*

INDUCTOR (IR)	OXIDIZING AGENT (Ox)	SUBSTANCE OXIDIZED (ACCEPTOR) (H_2A)	INDUCTION FACTOR	REFERENCE
Fe^{++}	CrO_3	I^-	2	Manchot and Wilhelms(a) Benson(b)
H_2AsO_3	CrO_3	I^-	2	De Lury(c)
$VOSO_4$	CrO_3	I^-	2	Luther and Rutter(e)
$(VO)_2SO_4$	CrO_3	I^-	2	
VSO_4	CrO_3	I^-	2	
Ti^{+++}	CrO_3	I^-	2	Manchot and Richter(f)
$UOSO_4$	CrO_3	I^-	0.5–0.7	Luther and Rutter(e); Manchot(g)
H_2AsO_3	CrO_3	Mn^{++}	0.5	Lang and Zwerina(d)
$CH_3CHOHCH_3$	CrO_3	Mn^{++}	0.5	Watanabe and Westheimer(h)
Fe^{++}	CrO_3	Br^-	Unknown	Luther and Rutter(e)
$VOSO_4$	CrO_3	Br^-		
Ti^{+++}	CrO_3	Br^-		
H_2TeO_3	CrO_3	Ferrion	Unknown	Lang(i)
Ferrion	CrO_3	H_2TeO_3		
$K_4Fe(CN)_6$	CrO_3	Tartaric acid	Unknown	Kessler(j)
SO_2	CrO_3	Tartaric acid		
Sb_2O_3	CrO_3	Tartaric acid		
SnO	CrO_3	Tartaric acid		
As_2O_3	CrO_3	Tartaric acid		
Oxalic acid	CrO_3	Indigo	Unknown	Schönbein(k)

(a) Manchot, W., and Wilhelms, O.: Ann. **325**, 105, 125 (1902).
(b) Benson, C.: J. Phys. Chem. **7**, 1 (1903).
(c) De Lury, R. E.: J. Phys. Chem. **11**, 239 (1907).
(d) Lang, R., and Zwerina, J.: Z. anorg. Chem. **170**, 389 (1928).
(e) Luther, R., and Rutter, T. F.: Z. anorg. Chem. **54**, 1 (1907).
(f) Manchot, W., and Richter, P.: Ber. **39**, 488 (1906).
(g) Manchot, W.: Ber. **39**, 1352, 3510 (1906).
(h) Watanabe, W., and Westheimer, F. H.: J. Chem. Phys. **17**, 61 (1949).
(i) Lang, R.: Mikrochim. Acta **3**, 113 (1938).
(j) Kessler, F.: Pogg. Ann. **119**, 218 (1863).
(k) Schönbein, C. F.: J. prakt. Chem. **75**, 108 (1858).

To explain the induced oxidations of the type listed in table 3, it is probably necessary to assume the presence of bromites, or of compounds in which iron has a valence higher than three, etc. The reactions where chromic acid induces the oxidation of arsenite or stannous chloride by atmospheric oxygen will be discussed later.

III. KINETICS OF CHROMIC ACID OXIDATIONS

A. The oxidation of isopropyl alcohol

The chromic acid oxidation of isopropyl alcohol (79) has been studied with care and in detail. The reaction proceeds smoothly to completion as shown in equation 16. An essentially quantitative yield of acetone is obtained.

$$3CH_3CHOHCH_3 + 2HCrO_4^- + 8H^+ \rightarrow 3CH_3COCH_3 + 2Cr^{+++} + 8H_2O \quad (16)$$

Here kinetic studies have been used to identify the particular compound of hexavalent chromium which, under given conditions, serves as the oxidizing agent. Since this part of the investigation is independent of the rest of the study, it can be treated separately.

An aqueous solution of chromic acid certainly contains the following ions: CrO_4^{--}, $HCrO_4^-$, and $Cr_2O_7^{--}$. In addition, it may possibly contain other species such as $HCr_2O_7^-$, $H_2Cr_2O_7$, or H_2CrO_4. The ionization constant, K_{17}, for the $HCrO_4^-$ ion (*cf.* equation 17) is about 10^{-7}; hence, in dilute aqueous acid, the concentration of CrO_4^{--} ions is negligible. The ionization constant, K_{18}, for the $HCr_2O_7^-$ ion is not known, but careful work (42) has shown that this constant is arge; hence, in solutions where $pH \geqslant 1$ the ionization (*cf.* equation 18) may be

$$HCrO_4^- \rightleftarrows H^+ + CrO_4^{--} \quad (17)$$

$$HCr_2O_7^- \rightleftarrows H^+ + Cr_2O_7^{--} \quad (18)$$

considered essentially complete. Consequently, of all the ions involving hexavalent chromium, the only ones present in large concentrations in solutions of dilute mineral acid are $HCrO_4^-$ and $Cr_2O_7^{--}$. These ions are in equilibrium with each other, according to the equation:

$$H_2O + Cr_2O_7^{--} \rightleftarrows 2HCrO_4^- \quad (19)$$

Reaction 19, unlike reactions 17 and 18, has an equilibrium the position of which is independent of pH. This position varies with the total concentration of hexavalent chromium (hereafter referred to as the gross concentration of chromic acid). There have been several attempts (36, 59, 62, 80) to measure the equilib-

TABLE 3

Induced oxidations in which Cr^6 *is the inductor*

INDUCTOR (IOx)	OXIDIZING AGENT (Ox)	SUBSTANCE OXIDIZED (ACCEPTOR) (H_2A)	REFERENCE
Cr^6	O_2	H_2AsO_3	Luther and Rutter[a]
Cr^6	$HBrO_3$	H_2AsO_3	Luther and Rutter
Cr^6	$FeCl_3$	H_2AsO_3	Luther and Rutter
Cr^6	$HClO_3$	H_2AsO_3	Luther and Rutter
Cr^6	$H_2S_2O_8$	H_2AsO_3	Luther and Rutter
Cr^6	O_2	$SnCl_2$	Luther and Rutter

(a) LUTHER, R., AND RUTTER, T. F.: Z. anorg. Chem. 54, 1 (1907).

rium constant, K_{19}. Methods based on the spectrophotometric analysis of chromic acid solutions have so far failed (30), because the absorption spectra of these solutions deviate only slightly from Beer's law. Hence it must be concluded that the acid chromate ion ($HCrO_4^-$) and the dichromate ion ($Cr_2O_7^{--}$) have approximately the same absorption spectra. Methods based on the freezing points of potassium dichromate solutions have been more successful. The observed freezing-point depressions are considerably greater than those which would be expected if the only ions present were K^+ and $Cr_2O_7^{--}$. Since the second ionization constant of chromic acid, K_{17}, is very small (about 10^{-7}), the additional ions necessary to account for the observed depressions cannot be H^+ ions; hence they must be $HCrO_4^-$ ions. The only precise freezing-point data are those of Sherrill (62), which were obtained before the idea of activity coefficients had been introduced. These data have, however, recently been recomputed (22, 73) by a method which involves activity coefficients based on the interionic attraction theory. The results confirm those obtained by Neuss and Rieman, whose work is next described.

The best quantitative determination of the equilibrium constant, K_{19}, is that of Neuss and Rieman (54), who used a glass electrode to study the acidity of solutions of potassium dichromate. They evaluated their data in terms of the two equilibrium constants, K_{17} and K_{19}. Since this evaluation was complicated by ionic strength effects, extrapolation to infinite dilution proved very difficult. Nevertheless the treatment was successful, and the two equilibrium constants (K_{17} and K_{19}) were evaluated. The constant (K_{17}) thus obtained proved to be of the same order of magnitude as that obtained by other investigators. The equilibrium constant for the acid chromate–dichromate equilibrium at infinite dilution, is 0.023.

$$\frac{(HCrO_4^-)^2}{(Cr_2O_7^{--})} = 0.023 \text{ mole/liter} \tag{20}$$

In the investigation of the chromic acid oxidation of isopropyl alcohol it was possible to determine which of the two chromium-containing species (*cf.* equation 19) is the active oxidizing agent (79). As a rough approximation, the rate of this oxidation is proportional to the first powers of the concentrations of the alcohol and of the gross chromic acid; it is proportional to the second power of the concentration of the hydrogen ions. More precisely, the rate of oxidation depends in a complex way upon the gross chromic acid concentration. But when the initial gross concentration of chromic acid is varied stepwise over an eightyfold range, a definite pattern becomes clear. In the very dilute solutions (0.0005–0.005 M) the rate is proportional to the gross chromic acid concentrations; in more concentrated solutions, the rate is less than that to be expected from the results obtained with dilute solutions. Furthermore, individual experiments with concentrated solutions no longer lead to good rate constants. But when the same data are recomputed on the assumption that the only active oxidizing species is the acid chromate ion, $HCrO_4^-$, the data all lead to the same satisfactory rate constant. In order to make this latter computation, the equilibrium constant,

K_{20}, of Neuss and Rieman was used in a slightly modified form which takes account of the ionic strengths of the solutions employed. The conclusion (i.e., that the active oxidizing agent is the acid chromate ion, $HCrO_4^-$) does not depend upon the exact value of the equilibrium constant, K_{20}, but only upon its approximate magnitude. The experiments in question are illustrated by figures 1 and 2. It will later be shown that other chromic acid oxidations besides that of isopropyl alcohol can be simplified and explained in terms of the equilibrium of equation 19.

The more precise kinetic picture thus obtained of the chromic acid oxidation of isopropyl alcohol indicates that the reaction rate is proportional to the first power of the acid chromate ion concentration, the first power of the isopropyl alcohol concentration, and the second power of the hydrogen-ion concentration. The rate-determining step therefore involves one acid chromate ion, one alcohol molecule, and two hydrogen ions. Since the chromium atom must change valence by three units, and the alcohol molecule must change by only two, some ion or molecule containing chromium in an intermediate valence state (Cr^4 or Cr^5) must take part in the reaction.

A further fact which supports the conclusion just reached is that isopropyl alcohol, like arsenious acid, induces the chromic acid oxidation of manganous ion to manganese dioxide. A quantitative study (72) of this induced oxidation has shown that one equivalent of manganese dioxide is produced for every two equivalents of isopropyl alcohol oxidized. That is to say, the induction factor is 0.5. This result indicates that the substance which oxidizes manganous ion is very probably tetravalent, not pentavalent, chromium, but it does not indicate whether the tetravalent chromium is produced directly from hexavalent chromium or indirectly from pentavalent chromium. The reaction kinetics, however, settle this point. The rate at which chromic acid is consumed in the oxidation of isopropyl alcohol is decreased by manganous ion to an extent which depends on the concentration of manganous ion present. The effect of even 10^{-5} moles per liter of manganous ion can easily be detected; when the concentration of manganous ion is greater than 0.001 mole per liter, the rate approaches asymptotically a value approximately one-half of that found in the absence of this ion.

A satisfactory mechanism for the chromic acid oxidation of isopropyl alcohol must account quantitatively for the diminution in reaction rate produced by manganous ion. One mechanism which fulfills this condition is:

$$HCrO_4^- + CH_3CHOHCH_3 \rightarrow Cr^4 + CH_3COCH_3 \qquad (21)$$

$$Cr^4 + CH_3CHOHCH_3 \rightarrow Cr^2 + CH_3COCH_3 \qquad (22)$$

$$Cr^2 + Cr^6 \rightarrow Cr^3 + Cr^5 \qquad (23)$$

$$Cr^5 + CH_3CHOHCH_3 \rightarrow Cr^3 + CH_3COCH_3 \qquad (24)$$

and

$$Cr^4 + Mn^2 \rightarrow Cr^3 + Mn^3 \qquad (13)$$

$$2Mn^3 + 2H_2O \rightarrow MnO_2 + Mn^2 + 4H^+ \qquad (14)$$

In most of these reactions, the hydrogen ion is omitted for the sake of convenience. It will later be shown that the mechanism given in equations 21 to 24 is one of four possibilities.

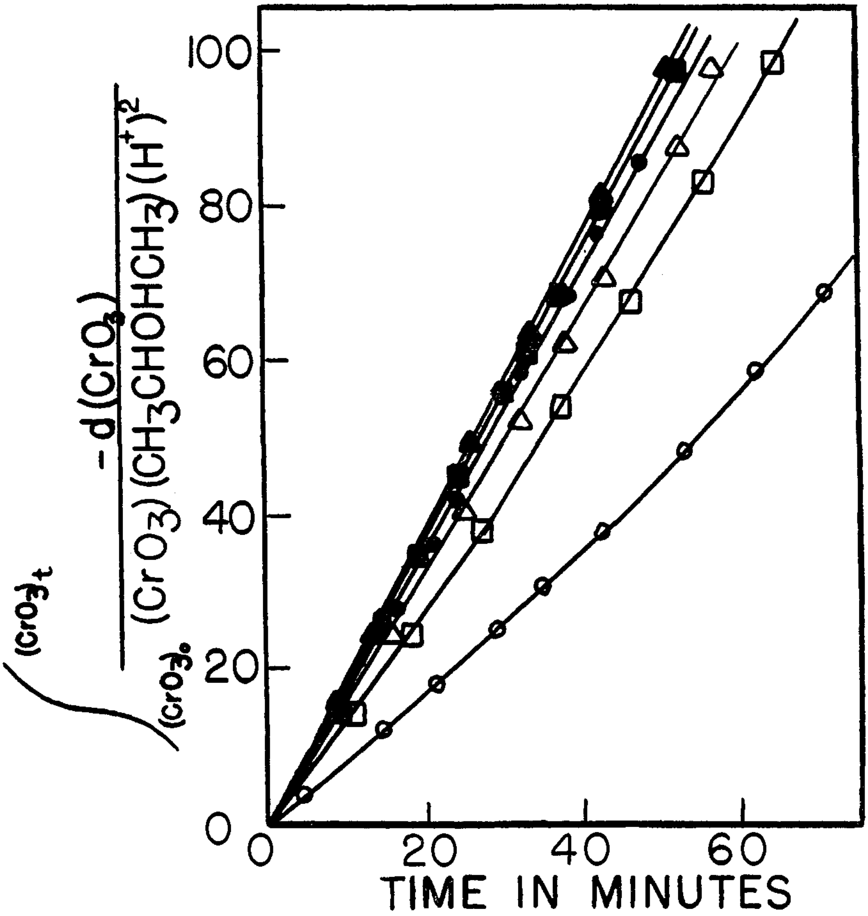


Fig. 1. Graphical representation of the equation

$$\int_{(CrO_3)_0}^{(CrO_3)_t} \frac{-d(CrO_3)}{(CrO_3)(CH_3CHOHCH_3)(H^+)^2} = kt$$

which assumes that all ions or molecules containing hexavalent chromium are oxidizing agents for isopropyl alcohol. Concentrations of H^+ and $CH_3CHOHCH_3$ were 0.2694 *M* and 0.2001 *M*, respectively. The various chromic acid concentrations are represented by the following symbols:

○ = 0.04316 *M*
□ = 0.01079 *M*
△ = 0.004316 *M*
● = 0.002158 *M*
■ = 0.001079 *M*
▲ = 0.0005316 *M*

The scheme just given accounts for all the facts now known. First, since it involves the oxidation of manganous ions by tetravalent chromium, it accounts for the induction factor of 0.5. Second, it accounts for the fact that manganous ion cuts in half the total rate at which hexavalent chromium is consumed. For hexavalent chromium is consumed not only in reaction 21 but also in reaction 23. If tetravalent chromium is reduced by manganous ion (reaction 13) before

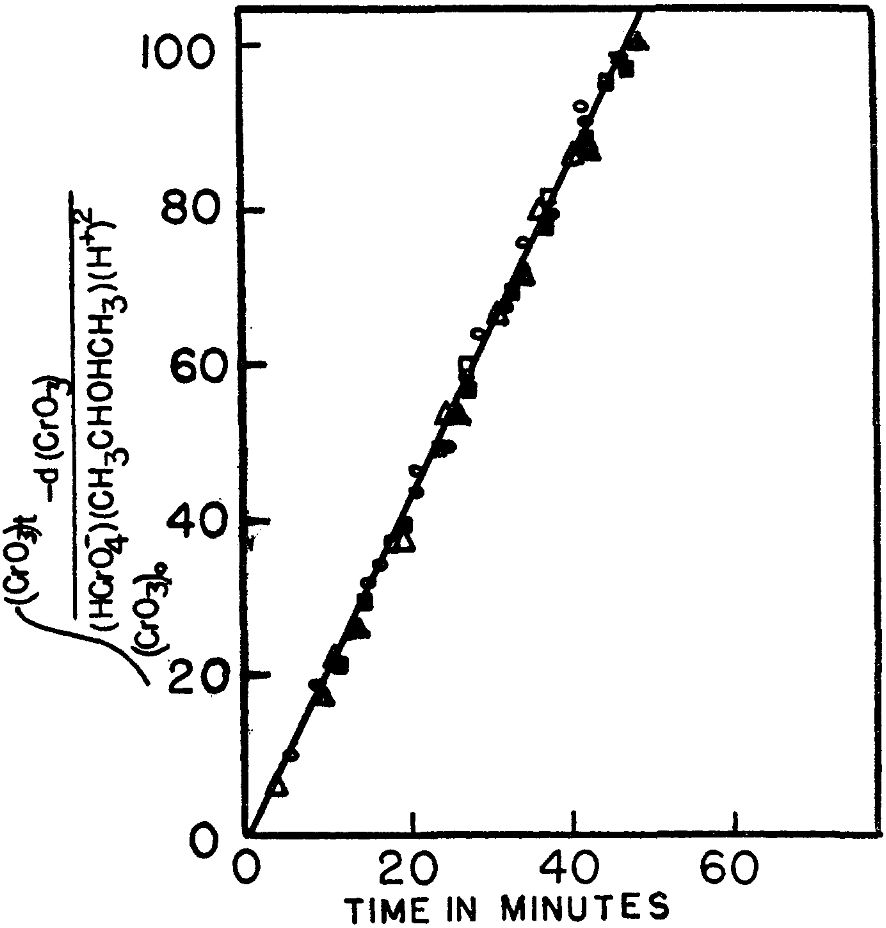


FIG. 2. Graphic representation of the equation

$$\int_{(CrO_3)_0}^{(CrO_3)_t} \frac{-d(CrO_3)}{(HCrO_4^-)(CH_3CHOHCH_3)(H^+)^2} = kt$$

which assumes that only $HCrO_4^-$ ions oxidize isopropyl alcohol. The data are the same as those shown in figure 1.

it has a chance to undergo reactions 22 and 23, the rate of consumption of Cr^6 is necessarily cut exactly in half.

As already stated, the scheme just advanced is consistent with all the known facts. To show that no other scheme will fit these facts is, as in all such cases, impossible. But in the present instance it may be shown that, within certain limits, four mechanisms are the only ones possible. The limits here chosen are logically arbitrary but chemically reasonable. The most important conditions are (*a*) only the chemical species $\mathrm{HCrO_4^-}$, $\mathrm{Cr^5}$, $\mathrm{Cr^4}$, $\mathrm{Cr^3}$, $\mathrm{Cr^2}$, $\mathrm{H_2A}$, $\mathrm{HA\cdot}$, A, and $\mathrm{HO\cdot}$ need be considered and (*b*) when relatively stable and relatively unstable particles occur together in a reaction mixture, the unstable particles (especially when they belong to a species present only at high dilution) do not react with one another to the practical exclusion of reactions between unstable and stable particles. When such is the fact, reactions between unstable particles may be neglected. A full discussion of this point and the other necessary limitations is included in the paper by Watanabe and Westheimer (72).

The kinetic data can be explained by reaction schemes other than the ones here advanced if the limitations described above are discarded (16). However, until and unless, at some future time, evidence is discovered inconsistent with the mechanism here advanced, this mechanism appears relatively probable; if such conflicting evidence is eventually discovered, it will probably be apparent which of the assumptions (*a*), (*b*), etc., here made is at fault. According to the limitation just set forth, reactions such as

$$\mathrm{Cr^5 + HA\cdot \rightarrow Cr^4 + A} \tag{25}$$

or

$$\mathrm{2Cr^5 \rightarrow Cr^6 + Cr^4} \tag{26}$$

may be neglected.

Thus the only reactions which need be considered are:

$$\mathrm{Cr^6 + H_2A \rightarrow Cr^4 + A} \tag{27a or 21}$$

$$\mathrm{Cr^6 + H_2A \rightarrow Cr^5 + HA\cdot} \tag{27b}$$

$$\mathrm{Cr^5 + H_2A \rightarrow Cr^3 + A} \tag{27c}$$

$$\mathrm{Cr^5 + H_2A \rightarrow Cr^4 + HA\cdot} \tag{27d}$$

$$\mathrm{Cr^4 + H_2A \rightarrow Cr^2 + A} \tag{27e}$$

$$\mathrm{Cr^4 + H_2A \rightarrow Cr^3 + HA\cdot} \tag{27f}$$

$$\mathrm{Cr^6 + HA\cdot \rightarrow Cr^5 + A} \tag{27g}$$

$$\mathrm{Cr^6 + Cr^4 \rightarrow 2Cr^5} \tag{27h}$$

$$\mathrm{Cr^6 + Cr^2 \rightarrow Cr^5 + Cr^3} \tag{27i}$$

$$\mathrm{Cr^6 + Cr^2 \rightarrow 2Cr^4} \tag{27j}$$

$$\mathrm{Cr^4 + H_2O \rightarrow Cr^3 + HO\cdot} \tag{27k}$$

$$\mathrm{HO\cdot + H_2A \rightarrow H_2O + HA\cdot} \tag{27l}$$

This list includes all the possible reactions where isopropyl alcohol is oxidized in a one-electron step to form a free radical or in a two-electron step to form acetone.

In the presence of manganous ion, the reactions of the following set (set 28) must also be taken into account:

$$Mn^2 + Cr^5 \rightarrow Mn^3 + Cr^4 \qquad (28a)$$

$$Mn^2 + Cr^5 \rightarrow MnO_2 + Cr^3 \qquad (28b)$$

$$Mn^2 + Cr^4 \rightarrow Mn^3 + Cr^3 \qquad (28c\ or\ 13)$$

$$Mn^2 + Cr^4 \rightarrow MnO_2 + Cr^2 \qquad (28d)$$

$$2Mn^3 + 2H_2O \rightarrow MnO_2 + Mn^2 + 4H^+ \qquad (28e\ or\ 14)$$

In terms of the reactions of sets 27 and 28, there is only one mechanism (reactions 27a, 28c, 28e; earlier presented as reactions 21, 13, 14) which is consistent with observed effects of manganous ions; there are exactly four mechanisms (those represented by the set of reactions 27a, 27e, 27i, 27c, by the set 27a, 27h, 27c, by the set 27a, 27f, 27g, 27c, and by the set 27a, 27k, 27l, 27g, 27c) which are consistent with the facts observed in the absence of manganous ions. Each of these four mechanisms, however, starts with the reaction:

$$HCrO_4^- + CH_3CHOHCH_3 \rightarrow Cr^4 + CH_3COCH_3 \qquad (21\ or\ 27a)$$

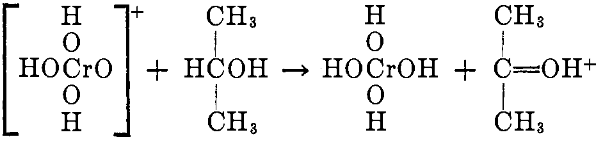
It is therefore highly probable that this two-electron change is the first step in the oxidation of isopropyl alcohol by chromic acid.

So far, it has been established that the reaction between acid chromate ion and isopropyl alcohol is a two-electron change. It will next be shown that, during the rate-controlling step of this reaction, the secondary hydrogen atom is the one removed. This conclusion follows from the following experiments.

The rate of oxidation of 2-deutero-2-propanol (1) has been measured (78) under experimental conditions identical with those used for the oxidation of ordinary isopropyl alcohol. The deuterium compound reacts only about one-sixth as fast as does the hydrogen compound. This fact is considered to prove that the secondary hydrogen atom is removed in the rate-controlling step of the oxidation. For if the attack were elsewhere (e.g., upon the hydroxylic hydrogen atom), replacement of the secondary hydrogen atom by deuterium could scarcely cause so large a change in rate. If and only if the secondary hydrogen is directly involved in the rate-controlling step does so large a change of rate become reasonable.

Decreases in rate similar to the one here adduced have been noted in other instances (50, 57, 81) where the transfer of a hydrogen (or deuterium) atom is involved in the rate-controlling step of a reaction. Furthermore, the experimental facts are reinforced by a simple theory. The zero-point energy of a bond is equal to $h\nu_0/2$, where ν_0 is the fundamental vibration frequency of the bond in question. Both theoretically and experimentally, it is found that a hydrogen atom vibrates faster with respect to the molecule than does a heavier deuterium atom. The zero-point energy of a carbon–hydrogen bond is therefore considerably greater than that of a carbon–deuterium bond. If, during a reaction, the carbon–hydrogen (or carbon–deuterium) bond is broken, the vibration in question can no longer occur; there is then no longer any difference in zero-point energy between the system which originally had the C—H bond and that which originally had the C—D bond. (Actually, this statement is an oversimplification of the facts; the idea here presented is only approximately correct.) A little consideration shows that in the case under discussion, the activation energy for the reaction of the deuterium compound should exceed that for the reaction of the hydrogen compound by (approximately) the difference in zero-point energies between the C—H and the C—D bonds. It follows, therefore, that the deuterium compound should react more slowly than does the hydrogen compound.

The facts so far established do not completely determine the mechanism of the chromic acid oxidation of isopropyl alcohol; consistent with these facts are the two reaction schemes 29 and 30a, 30b.



$$\left[\begin{array}{c}\mathrm{H}\\\mathrm{O}\\\mathrm{HOCrO}\\\mathrm{O}\\\mathrm{H}\end{array}\right]^{+} + \begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{HCOH}\\|\\\mathrm{CH_3}\end{array} \rightarrow \begin{array}{c}\mathrm{H}\\\mathrm{O}\\\mathrm{HOCrOH}\\\mathrm{O}\\\mathrm{H}\end{array} + \begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{C{=}OH^+}\\|\\\mathrm{CH_3}\end{array} \qquad (29)$$

$$HCrO_4^- + 2H^+ + CH_3CHOHCH_3 \overset{\text{fast}}{\rightleftharpoons} [(CH_3)_2CHOCrO_3H_2]^+ + H_2O \qquad (30a)$$

$$[(CH_3)_2CHOCrO_3H_2]^+ + H_2O \xrightarrow{\text{slow}} (CH_3)_2CO + H_2CrO_3 + H_3O^+ \qquad (30b)$$

Consistent with the esterification mechanism (equations 30a, 30b) is the fact that unstable chromic acid esters of several tertiary alcohols have been prepared (34, 53, 76); consistent with the direct removal of a hydride ion by chromic acid (equation 29) is the fact that diisopropyl ether can be oxidized to acetone by chromic acid in sulfuric acid solution (13), and that this oxidation is not preceded by a hydrolysis of the ether to isopropyl alcohol. Further study is needed to decide between the two mechanisms cited (*cf.*, however, the work of Mosher discussed below).

The mechanism of the chromic acid oxidation of isopropyl alcohol in aqueous solution has so far been partly elucidated. It should not, however, be inferred that this mechanism applies to the chromic acid oxidation of any other compound in aqueous solution, or to the chromic acid oxidation of any substance in any non-aqueous solvent (e.g., acetic acid). More such oxidation reactions must be investigated before generalization will be safe.

Here it is well to consider certain evidence obtained from other oxidations which may perhaps bear upon the mechanism of the isopropyl alcohol oxidation already discussed. Waters (58, 74, 75) has shown that oxygen is absorbed during the chromic acid oxidation in acetic acid solution of many alcohols, ethers, etc. Reference has already been made (see table 3) to the absorption of oxygen during chromic acid oxidations. Waters interpreted his observations to mean that chromic acid oxidation must necessarily involve organic free radicals as unstable intermediates. But since oxygen absorption is characteristic of chromic acid oxidations, both inorganic and organic, it is more probable that some compound containing pentavalent, tetravalent, or divalent chromium is the species which absorbs oxygen. Nevertheless, the possibility of free-radical intermediates remains open; they have been ruled out only in the first step of the oxidation of isopropyl alcohol in dilute chromic acid.

Mosher (51, 52) has advanced the hypothesis that chromic acid oxidation of certain alcohols proceeds by way of a transitory intermediate formed by removing a hydride ion from the hydroxyl group of the alcohol. His theory implies that the rate-controlling step is the formation of this intermediate, which subsequently reacts by either one or both of two indicated paths. Clearly, no such intermediate can occur in the oxidation of isopropyl alcohol under the conditions already discussed; the experiments with the deuterated alcohol rule out this possibility. Mosher advanced his hypothesis to explain his discovery that methyl-*t*-amylcarbinol when oxidized by chromic acid yields 10 per cent of *t*-amyl alcohol; this and similar facts can be explained equally well by mechanisms other than the one he gives (e.g., a decomposition of a chromic acid ester along somewhat different lines than those indicated by equation 30b). An alternative mechanism (by way of carbonium ions) for the chromic acid oxidation of certain tertiary alcohols has recently been suggested by Zeiss (83).

B. The oxidation of arsenious acid

In 1904, the oxidation of arsenious acid by chromic acid was studied by De Lury (18, 19) under the direction of Professor Lash Miller. De Lury acidified his solutions with sulfuric acid; unfortunately he happened to work in a region (0.01–0.05 *M* acid) where the second ionization of this acid is incomplete. His data have therefore been recomputed (table 4) using 0.02 mole per liter for the ionization constant for the HSO_4^- ion at 0°C. (31, 43). The data thus recomputed show that the reaction rate is roughly proportional to the square of the concentration of hydrogen ion. Investigations over a broader range of acidity are required to determine whether the discrepancies shown by these and similar data are significant or whether they fall within the experimental error.

De Lury also found, at least as a first approximation, that the rate in the oxidation of arsenious acid is proportional to the 0.7 power of the concentration of the chromic acid. However, when his data are recomputed, taking into account the equilibrium (equation 20) between dichromate and acid chromate ion, it appears that this rate (as in the oxidation of isopropyl alcohol) is nearly proportional to the concentration of acid chromate ion (see table 5). Thus clearly the true rate equation for the chromic acid oxidation of arsenious acid is

$$-d(CrO_3)/dt = k(H_3AsO_3)(HCrO_4^-)(H^+)^2 \qquad (31)$$

This equation is strictly analogous to the one for the oxidation of isopropyl alcohol.

Several interesting oxidations are induced by the chromic acid–arsenious acid reaction; among them are those of iodide, bromide, and manganous ions. The last of these will be considered first.

Lang (44, 45) showed that arsenite induces the chromic acid oxidation of manganous ion to manganese dioxide and manganic ion. (In dilute aqueous acid, these species are in equilibrium with manganous ion.) Since, under the given experimental conditions, the oxidation of manganous ion to manganic ion (or MnO_2) is thermodynamically impossible, it follows that the observed oxidation

TABLE 4

Recomputation of De Lury's data (influence of H^+ *concentration)*

EXPERIMENT NO.	CONCENTRATION OF CHROMIC ACID AS $Cr_2O_7^{--}$	CONCENTRATION OF H^+ (RECOMPUTED)	k(De Lury)/$(H^+)^2$
	moles per liter	*moles per liter*	*(moles per liter)*$^{-2}$ *min.*$^{-1}$
5	0.00298	0.164	214
1 and 4	0.00298	0.055	238

TABLE 5

Recomputation of De Lury's data (influence of chromic acid concentration)

EXPT. NO.	$K_2Cr_2O_7$	As_2O_3	H_2SO_4	k(De Lury) or $\frac{1}{2.3} k_1$	$(HCrO_4^-)$	(H^+)	$\frac{10^{-3} k_1}{(HCrO_4^-)(H^+)^2}$
	moles per liter $\times$ *10*^{3}	*moles per liter* $\times$ *10*^{3}	*moles per liter* $\times$ *10*^{3}	*min.*$^{-1}$	*moles per liter* $\times$ *10*^{3}	*moles per liter* $\times$ *10*^{3}	*min.*$^{-1}$ *(moles per liter)*$^{-3}$
1	2.98	0.0497	9.68	0.058	4.19	15.2	1.38
2	5.96	0.0497	9.68	0.110	7.00	15.2	1.57
3	11.94	0.0497	9.68	0.178	11.25	15.2	1.57
4	2.98	0.0298	9.68	0.052	4.19	15.2	1.24
5	2.98	0.0497	19.36	0.164	4.19	27.6	1.18
6	2.98	0.0497	15.50	0.107	4.19	22.7	1.14
7	0.67	0.0833	8.07	0.115	1.19	13.1	1.30
8	0.67	0.0833	8.07	0.114	1.19	13.1	1.29
9	0.67	0.1667	8.07	0.116	1.19	13.1	1.31
10	0.67	0.0833	16.14	0.318	1.19	23.7	1.10
11	0.67	0.0417	8.07	0.114	1.19	13.1	1.29
12	0.67	0.0417	16.14	0.300	1.19	23.7	1.03
13	1.33	0.0833	8.07	0.217	2.17	13.1	1.34
14	1.33	0.0417	8.07	0.200	2.17	13.1	1.23
15	0.67	0.0417	4.03	0.044	1.19	7.05	1.71
Average							1.31 ± 0.13

of manganous ion must involve an intermediate containing tetravalent or pentavalent chromium. For this particular reaction, Lang showed that the induction factor is 0.5, i.e., two electrons are contributed by the arsenite for each electron contributed by the manganous ion. More precisely, the induction factor approaches 0.5 as a limit (see table 1) when the manganous-ion concentration is high. This fact indicates that the intermediate contains tetravalent chromium.

On the other hand, when an arsenite in dilute aqueous acid is oxidized by chromic acid in the presence of iodide the induction factor is 2, i.e., two equivalents of iodide are oxidized for each one of arsenite. This fact indicates that iodide is here oxidized by pentavalent chromium. Thus, in the oxidation of arsenite by chromic acid either tetravalent or pentavalent chromium may, under suitable conditions, occur as an intermediate. With regard to the reaction induced by iodide, it is of interest that the overall rate of reduction of chromic acid is unaffected by the iodide. This fact was discovered by De Lury. He found that, with increasing iodide concentration, the induction factor approached 2. In any particular experiment, however, the sum of the rates of production of iodine and arsenate was just equal to the rate at which chromate was reduced in a reaction mixture containing no iodide. His data are illustrated in figure 3.

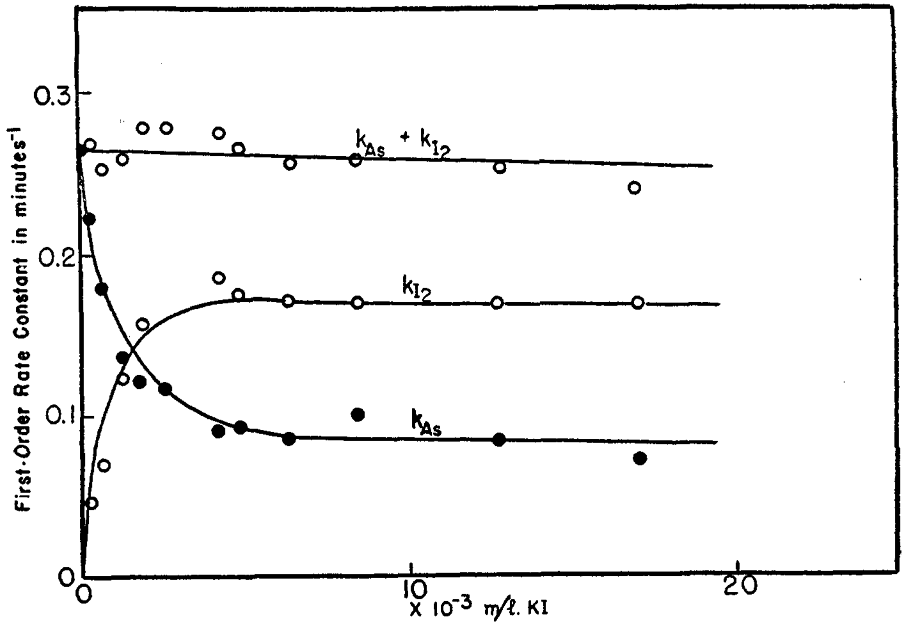


FIG. 3. The arsenate-induced oxidation of iodide by dichromate. Rate constant for the formation of iodine is k_{I_2}, that for the formation of arsenate is k_{As}.

The most satisfactory reaction scheme so far proposed to account for the above facts is the following:

$HCrO_4^- + As^3 \rightarrow Cr^4 + AsO_4^-$ (32a; *cf.* 12)

$Cr^4 + Cr^6 \rightarrow 2Cr^5$ (32b or 4)

$Cr^5 + As^3 \rightarrow Cr^3 + AsO_4^-$ (32c)

This scheme calls for the formation of both tetravalent and pentavalent chromium as intermediates. Either of these can then function as an oxidizing agent in an induced oxidation, as shown in the following equations:

$$Cr^4 + Mn^2 \rightarrow Cr^3 + Mn^3 \qquad (15)$$

$$Cr^5 + 2I^- \rightarrow Cr^3 + I_2 \qquad (33)$$

Furthermore, according to the given scheme the overall rate of reduction of hexavalent chromium should be (as it is) unaffected by the addition of iodide. As previously noted (see equation 4) equations 32b and 32c are only stoichiometrically correct; they may represent the sum of other more complex reactions.

Most of the schemes which might be proposed as alternatives to scheme 32 involve the assumption that some compound containing tetravalent arsenic occurs as a transitory intermediate in the reaction. Such an assumption cannot now be shown to be erroneous. But it seems unwise to postulate a reaction in which two very unstable compounds (one of pentavalent chromium and one of tetravalent arsenic) are simultaneously produced.

$$HCrO_4^- + As^3 \rightarrow Cr^5 + As^4 \qquad (34)$$

However, if this unlikely postulate is accepted, it is still difficult to plan a proper sequence of subsequent reactions which involve tetravalent chromium and at the same time account for the kinetics of the overall reaction. Most of those schemes which involve tetravalent arsenic, tetravalent chromium, and pentavalent chromium lead to the conclusion that the reaction should be autocatalytic —a conclusion incompatible with experiment. In the absence of any evidence to the contrary, mechanism 32 appears adequate for the chromic acid oxidations of arsenious acid.

C. The oxidation of ferrous ion

The kinetics of the oxidation of ferrous ion by chromic acid was developed in 1903. In two excellent papers, Clara Benson (4), who also worked under the direction of Professor Lash Miller, determined the rate of the reaction, varying the initial concentration of each of the reactants (ferrous ion, ferric ion, chromic acid, and hydrogen ion) independently, and by a factor not less than 2. Her work strongly suggests the following rate equation:

$$\frac{-\,d(Cr^6)}{dt} = k\,\frac{(Cr^6)^{1.7}(Fe^{++})^2(H^+)^2}{(Fe^{+++})} \qquad (35)$$

The unusual fractional exponent of the chromic acid concentration which appears in this equation will be discussed later. Attention is here directed to the fact that the rate is proportional directly to the square of the ferrous-ion concentration[3] and inversely to the first power of the ferric-ion concentration. The

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[3] The dependence of the rate on the square of the ferrous-ion concentration was established by experiments in which the initial concentration of ferrous ion was varied. Regret-

inverse dependence of the reaction rate on ferric-ion concentration is further supported by Gortner (28). He found that fluoride (which forms a strong complex with ferric but not with ferrous ion (26)) greatly accelerates the oxidation, probably by reducing the concentration of ferric ion. But all of this work does not fully establish the quantitative dependence of the rate on the inverse first power of the ferric-ion concentration. Here (for want of evidence to the contrary) this dependence will be assumed.

Wagner (70) interprets the observed decrease in reaction rate with increase in concentration of ferric ion as follows. The first step in the reaction is a reversible one in which ferric ion is produced.

$$\mathrm{Cr^6 + Fe^{++} \rightleftarrows Cr^5 + Fe^{+++}} \qquad (9)$$

Subsequently pentavalent chromium reacts, in a rate-controlling step, with ferrous ion. Such a pair of reactions leads to the observed dependence of the reaction rate upon the concentrations of ferrous and ferric ions. Wagner has suggested two alternative schemes for the second (rate-controlling) step.

$$\mathrm{Cr^5 + Fe^{++} \rightarrow Cr^4 + Fe^{+++}} \text{ (rate controlling)} \qquad (36)$$

$$\mathrm{Cr^4 + Fe^{++} \rightarrow Cr^3 + Fe^{+++}} \qquad (37)$$

or

$$\mathrm{Cr^5 + Fe^{++} \rightarrow Cr^3 + Fe^4} \text{ (rate controlling)} \qquad (38)$$

$$\mathrm{Fe^4 + Fe^{++} \rightarrow 2Fe^{+++}} \qquad (39)$$

In 1903 Benson (4) studied quantitatively the ferrous ion-induced oxidation of iodides by chromic acid. The induction factor is 2, i.e., two iodide ions are oxidized for each ferrous ion. This fact strongly suggests that the iodide ions are oxidized by some compound of pentavalent chromium. Probably the reaction is

$$\mathrm{Cr^5 + I^- \rightarrow Cr^3 + IO^-} \qquad (10)$$

$$\mathrm{2H^+ + IO^- + I^- \rightarrow I_2 + H_2O} \qquad (11)$$

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tably there is a typographical error (revealed by recomputation of the original data) in Miss Benson's record of her experiment No. 1. The appropriate constants are

EXPERIMENT	*k*, COMPUTED FOR A REACTION OF ORDER *n* IN FERROUS ION		
	$n = 1$	$n = 2$	$n = 3$
No. 1	0.21	0.66	2 (approx.)
No. 2	0.12	0.71	4 (approx.)

The ferrous-ion concentration was twice as high in experiment No. 2 as in No. 1; only for the second order of this concentration is k approximately constant.

At high concentrations of iodide, the equation for the rate of formation of iodine is

$$d(I_2)/dt = k\,(H^+)_4(CrO_3)^{1.5}\,\frac{(I^-)(Fe^{++})}{(Fe^{+++})} \tag{40}$$

This equation indicates that iodide competes successfully with ferrous ion for the pentavalent chromium. Furthermore, at high concentrations of iodide, chromic acid disappears several times as fast as it does in the absence of iodide. This fact supports the hypothesis that iodide reacts with pentavalent chromium. If reaction 10 (instead of 36 or 38) is the rate-controlling step, then the overall rate of formation of iodine must depend on the concentrations of I^- and Fe^{++} in the way shown by the experimentally determined kinetic equation (equation 40).

The asserted dependence of the rate on the fourth power (see equation 40) of the hydrogen-ion concentration should be reinvestigated; the later and more precise work of Wagner (*vide infra*) suggests that the third power is more probable.

Wagner and Preiss (70) have carefully studied the competition between ferrous ion and iodide for pentavalent chromium. In successive experiments they varied the concentrations of ferrous ion, chromate, iodide, and acid over wide ranges. Assuming the mechanism already proposed (*cf.* equations 9–11 and 36–39), the amount of iodine formed depends primarily upon the relative concentrations of the iodide and ferrous ions.

$$Cr^6 + Fe^{++} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cr^5 + Fe^{+++} \tag{9}$$

$$Cr^5 + Fe^{++} \xrightarrow{k_3} \text{products} \tag{36 or 38}$$

$$Cr^5 + I^- \xrightarrow{k_4} Cr^3 + IO^- \tag{10}$$

If v_1 is the rate of reactions 36 or 38, and v_2 is that of reaction 10, then

$$\frac{v_1}{v_2} = \frac{k_3(Fe^{++})}{k_4(I^-)} \quad \text{and} \quad \frac{k_3}{k_4} = \frac{(I^-)}{(Fe^{++})}\,\frac{v_1}{v_2} \tag{41}$$

The ratio v_1/v_2 is the ratio of the rate of formation of ferric ion (after allowing for reaction 9) to the rate of formation of iodine; near the beginning of the reaction the ratio of these rates is measured by the ratio of the yields. Wagner and Preiss found that, at constant acidity, the ratio k_3/k_4 (based upon yield determinations in accordance with equation 41) is in fact constant. This result agrees with the interpretation of the reaction given above. They also found that, with varying acidity, $k_3(H^+)/k_4$ rather than k_3/k_4 is constant; this fact means that the rate-controlling step of the reaction of pentavalent chromium with iodide involves one more hydrogen ion than does the reaction of pentavalent chromium with ferrous ion. Since the overall rate of the chromate–ferrous ion reaction depends (*cf.* equation 35) on the square of the hydrogen-ion concentration, the induced oxidation of iodide should depend upon the third power (rather than the fourth power; *cf.* equation 40) of the hydrogen-ion concentration.

Although the mechanism of the oxidation of iodide by chromate, as induced by ferrous ion, is thus satisfactorily explained, there remain two alternative paths for the oxidation of ferrous ion by pentavalent chromium. One of these involves tetravalent chromium, the other tetravalent iron. (There are other oxidations (11, 27, 33) which can be explained by assuming the formation of unstable intermediate compounds of tetravalent iron.) The data so far available do not fully justify a choice between the two.

According to equations 35 and 40, in the chromic acid oxidation of ferrous ion the observed reaction rate is approximately proportional to the 1.5–1.7 power of the chromic acid present. This fractional power in the kinetic equation remains to be explained. When the acid chromate ion is the sole oxidizing agent (e.g., in the oxidation of arsenite; see equation 31), the oxidation rate is apparently proportional to a fractional power (between 0.5 and 1.0) of the total chromic acid. The exponent greater than unity (that is, 1.5–1.7) for the chromic acid concentration in the rate equation 35 or 40 suggests that here the active oxidizing agent is the dichromate ion, $Cr_2O_7^{--}$. The concentration of this ion must vary (*cf.* equation 20) as the square of the gross concentration of chromic acid, wherever that concentration is small. The observations of Benson, although not in good quantitative agreement with the hypothesis that $Cr_2O_7^{--}$ is the active oxidizing agent, certainly suggest that such is the fact.

Since, however, the hexavalent chromium and ferrous ion are assumed to be in equilibrium (see equation 9) with pentavalent chromium and ferric ion, this explanation is valid only if the pentavalent chromium is here present as a complex with hexavalent chromium. (For example, if equation 9 may be rewritten

$$Cr_2O_7^{--} + Fe^{++} \rightleftarrows Cr_2O_7^{---} + Fe^{+++} \tag{42}$$

the ion $Cr_2O_7^{--}$ is given merely as a hypothetical example of a Cr^5–Cr^6 complex.)

Such an assumption of a new chromium-containing species, however, would require reconsideration of the reaction schemes for the chromic acid oxidation of isopropyl alcohol (72).

D. The oxidation of formic acid

Quantitative investigations of chromic acid oxidations, with the exception of the studies already discussed, have not been highly successful. Nevertheless, some of them deserve further mention, and among such is the oxidation of formic acid. The rate of this reaction has not yet been investigated over a wide range of initial concentrations of chromic acid; consequently the appropriate kinetic equation is still unknown. The reaction rate, like that of the oxidation of isopropyl alcohol, is diminished by manganous ion, but where the concentration of Mn^{++} is moderate, this rate approaches one-third (rather than one-half) of the rate when no Mn^{++} is present (21). These facts suggest (but do not prove) that the mechanism for the oxidation of formic acid is similar to that for the oxidation of isopropyl alcohol. The difference in the factor by which Mn^{++} diminishes the rate is easily explained. In the oxidation of formic acid, the conditions are such that no MnO_2 accumulates in the solution. Wagner therefore suggested that manganous ion catalyzes the disproportionation of tetravalent or pentavalent chromium to chromic ion and to chromate. Of the several sets of reactions which would account for the experimental facts, reaction 43 is a sequence which may occur in the absence of manganous ion and reaction 44 is a sequence which may occur in the presence of that ion. (These sequences, although tentative, are here preferred to the ones suggested by Wagner.)

$$HCrO_4^- + HCOOH \rightarrow CO_2 + Cr^4 \tag{43a}$$

$$Cr^4 + Cr^6 \rightarrow 2Cr^5 \tag{43b or 4}$$

$$Cr^5 + HCOOH \rightarrow Cr^3 + CO_2 \tag{43c}$$

and

$$HCrO_4^- + HCOOH \rightarrow CO_2 + Cr^4 \tag{44a}$$

$$3Cr^4 \text{ (in steps, catalyzed by } Mn^{++}) \rightarrow 2Cr^3 + HCrO_4^- \tag{44b}$$

The sets of equations 43 and 44 account for the observed fact that in the presence of manganous ion the rate of disappearance of chromic acid is only one-third as great as it is in the absence of that ion.

The rate of oxidation of formic acid by chromic acid is also diminished by addition of cerous salts. A complete kinetic study of the oxidation under these conditions has not yet been carried out, but since the only known valence states of cerium are three and four, the valence of the cerium must increase by one during the reaction. Hence, the cerous salt probably reacts with a compound containing tetravalent chromium. This conclusion is consistent with the general mechanism (equations 43 and 44) already proposed for the reaction.

Snethlage (64) investigated the chromic acid oxidation of formic acid in solutions containing 1–60 per cent sulfuric acid. The function pH as applied to such solutions has little or no meaning; the only acidity function useful under the stated conditions is Hammett's H_0 function (29). This function, applied to dilute aqueous solutions, approaches pH asymptotically; applied to concentrated sulfuric acid, it is a logarithmic function of the tendency of the solvent to transfer a proton to an uncharged base. Any reaction which proceeds by way of an activated complex made up of various (electrically neutral) molecules and one proton obeys the relation:

$$\log k + H_0 = \text{constant} \tag{45}$$

This relation agrees approximately with Snethlage's finding that the oxidation rate in 60 per cent sulfuric acid is 30,000 times as fast as the rate in 5 per cent sulfuric acid. This agreement supports the hypothesis that one proton reacts with a formic acid molecule and the appropriate chromate ion. It is reasonable to assume that the mechanism for the chromic acid oxidation of formic acid is similar to that for the oxidation of isopropyl alcohol.

E. The oxidation of phosphorous acid

The oxidation of phosphorous acid by chromic acid has been investigated by Dhar (21). Manganous ion diminishes the oxidation rate by two-thirds, a fact which suggests a reaction scheme analogous to that proposed for formic acid (equations 43 and 44).

F. The oxidation of aldehydes

The rates of the chromic acid oxidations of some aromatic aldehydes (48) in acetic acid–sulfuric acid solutions have been studied in some detail. From the data available, it is impossible to determine which particular ion of hexavalent chromium is the active oxidizing agent. On the other hand, the effect which the structure of the aldehyde exercises on the oxidation rate has been thoroughly tested. The nitrobenzaldehydes are oxidized considerably more rapidly than is benzaldehyde, which in turn is oxidized more rapidly than is *p*-methoxybenzaldehyde. The interpretation of these facts is by no means unambiguous; further investigations are needed to permit valid conclusions concerning the mechanisms of the various reactions.

G. The oxidation of inorganic iodides

Studies of the chromic acid oxidation of iodide ion, although they have been extensive, have not led to any fully satisfactory reaction mechanism. In dilute solutions of chromic acid the oxidation rate is proportional to a power of the chromic acid concentration (18) slightly less than 1; very probably the true oxidizing agent (as in the oxidations of isopropyl alcohol and arsenite) is the acid chromate ion. The reaction rate depends in a complex way on the concentrations of the iodide and hydrogen ions (2); apparently there is in the rate equation a term in $(H^+)(I^-)$ and one in $(H^+)^2(I^-)^2$. But at present little more can be said about this highly important reaction.

H. The oxidation of uranyl ion

The chromic acid oxidation of uranyl ion (49) has not been investigated in detail. However, in this reaction, the induction factor for iodide is not 2 but approximately 1; and this fact sets the reaction in question apart from all other induced oxidations of iodide. Without further experimentation, no mechanism can here be definitely established. Nevertheless, the fact that compounds of pentavalent uranium are known suggests the following scheme as a working hypothesis.

$$UO^{++} + Cr^6 \rightarrow UO_2^{++} + Cr^4 \qquad (46a)$$

$$UO^{++} + Cr^4 \rightarrow U^5 + Cr^3 \qquad (46b)$$

$$U^5 + Cr^6 \rightarrow U^6 + Cr^5 \qquad (46c)$$

$$UO^{++} + Cr^5 \rightarrow UO_2^{++} + Cr^3 \qquad (46d)$$

or

$$Cr^5 + 2I^- \rightarrow Cr^3 + I_2 \qquad (46e\text{ or }33)$$

Competition between a set of reactions such as 46 (which implies an induction factor of 0.5) and the normal type of induced oxidation of iodide (which implies an induction factor of 2) would account for the intermediate values (0.7–1.0) experimentally obtained for the induction factor in the oxidation of uranyl ion.

I. The oxidation of oxalic, lactic, and malic acids

Studies of the chromic acid oxidation of oxalic, lactic, and malic acids have shown that the kinetics of these reactions are extremely complex. First and foremost, there are wide differences in reaction products. Oxalic acid, as expected, is oxidized to carbon dioxide, but lactic acid is oxidized not at the hydroxyl but at the carboxyl group (14):

$$8H^+ + 2HCrO_4^- + 3CH_3CHOHCOOH \rightarrow$$
$$3CH_3CHO + 3CO_2 + 2Cr^{+++} + 8H_2O \qquad (47)$$

Reaction 47 probably does not involve an oxidation of lactic acid to pyruvic acid, followed by a decarboxylation; for pyruvic acid, under the experimental conditions in question, undergoes further oxidation (15) much more rapidly than it undergoes decarboxylation (3). Presumably the lactic acid is attacked at the carboxyl group. Although the nature of the products obtained by chromic acid oxidation from other hydroxy acids has not been fully determined, reactions analogous to 47 are probably not infrequent.

The rate of the chromic acid oxidation of oxalic acid does not depend in any simple manner upon the concentrations of the reactants (20, 35), nor does it increase monotonically with increase in the concentration of added sulfuric acid (63). The rate constant for the oxidation in sulfuric acid solution is much greater than that for the thermal decomposition in the same solution (12, 47).

$$HOOCCOOH \rightarrow CO_2 + CO + H_2O \qquad (48)$$

Hence, the oxidation must clearly involve a direct attack of the oxidizing agent upon the organic acid (or ion). Furthermore, the rates of oxidation of both oxalic and lactic acids are considerably increased by the addition of small amounts of manganous ion (20, 21). Further information about these oxidations has been obtained from photochemical studies.

J. Photochemical oxidations

Although most chromic acid oxidations have been studied only in the dark, experiment has shown that some of them are accelerated by light. Bhattacharya and Dhar (6) showed that, in the chromic acid oxidation of citric, tartaric, and lactic acids, the quantum yields range from 100 to 1000. The reactions are thus clearly photochemical chain reactions of some sort. By contrast, Bowen (7, 8, 9, 10) and his coworkers showed that when the lower aliphatic alcohols are photochemically oxidized by dichromates,[4] the quantum yield never exceeds 2. There is of course no assurance that the mechanism of any particular photochemical oxidation by chromic acid bears any resemblance to the mechanism of the corresponding dark reaction. However, the results of the two photochemical investigations just quoted are consistent with the mechanisms hereafter proposed for the dark reactions.

The oxidation of isopropyl alcohol by chromic acid is kinetically simple. It is characterized by the following facts: (*1*) The only organic product is acetone. (*2*) The reaction rate depends upon small integer powers of the concentrations of the reactants (isopropyl alcohol, hydrogen ion, and $HCrO_4^-$ ion). (*3*) Manganous ion decreases the reaction rate; the reaction induces the oxidation of Mn^{++} to MnO_2. (*4*) The corresponding photochemical oxidation has a low integer quantum yield. On the other hand, the oxidation of lactic acid, for example, is very complex: (*1*) The point of oxidative attack is at the carboxyl, not at the hydroxyl group. (*2*) The reaction rate does not depend upon small integer powers of the concentrations of the reactants. (*3*) The reaction is catalyzed, not retarded, by the addition of manganous ion. (*4*) The corresponding photochemical oxidation is characterized by a long reaction chain. Evidently the mechanism for the oxidation of lactic acid (and of oxalic and malic acids) must be quite different from that for the oxidation of isopropyl alcohol. A detailed study of the oxidations of the acids mentioned may well reveal that these reactions involve organic free radicals as intermediates.

IV. COMPOUNDS OF PENTAVALENT AND TETRAVALENT CHROMIUM

In the preceding discussions of the mechanisms of chromic acid oxidations, the existence of unstable intermediates containing pentavalent and tetravalent chromium has been inferred from kinetic data. Hence, it is appropriate to examine the evidence for the existence of stable compounds containing chromium in these unusual valence states.

There are several known compounds which probably contain pentavalent chromium. The most important series (77) of such compounds was discovered by Wienland; it consists of the potassium, rubidium, cesium, ammonium, pyridinium, and quinolinium salts of the anion $CrOCl_4^-$. These salts are prepared by treating acetic acid solutions of chromium trioxide with dry hydrogen chloride, and then adding to the mixture a solution of the appropriate metal (or substituted ammonium) chloride. The formulas of the substances thus prepared suggest that they contain pentavalent chromium. Their oxidizing power corresponds to that anticipated for compounds containing chromium with this valence; and in non-ionizing solvents the molecular weight of the pyridinium compound corre-

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[4] Bowen and his coworkers were the first to consider the possibility that the equilibrium

$$Cr_2O_7^{--} + H_2O \rightleftharpoons 2HCrO_4^- \qquad (19)$$

might be important in determining the mechanism of chromic acid oxidations. Unfortunately the work of Neuss and Rieman was not available to them; hence they chose for the equilibrium constant of reaction 19 a value which now appears to be in error.

sponds to the monomeric formula $C_5H_5NHCrOCl_4 \cdot H_2O$. Moreover these salts (e.g., Rb_2CrOCl_5) are isomorphous with the corresponding salts of pentavalent niobium (e.g., Rb_2NbOCl_5). Although these facts support the conclusion that these compounds contain pentavalent chromium, the low magnetic susceptibility (5) of the pyridinium salt implies that the compound contains only hexavalent chromium. No explanation of the discrepancy is at present available.

When the compound $C_5H_5NHCrOCl_4$ (or any other compound of the same series) is treated with water, it quickly disproportionates to give two compounds, one of trivalent and one of hexavalent chromium. But since the rate of this process is measurable (see below) the compound cannot initially contain chromium in these different valence states. Wagner (69) showed that Weinland's pyridinium salt of $CrOCl_4^-$ oxidized iodide in neutral or slightly acid solutions, whereas it is well known that ordinary dichromates do not. These facts are clearly consistent with the conclusion that $C_5H_5NHCrOCl_4$ is a compound of pentavalent chromium, and with the conclusion (*cf.* equation 33) that such pentavalent chromium compounds cause the induced oxidation of iodide in dilute acid solution.

The oxidizing properties of pentavalent chromium may be expected to vary considerably with the composition and structure of the particular pentavalent chromium intermediate present. Hence, the intermediate formed in a given chromic acid oxidation need not behave exactly like any of the oxychlorides just discussed. However, Wagner (69) in his investigations of the chromic acid oxidation of oxalic and lactic acids showed that in these reactions the intermediate formed does act very much like $C_5H_5NHCrOCl_4$. The latter compound oxidizes iodide ions in solutions containing far less acid than is required for the oxidation of iodide ions by compounds of hexavalent chromium. To demonstrate the similarity between this compound and the postulated pentavalent chromium intermediate, he neutralized a reaction mixture in which chromic acid had partially oxidized either lactic or oxalic acid, and then added an inorganic iodide to the mixture. Iodine was liberated under conditions of acidity where chromates alone do not oxidize iodide at all. Clearly, some metastable compound containing chromium in an intermediate valence state must be responsible for this action. In his most spectacular experiment, Wagner reduced the acidity of his reaction mixture with acetate ion and at the same time precipitated the unreacted hexavalent chromium as barium chromate. That is, he started with 30 cc. of a solution 0.17 *N* with respect to sulfuric acid, 0.067 *N* with respect to potassium dichromate, and containing a large excess of lactic acid. After the oxidation had proceeded 30 per cent to completion, he poured the solution with violent stirring into a large excess of barium acetate solution. Finally, to equal successive samples of this mixture he added, at various times, an excess of a solution of potassium iodide. The amounts of iodine formed are shown in table 6. Evidently the intermediate (and probably pentavalent) chromium compound which constitutes an appreciable fraction (about 5 per cent) of the total chromium present, does not disappear instantaneously when the pH of the solution is about 5. Wagner also showed that, when the pH is about 7, the rate of disappearance is much greater.

Other compounds of pentavalent chromium have been reported, but their oxidizing properties are of relatively little interest in connection with the present study. The magnetic susceptibilities (66) of salts of perchromic acid (e.g., K_3CrO_8) show that these compounds must contain either pentavalent or heptavalent chromium; the former is much more probable. F. Hein (32) prepared a series of polyphenylated derivatives of chromium including $(C_6H_5)_5CrOH$, $(C_6H_5)_4CrI$, and $(C_6H_5)_3CrI \cdot (C_6H_5)_2O$. The magnetic susceptibilities (41) of these substances indicate that they all are compounds of pentavalent chromium. This valence is fairly evident for the compound $(C_6H_5)_4CrI$, but the others appear to be compounds of hexavalent or tetravalent chromium. Clearly the entire series needs further investigation.

Recently Wartenberg (71) has prepared both CrF_4 and $CrCl_4$; these are relatively stable and are unquestionably compounds of tetravalent chromium.

The dioxide is well known, but the magnetic susceptibility data (5) do not unambiguously distinguish between a true compound of tetravalent chromium and a mixed oxide, $CrO_3 \cdot Cr_2O_3$. There are no data to exclude either one of these possibilities. Of somewhat more interest are the compounds which Étard (23) obtained by treating toluene (or related compounds) with chromyl chloride, CrO_2Cl_2. Where toluene is used, the reaction product contains two molecules of the chloride to one of the hydrocarbon, e.g., $C_6H_5CH_3 \cdot 2CrO_2Cl_2$. This compound, when hydrolyzed, decomposes to give benzaldehyde and compounds of both trivalent and hexavalent chromium:

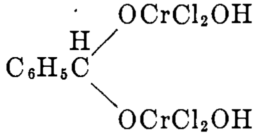
TABLE 6

Oxidation of iodide by transitory chromium compound

TIME BEFORE ADDITION OF KI	0.1 *N* $Na_2S_2O_3$ USED TO TITRATE IODINE
seconds	*cc.*
0	0.70
10	0.60
30	0.65
60	0.40
120	0.25
300	0.10

$$3[C_6H_5CH_3 \cdot 2CrO_2Cl_2] \rightarrow 3C_6H_5CHO + 4CrCl_3 + 2H_2CrO_4 + H_2O \qquad (49)$$

These hydrolysis products suggest for Étard's compounds structures like



$$C_6H_5CH(OCrCl_2OH)_2$$

Such structures indicate that the compounds in question contain tetravalent chromium. No magnetic investigations of these substances have yet been made.

V. PROPERTIES OF TETRAVALENT AND PENTAVALENT CHROMIUM

The data so far presented can be used to make approximate estimates of the oxidizing powers of compounds containing pentavalent chromium. In each instance the exact potential must depend upon the particular compound of pentavalent chromium present, but the estimates given hereafter are so rough that such variations may be neglected.

The kinetics of the initial reaction between ferrous ion and a compound of hexavalent chromium show that the process is a reversible one, and that the equilibrium is displaced toward the starting materials.

$$Cr^6 + Fe^{++} \rightleftarrows Cr^5 + Fe^{+++} \qquad (9)$$

Since the equilibrium is displaced toward the left, the standard oxidation potential for the ferric ion–ferrous ion couple must exceed that for the Cr^6–Cr^5 couple. Therefore, since (46) for the reaction

$$Fe^{+++} + e \rightleftarrows Fe^{++} \qquad (50)$$

the standard potential, E^0, is equal to 0.74 volt, for the reaction

$$Cr^6 + e \rightleftarrows Cr^5 \qquad (51)$$

the standard potential must be $E \leq 0.62$ volt. That is to say, if the equilibrium 9 is displaced at least 99 per cent to the left, the difference between the standard potentials of reactions 50 and 51 must be at least 0.12 volt. The effect of hydrogen ions is here omitted; but since all the data under consideration have been obtained in the region between 0.001 and 1 M acid, this omission is unlikely to cause an error in potential of more than a few tenths of a volt, and most of this error cancels out when the figures here given are applied (uncorrected for H^+ effect) to a system other than the one from which the data were secured.

The assignment of a potential of 0.6 volt or less to the Cr^6–Cr^5 couple permits the assignment of a potential of 1.75 volt or more for the reaction:

$$Cr^5 + 2e \rightleftarrows Cr^3 \qquad (52)$$

This conclusion follows from the fact that, for the reaction

$$7H^+ + HCrO_4^- + 3e \rightleftarrows Cr^3 + 4H_2O \qquad (53)$$

the potential (46), E^0, is 1.36 volt. Further, the conclusion would not be greatly modified if a moderately stable Cr^5–Cr^6 complex (see equation 42) exists.

The lower limit (1.75 volt) for the potential of the Cr^5–Cr^3 couple is consistent with the chromic acid oxidation of bromide induced by arsenite. This reaction very probably parallels the induced oxidation of iodide. It will later be shown that iodide is oxidized by pentavalent chromium to hypoiodite; hence bromide is presumably oxidized to hypobromite

$$Cr^5 + Br^- \rightarrow Cr^3 + BrO^- \qquad (54)$$

The potential for the Br^-–BrO^- couple is 1.6 volt. Clearly, then, the Cr^5–Cr^3 couple has sufficient potential to cause reaction 54.

Although it is thus possible to set a lower limit to the potential of the Cr^5–Cr^3 couple, it is not possible to assign a precise upper limit to this potential. A rough idea of this upper limit may be obtained by applying the theory of absolute reaction rates (25) to Benson's data (4). The argument is rather tenuous; it has, however, led the author to the opinion that the potential of the Cr^5–Cr^3 couple probably does not exceed 2 volts.

It has not proved possible to make even an approximate estimate of the potential for the reactions

$$Cr^5 + e \rightleftarrows Cr^4 \tag{55}$$

and

$$Cr^4 + e \rightleftarrows Cr^3 \tag{56}$$

To the second of these, a minimum potential of 1.5 volts may be assigned, on the basis of the quantitative oxidation of manganous ion to manganic ion (or MnO_2) by tetravalent chromium. But by how much the potential exceeds 1.5 volts is quite uncertain.

Stefanovskiĭ (82) attempted to measure the potentials involved in equations 55 or 56 directly. Although his experiments clearly reveal that compounds containing chromium in intermediate valence states have high oxidizing power, his data do not permit the exact determination of the potentials which he was seeking.

It should be noted that tetravalent chromium is not only a strong oxidizing agent but also (in all probability) a good reducing agent. Since the potential for reaction 56 is greater than 1.5 volts, the potential for the reaction

$$Cr^6 + 2e \leftrightarrows Cr^4 \tag{57}$$

cannot exceed 1.3 volts; it may, however, be much less than 1.3 volts, and if such is the fact, then tetravalent chromium can be oxidized with moderate ease.

Finally, it is necessary to present the argument that pentavalent chromium oxidizes iodide to hypoiodite rather than to iodine. First, it should be noted that the direct oxidation of iodide to iodine requires the formation of iodine atoms:

$$Cr^5 + I^- \rightarrow Cr^4 + I^0 \tag{58}$$

and

$$Cr^4 + I^- \rightarrow Cr^3 + I^0 \tag{59}$$

But the assumption that these reactions occur involves an internal contradiction. In a reaction such as the oxidation of arsenite, tetravalent chromium is first produced (see equation 32a). In order to explain the observed induction factor of 2, it is necessary to assume that this tetravalent chromium is converted quantitatively (by direct or indirect reaction with hexavalent chromium) to pentavalent chromium. Hence the tetravalent chromium cannot react with iodide. On the other hand, in order that iodine be produced in reaction 59 (also a necessary requisite for the induction factor of 2) the compound containing tetravalent chromium must react quantitatively with iodide, and may not react either directly or indirectly with a compound of hexavalent chromium. In view of this internal contradiction, it must be concluded that pentavalent chromium oxidizes iodide to something other than iodine atoms—most probably to hypoiodite ions. The analogous conclusion can be reached (with high probability if not with certainty) by considering the potentials involved in the induced oxidation of bromide to bromine by way of bromine atoms.

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