

## The Kinetics of the Chromic Acid Oxidation of Isopropyl Alcohol: The Induced Oxidation of Manganous Ion

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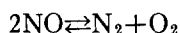


value of the partial pressure of nitric oxide  $\bar{p}_{\text{NO}}$  was calculated by taking into account the adiabatic change of state and a correction term for the extent of the chemical reaction by means of the equation

$$\bar{p}_{\text{NO}} = 0.0610(\bar{T}/3000)^{\gamma/(\gamma-1)} - \Delta p_{\text{NO}} \bar{T}, \quad (21)$$

where  $\Delta p_{\text{NO}} \bar{T}$  equals the reduction of partial pressure resulting from chemical reaction and  $\bar{T}$  is the average temperature in the interval.

Comparison of the last two columns of Table II shows that significant departures from equilibrium occur in the temperature interval between 2900 and 2800°K and that the equilibrium



is practically frozen below about 2800°K.

A calculation similar to the one just described has also been carried out for a gas with  $\gamma = 1.67$  and  $\bar{M} = 4$  g/mol using the same initial concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$ . Again it was found

that practically no composition changes occur below about 2800°K. This result is not surprising since the thermodynamic constants of a gas do not produce a significant change in the term  $(-dt/dT)$  or in the rate of decomposition of nitric oxide. Reference to Eq. (14) shows that the design parameters which affect some control over the composition changes are  $\tau$  and  $\delta$ . In general, however, it is not practical to design a nozzle so as to give either constant-composition or equilibrium flow since design parameters  $\tau$  and  $\delta$  are of secondary importance when compared with the reaction rate constants.

In conclusion, it should be emphasized that the present analysis is concerned only with the decomposition of nitric oxide according to Eq. (16). If gases are present which react chemically with nitric oxide, then the over-all composition change should be analyzed in terms of the composition changes associated with each of the individual reactions.

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## The Kinetics of the Chromic Acid Oxidation of Isopropyl Alcohol: The Induced Oxidation of Manganous Ion

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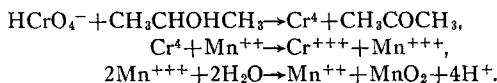
(Received July 23, 1948)

1. Isopropyl alcohol "induces" the chromic acid oxidation of manganous salts to  $\text{MnO}_2$ . The limiting induction factor (ratio of moles of  $\text{MnO}_2$  to moles of acetone formed) is one-half.

2. In the presence of manganous ion the rate at which chromic acid is reduced by isopropyl alcohol is decreased; the maximum decrease in rate observed under a wide variety of experimental conditions is 50 percent.

3. These facts, together with the previously determined reaction kinetics, demand the formation of an intermediate chromium compound in which chromium has the valence four or five.

4. Within chemically reasonable limits, *all* the reaction mechanisms involving such transitory intermediates have been examined. In the presence of manganous salts the only possible mechanism is



In the absence of manganous salts several mechanisms (all of which are listed) are possible.

### INTRODUCTION

IT has recently been shown<sup>1</sup> that, in the rate-controlling step of the chromic acid oxidation

<sup>1</sup>F. H. Westheimer and A. Novick, *J. Chem. Phys.* **11**, 506 (1943).

of isopropyl alcohol to acetone, one molecule of the alcohol reacts with one acid chromate ion and two hydrogen ions. In the over-all reaction, isopropyl alcohol undergoes a two electron oxidation; it follows, therefore, that the rate-deter-

mining step must be either a reaction which produces a ketyl-free radical and a compound of pentavalent chromium, or a reaction which produces acetone and a compound of tetravalent chromium.<sup>2</sup> A complete mechanism for the chromic acid oxidation of isopropyl alcohol should identify the valence states of the chromium intermediates actually involved, and specify the further reactions by which these transitory intermediates are converted into the final reaction products. A tool with which to investigate the details of the reaction in question is supplied by the observation<sup>1</sup> that the chromic acid oxidation of isopropyl alcohol "induces"<sup>3</sup> the oxidation of manganous salts to manganese dioxide.

Chromic acid in dilute acid solution, or in acid solution containing acetone and a chromic salt, does not oxidize  $\text{Mn}^{++}$  to  $\text{MnO}_2$ . The active reagent in the reaction induced by isopropyl alcohol must therefore be one of the already

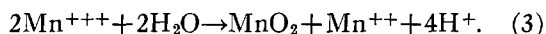
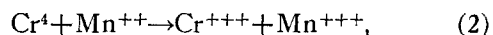
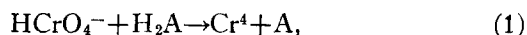
TABLE I. The induction factor: variation in  $\text{Mn}^{++}$  concentration.

Conc. of $\text{MnSO}_4$ , mole/liter	Millieq. chromic acid reduced	Millieq. $\text{Mn}^{++}$ oxidized (calc.)	Induction factor
0.053	0.137	0.036	0.36
0.106	0.141	0.040	0.40
0.213	0.148	0.047	0.47
0.331	0.153	0.050	0.50
0.426	0.149	0.048	0.48

postulated transitory compounds of tetravalent or pentavalent chromium. Furthermore, in the presence of manganous ion, the rate at which chromic acid is reduced is decreased by about fifty percent.<sup>1</sup> In the present investigation, the induced oxidation of manganous salts to  $\text{MnO}_2$  and the concurrent decrease in reaction rate (hereafter called "inhibition") have been carefully studied. The results thus obtained show that the reaction sequence in the presence of manganous salts is that represented by Eqs. (1)–(3).

<sup>2</sup> For other cases in which compounds of pentavalent or tetravalent chromium have been described or inferred, see R. F. Weinland and M. Fiederer, *Ber.* **39**, 4042 (1906); C. Wagner and W. Preis, *Zeits. f. anorg. allgem. Chemie* **168**, 265 (1928); C. Wagner, *ibid.* **168**, 279 (1928).

<sup>3</sup> For other examples of induced chromic acid oxidations see C. F. Schönbein, *J. pract. Chem.* **75**, 108 (1858); F. Kessler, *Pogg. Ann.* **119**, 218 (1863); R. Lang, *Zeits. anorg. f. allgem. Chemie* **170**, 387 (1928); E. H. Land and J. Zwerina, *ibid.* **170**, 389 (1928).

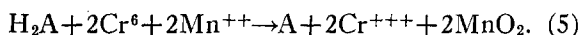
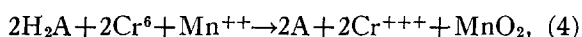


(In these and subsequent equations, acetone is represented by A, isopropyl alcohol by  $\text{H}_2\text{A}$ , the ketyl free radical by  $\text{HA}^\cdot$ , compounds of pentavalent and tetravalent chromium by  $\text{Cr}^5$  and  $\text{Cr}^4$ . Hydrogen ions are omitted wherever it is possible to do so without ambiguity.)

In the absence of manganous ions, Eq. (1) represents the first stage of the reaction; no decision can as yet be made among several possibilities for subsequent stages.

### THE INDUCTION FACTOR

The oxidation of manganous salts to manganese dioxide by chromic acid alone is thermodynamically impossible<sup>4</sup> at  $\text{pH} > 0$ . Under these conditions the reverse reaction occurs slowly (see below). Since isopropyl alcohol induces the chromic acid oxidation of manganous salts, the stoichiometry of the reaction must be represented by (4) or (5), or by a combination of (4) and (5).



The ratio of the number of moles of  $\text{MnO}_2$  produced to the number of moles of alcohol oxidized is called the "induction factor" for the reaction in question; the induction factor for reaction (4) is one-half, whereas that for (5) is two. Since experiment has shown that the induction factor is approximately one-half, Eq. (4) is stoichiometrically correct.

In every actual experiment, however, the value of the induction factor was found to be below 0.5; in fact this latter value was obtained only as a limit which was approached asymptotically when the manganous ion concentration was high, and when other special precautions (see below) were observed. Asymptotic approach to a definite induction factor has been observed in other cases,<sup>3</sup> and was here to be anticipated for the following reasons: In the absence of manganous ion the transitory chromium intermediates are

<sup>4</sup> W. M. Latimer, *Oxidation Potentials* (Prentice-Hall, Inc., New York, 1938).

somehow consumed (e.g., by reaction with isopropyl alcohol). Consequently in the presence of manganous ion, isopropyl alcohol (or whatever it is with which the transitory compounds react) must compete for the transitory tetravalent or pentavalent chromium compounds. The manganous ion will compete successfully for the intermediate (and the stoichiometry will be that of Eq. (4)) only when the concentration of this ion is high; hence only under these conditions will the limiting value of the induction factor be attained.

In the experiments here performed, measured amounts of isopropyl alcohol in dilute perchloric acid solution were allowed to react essentially to completion with excess chromic acid and manganous ion. Then the amount of precipitated  $\text{MnO}_2$  and the amount of unreacted chromic acid were independently determined. Since under like conditions but in the absence of manganous ion the oxidation of isopropyl alcohol to acetone is quantitative,<sup>1</sup> it was possible to compute the amount of manganous ion oxidized to  $\text{MnO}_2$  from the amounts of chromic acid and alcohol consumed. Since the two methods led to the same result, both were employed. Table I gives the data and the induction factor obtained in a series of experiments in which the manganous ion concentration was varied and in which the other conditions were favorable to the formation of  $\text{MnO}_2$ . All the reaction mixtures had a total volume of 61 cc and were 0.0162 molar in chromic acid, 0.82 molar in perchloric acid, and 0.166 molar in isopropyl alcohol.

Although it was never possible to obtain an induction factor greater than 0.5, many experiments led to lower values for this factor. These lower values were obtained not only in those experiments where insufficient manganous ion was used, but also in many experiments where the concentration of this ion was high. Careful tests, however, revealed that the  $\text{MnO}_2$  produced in the induced oxidations is not indefinitely stable; in the solutions in which it is formed it slowly oxidizes chromic salts to chromates and isopropyl alcohol to acetone. Reaction (3) between  $\text{Mn}^{++}$ ,  $\text{Mn}^{+++}$ , and  $\text{MnO}_2$  was also considered; it proved, however, to be unimportant compared to the reactions of  $\text{MnO}_2$  with chromic salts and isopropyl alcohol. When the induced

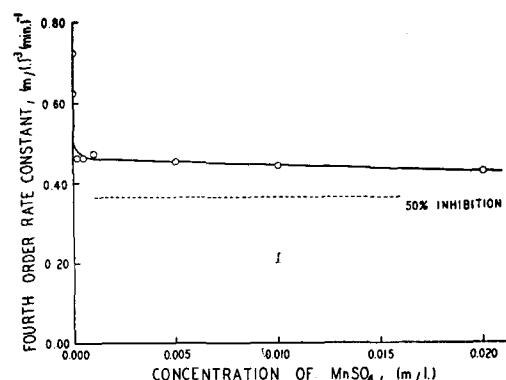


FIG. 1. Set of 8 determinations of the rate constant for the oxidation of isopropyl alcohol by chromic acid. Initial  $(\text{H}^+) = 0.345M$ , initial  $(\text{CH}_3\text{CHOHCH}_3) = 0.200M$ , initial  $(\text{CrO}_3) = 0.0100M$ ;  $(\text{Mn}^{++})$  shown in graph.

oxidation was allowed to proceed to completion, good yields of  $\text{MnO}_2$  could be obtained only when the amount of alcohol oxidized was small. Hence there is evidently a relatively narrow range of concentrations of isopropyl alcohol and manganous salts over which the limiting value of 0.5 for the induction factor can actually be attained. (Some of the data leading to this conclusion are presented in the experimental section.) Since, however, the only two limiting values of the induction factors in question are 2.0 and 0.5, there can be no doubt that the latter is the correct one.

### THE INHIBITION

It has already been noted that manganous ion decreases the rate at which chromic acid is reduced by isopropyl alcohol. This effect may easily be detected when solutions of manganous ion containing as little as  $10^{-6}$  mole/liter are used. The maximum effect (a diminution in rate of about 50 percent) is achieved when the concentration of manganous ion is less than 0.01 mole/liter. A typical series of experiments is

TABLE II. Inhibition of the oxidation by  $\text{Mn}^{++}$ .

Chromic acid, mole/liter	Isopropyl alcohol, mole/liter	$k_4$ , (mole/ liter) $^{-1}$ min. $^{-1}$ No $\text{Mn}^{++}$	$k_4$ , (mole/ liter) $^{-1}$ min. $^{-1}$ $(\text{Mn}^{++}) = 0.01$ mole/liter	Percent inhibition
0.100	0.020	0.542	0.425	21.6
0.010	0.020	0.566	0.405	28.4
0.001	0.020	0.632	0.417	34.0
0.100	0.200	0.727	0.473	34.9
0.010	0.200	0.723	0.440	39.2
0.001	0.200	0.715	0.443	38.0
0.100	1.250	0.996	0.510	48.8
0.010	1.250	0.875	0.470	46.3
0.001	1.250	0.825	0.437	47.0

illustrated by Fig. 1. Here, with increasing concentration of manganous ion, the rate constant asymptotically approaches a limit, which is 61 percent of that obtained in the absence of manganous ion. The results obtained under widely differing experimental conditions are summarized in Table II.

A 50 percent diminution of rate is quite clearly the limit which can be obtained even under special conditions, i.e., when high isopropyl alcohol and manganous ion concentrations and low chromic acid concentrations are employed. If the reaction mechanism later advanced were precisely correct, then it would always be possible at high manganous ion concentrations to obtain a 50 percent diminution of rate. The slight but real deviation of the experimental from the theoretical results is considered in a later section (Secondary Effects).

At this point a word about rate constants is necessary. The statement (cf. Eq. (1)) that the effective oxidizing agent is the acid chromate ion,  $\text{HCrO}_4^-$ , is based on the application of a fourth-order kinetic equation,<sup>1</sup> ( $N$ ), in which the value<sup>5</sup> of 0.023 mole/liter is assigned to the equilibrium constant for the hydrolysis (Eq. (6)) of dichromate to acid chromate ions.



The appropriate kinetic equation, ( $N$ ), had previously been applied to results obtained at 40°; it applied equally well to those here obtained at 25° in the absence of manganous ion, or in the presence of either a very low (0.00001 mole/liter) or a considerable (0.01 mole/liter) concentration of manganous ion. But for intermediate concentrations (around 0.001 mole/liter) the rate constants, calculated by the use of Eq. ( $N$ ), tended to drift downward during the course of each experiment; after one-half life these constants were 10–20 percent below the initial values.

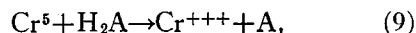
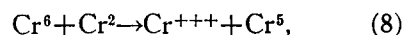
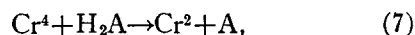
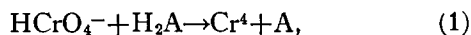
These rather poor rate constants are somehow related to the precipitation of  $\text{MnO}_2$  in the reaction mixtures. In the experiments where very little manganous ion is used no  $\text{MnO}_2$  precipitates during the reaction. Since inhibition nevertheless occurs in these experiments, man-

ganous ion must be oxidized and then regenerated. The manganic ions (or ions of tetravalent manganese) formed must be reduced, either by isopropyl alcohol or chromic ion or both. In experiments where the manganous ion concentration is high, manganese dioxide is promptly precipitated. However, in experiments where intermediate concentrations of manganous salts are used, only later does  $\text{MnO}_2$  precipitate. The precipitation of the  $\text{MnO}_2$  occurs approximately where the rate constant diminishes; further, if from the very beginning of the experiment  $\text{MnO}_2$  is suspended in the solution, the lower rate constant is obtained throughout.

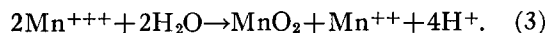
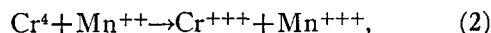
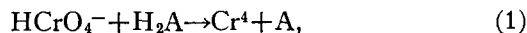
In order to be conservative, all the rate constants here reported are those which apply to the initial rate. If the average rate constant (or the rate constant obtained after  $\text{MnO}_2$  had precipitated) had been used, the values of the calculated percent of inhibition would have been closer to 50 percent than those shown in Table II.

## DISCUSSION

The experimental data just cited are consistent with the following reaction schemes: In the absence of manganous ion, the oxidation of isopropyl alcohol by chromic acid may occur by way of Eqs. (1) and (7)–(9).



or by one of several other paths to be later outlined. In the presence of manganous ion, the reaction occurs by way of Eqs. (1)–(3).



The stoichiometry of Eqs. (1)–(3) is consistent with a limiting value of 0.5 for the induction factor; the two sets of equations together account for the fact that manganous ion cuts in half the rate at which chromic acid is consumed. This latter effect is explained as follows: In the reaction scheme represented by Eqs. (1) and (7)–(9), one acid chromate ion is consumed in

<sup>5</sup> J. D. Neuss and W. Rieman, J. Am. Chem. Soc. 56, 2238 (1934).

reaction (1) and each molecule or ion of tetravalent chromium produced in (1) consumes (by way of reactions (7) and (8)) a second ion containing hexavalent chromium. On the other hand, if tetravalent chromium reacts with manganous ion instead of with hexavalent chromium (that is, if reaction (2) replaces reaction (7)), then the rate at which hexavalent chromium is consumed is cut in half.

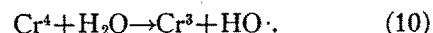
Although the mechanism just presented accounts satisfactorily for the observed induction and inhibition effects, there remains the question of whether this scheme is the only one which does so, or whether it is merely one of many satisfactory possibilities. Usually it is difficult, if not impossible, to show that any given kinetic mechanism is unique. In the present case, however, the mechanism advanced for the reaction in the presence of manganous ion appears to be the only one falling within certain logically arbitrary but chemically reasonable limits referred to below as assumptions (A)–(F); the mechanism advanced for the reaction in the absence of manganous ion is one of a clearly designated small set. In order to show that such is the fact, *all* possible mechanisms consistent with the above-mentioned limitations are considered individually.

The oxidation of isopropyl alcohol by chromic acid may involve any or all of the following chemical species: compounds of hexavalent, pentavalent, tetravalent, trivalent, or divalent chromium, isopropyl alcohol, the ketyl free radical, the OH free radical, and acetone. (The  $H^+$  ion, although it takes part in the reaction, may here be left out of account.) The first assumption (A) is that, for each valence state of chromium, there is only one effective oxidizing or reducing species; these are hereafter called  $Cr^6$ ,  $Cr^5$ ,  $Cr^4$ ,  $Cr^3$ , and  $Cr^2$ .

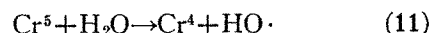
Any step in the over-all oxidation must then be a reaction in which one or more of the nine substances just mentioned take part. The simplest steps would be bimolecular oxidation-reduction reactions; it is assumed (B) that only such reactions need be considered. If each species is paired with itself and with each of the other eight, there are forty-five possible combinations. The members of some of these pairs (e.g.,  $Cr^3 + CH_3CHOHCH_3$ , or  $Cr^6 + Cr^6$ ) are obviously

stable toward one another, and some pairs are merely the products formed in more probable bimolecular reactions between members of the nine fundamental species. Elimination of pairs of the sorts just mentioned leads to a list of twenty-eight reactions; the list includes several cases where a given pair of reactants may react in two different ways to form two different sets of reaction products. The list may be further diminished by eliminating all reactions between two transitory intermediates (e.g., between a compound of tetravalent chromium and a ketyl free radical). Although this latter limitation seems drastic, it will later be shown to be equivalent to the reasonable assumption (C) that the transitory intermediates do not react preferentially with one another to the exclusion of their reaction with the stable species in solution.

It has further been assumed (D) that the chromium compounds containing  $Cr^4$  and  $Cr^6$  do not oxidize the solvent (water); except, perhaps, that tetravalent chromium may thus produce OH radicals.



The experiments later described show that two electron oxidations of the solvent do not occur. Such oxidations would produce hydrogen peroxide. Even in the presence of isopropyl alcohol, this peroxide reacts with chromic acid to form perchromic acid which, under the experimental conditions here employed, decomposes<sup>6</sup> (see experimental section) to yield chromic ion and oxygen. It follows that, if hydrogen peroxide were formed, some of the oxidizing power of the solution would be lost as oxygen, and the yield of acetone, based on the chromic acid consumed, would not be quantitative. Since this yield is in fact quantitative, it follows that no peroxide (or oxygen) is formed. Finally, the reaction

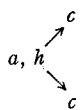
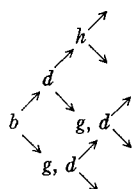
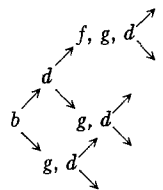
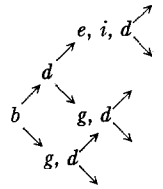
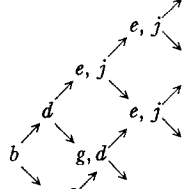
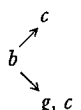
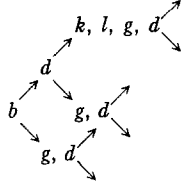
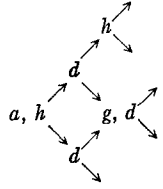
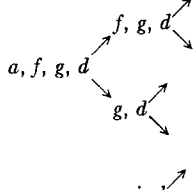
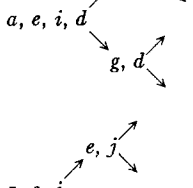
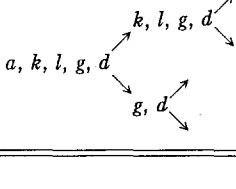
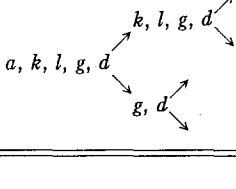


is eliminated because it is unlikely that the oxidation potential of the  $Cr^5$ – $Cr^4$  couple is large enough to decompose water.

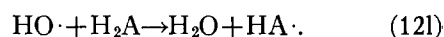
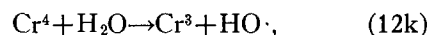
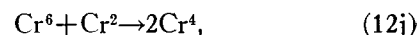
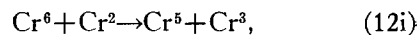
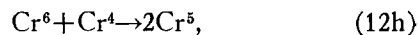
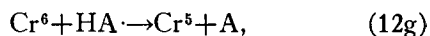
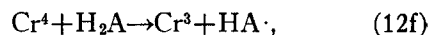
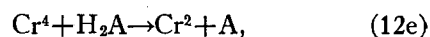
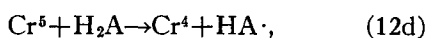
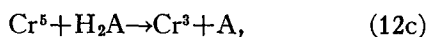
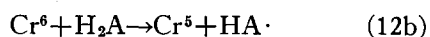
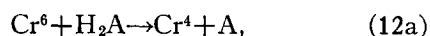
A fifth assumption (E) is that the reactions to be listed go essentially to completion in the direction indicated. The twelve reactions consistent with the assumptions (A)–(E) are listed

<sup>6</sup> N. D. Podobed, Chem. Abs. **32**, 25 (1938).

TABLE III. The mechanisms derived from the reactions of set (12).

(I)		(XI)	
(II)	$a, f, g, c$	(XII)	
(III)	$a, e, i, c$	(XIII)	
(IV)	$a, k, l, g, c$	(XIV)	
(V)		(XV)	
(VI)			
(VII)			
(VIII)			
(IX)			
(X)			

as set (12).



In constructing mechanisms from these basic reactions, the following rules are applied: The total mechanism must account for the stoichiometry of the over-all reaction; the first (and rate-controlling) step must be either (12a) or (12b), since these alone are consistent with the known kinetics.<sup>1</sup> When these two rules are applied, fifteen different reaction schemes can be constructed from the twelve basic reactions of set (12). These mechanisms are collected in Table III; for brevity, the reactions are designated by letter. That is, the reaction scheme previously presented as Eqs. (1) and (7)–(9) is here written as  $a, e, i, c$  (mechanism III). Since the reactions  $b, d, h$ , and  $j$  lead to the formation of two unstable reactive intermediates, these reactions cause "branching." Whenever in Table III the arrows indicating branching do not lead to the symbol for any reaction of set (12), the mechanism is of the "chain branching" (autocatalytic) type.

Mechanisms VI–XV of Table III are of this chain-branching (autocatalytic) type. And, since the kinetics<sup>1</sup> of the over-all reaction show that it is not autocatalytic, these schemes must be discarded. Only mechanisms I–V remain.

It is on the basis of this conclusion that the reasonableness of restriction C rests. By this restriction all reactions between transitory intermediates are disregarded. Consider the three species,  $X$ ,  $Y$ , and  $Z$ , of which  $X$  and  $Y$  are unstable intermediates and  $Z$  is a stable molecular species. If  $X$  reacts occasionally with  $Z$  and occasionally with  $Y$ , this latter chain-breaking step may serve to prevent autocatalysis of the simple-chain type, but cannot prevent autocatalysis of the branched-chain type. Only if  $X$  reacts almost exclusively with  $Y$  does this chain-

breaking mechanism serve to prevent autocatalysis of the branched chain type.<sup>7</sup> The autocatalytic mechanisms listed in Table III are all of the branched-chain type. Since they have been ruled out (by the fact that the chromic acid oxidation of isopropanol is not autocatalytic), only the following two hypotheses are possible:

(a) The unstable intermediates at least occasionally attack the stable molecular species. If such is the fact, then, since the over-all oxidation is not autocatalytic, only the mechanisms I–V listed in Table III are possible; and these would not be greatly modified by occasional reactions between two unstable intermediates (see Secondary Effects).

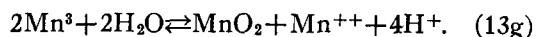
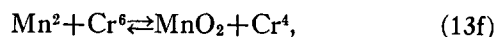
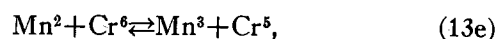
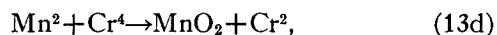
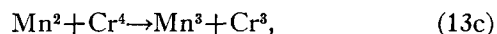
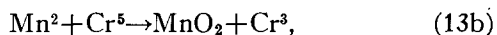
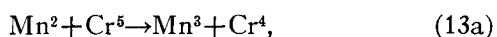
(b) The unstable intermediates react exclusively with one another. This behavior on their part would serve to prevent autocatalytic reactions of the branched-chain type such as VI–XV in Table III. But since these unstable inter-

TABLE IV. Non-chain mechanisms using the reactions of sets (12) and (13) and giving the stoichiometry of Eq. (4).

XVI (12a), (13e), (13g)	XXI (13e), (12c), (13g)
XVII (12a), (13d), (12i), (12c)	XXII (13f), (12e), (12i), (12c)
XVIII (12a), (12f), (12g), (13b)	XXIII (13f), (12f), (12g), (12c)
XIX (12a), (12e), (12i), (13b)	XXIV (13f), (12k), (12i), (12g), (12c)
XX (12a), (12k), (12i), (12g), (13b)	

mediates are present only at very high dilution in the reaction mixture, it is extremely improbable that they would behave in the manner indicated. For this reason, assumption C appears highly plausible.

Before trying to decide among mechanisms I–V, it is necessary to consider the possible mechanisms for the induced oxidation of manganous ion to  $\text{MnO}_2$ . It seems unlikely (assumption F) that the ketyl-free radical or the  $\text{OH}\cdot$  free radical can oxidize  $\text{Mn}^{++}$  to  $\text{MnO}_2$ ; the other possibilities are those of set (13).



(Reactions (13e) and (13f) are here listed even though they are not reactions of manganous ion with an unstable chromium intermediate; they are eliminated by the argument given below.)

For the induced oxidation, the twelve reactions of set (12) and the seven of set (13) must be considered together. The conditions imposed on the system are the same as those previously used, except that the stoichiometry must correspond to Eq. (4), which implies an induction factor of one-half. Most of the conceivable mechanisms correspond to chain reactions. But no chain reaction (whether of the simple or of the branched-chain type) can be correct, since no such mechanism can account for the inhibition of the oxidation in the presence of manganous ion. All of the non-chain mechanisms which fall within the limits already proposed are listed in Table IV.

Mechanisms XXI–XXIV may be immediately eliminated, since they correspond to catalysis, not inhibition by manganous ion. Each of the mechanisms XVI–XX must be considered in combination with each of the mechanisms I–V of Table III. The correct mechanism (or mechanisms) must account for the fact that the upper limit of the inhibitory effect of manganous ion corresponds to a diminution of about 50 percent in the rate of consumption of chromate. It is a fortunate fact that of the mechanisms involving manganous ion only one (XVI = (1), (2), and (3) on p. 3) will account for any inhibition at all; this mechanism, as earlier noted, accounts for an inhibition of exactly 50 percent.

The choice of a mechanism for the induced oxidation facilitates the re-examination of the reaction schemes possible in the absence of manganous ion. Of these, I–IV begin with the same reaction (12a), which involves the formation of tetravalent chromium. In mechanism V, however, the only chromium-containing intermediate which appears contains pentavalent chromium. Since, in the induced oxidation, manganous ion is oxidized by tetravalent chromium, the latter species must appear somewhere in the complete reaction scheme. Hence mechanism V

<sup>7</sup> N. N. Semenov, *Chemical Kinetics and Chain Reactions* (Oxford University Press, London, 1935). H. D. Smyth, *Atomic Energy for Military Purposes* (Princeton University Press, 1945).



is eliminated and only mechanisms I-IV remain. These four mechanisms all start with the oxidation of isopropyl alcohol to acetone, accompanied by the reduction of acid chromate ion to a compound of tetravalent chromium; they differ as to the subsequent path by which the tetravalent chromium is reduced to chromic ion.

### SECONDARY EFFECTS

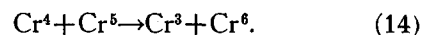
In order to understand completely the mechanism of the oxidation of isopropyl alcohol by chromic acid, it is necessary to consider some of the slight but real variations in the rate constant, and to explain why the inhibition of the reaction by excess manganous ion is in some cases significantly less than fifty percent. These secondary effects can already be in part accounted for; in part they remain as subjects for future research.

The rate constant in the presence of manganous ion is certainly satisfactory, since 100-fold variations in the initial chromic acid concentration and 60-fold variations in the initial isopropyl alcohol concentration do not cause the rate constant to deviate by more than 10 percent from the average. Although this deviation is greater than the experimental error, the constancy of  $k$  over such wide variations in the concentrations of reactants is gratifying. The slightly larger rate constants observed at isopropyl alcohol concentrations of 1.25 mole/liter may be due to the fact that such high concentrations of alcohol (about 70 grams/liter) may cause an appreciable change in the properties of the solvent.

On the other hand, in the absence of manganous salts, the largest and smallest rate constants hitherto determined differ from the average by almost  $\pm 30$  percent. This variation in the rate constant is the cause of the variation in the percent by which manganous salts inhibit the oxidation (see Table II). The results show an unmistakable trend; the inhibition approaches 50 percent when the isopropyl alcohol concentration is high and the chromic acid concentration low.

A possible explanation of the facts here observed is that the intermediate compounds of  $\text{Cr}^4$  and  $\text{Cr}^5$  disproportionate to a small extent. For example, the total rate at which chromic acid is consumed would be decreased by re-

action (14).



The rate of reaction (14) will be largest, relative to that of the normal reaction (e.g., mechanism III) when the isopropyl alcohol concentration is low and the chromic acid concentration high; the rate of (14) will be negligible when the chromic acid concentration is low and that of alcohol high. This explanation of a secondary effect is advanced only tentatively as a possible explanation for the low percent of inhibition observed under certain experimental conditions. However, this suggestion in no way invalidates the previous assumption (C) concerning the behavior of transitory intermediates. This assumption is only that transitory intermediates do not react with one another to the exclusion of their reactions with the stable species present. The tentative explanation here offered assumes only that transitory intermediates occasionally react with one another.

The reaction scheme which applies in the absence of manganous ion cannot now be selected with certainty. One of the four possible mechanisms, (II) involves the ketyl-free radical. This mechanism is not necessarily the correct one, despite the theory, recently advanced by Waters,<sup>8</sup> that chromic acid oxidations generally proceed by way of organic free radical intermediates. Waters showed that the chromic acid oxidation of many organic compounds is accompanied by the absorption of oxygen, and he stated correctly that many organic free radicals absorb oxygen. But many other compounds do so also. Further, it has been shown that the chromic acid oxidation of arsenious acid and of stannous salts is also accompanied by the reduction of oxygen.<sup>9</sup> Although these latter oxidations may proceed by way of transitory compounds involving, respectively, tetravalent arsenic and trivalent tin, it is possible (and with  $\text{Cr}^2$  it is certain) that chromium compounds of valence other than six or three may also absorb oxygen.

Nevertheless, it seemed desirable to determine the effect of oxygen upon the rate of the chromic acid oxidation of isopropyl alcohol in aqueous solution. Careful experiments showed this rate

<sup>8</sup> W. A. Waters, *J. Chem. Soc.* 1151 (1946).

<sup>9</sup> R. Luther and T. F. Rutter, *Zeits. anorg. f. allgem. Chemie* 54, 1 (1907).

to be identical, within experimental error, under oxygen, under carbon dioxide, and in vacuum.

Other aspects of the chromic acid oxidation of isopropyl alcohol have been treated elsewhere.<sup>10</sup>

### EXPERIMENTAL

#### Materials

The chromic acid used was Mallinckrodt reagent grade, purified by two recrystallizations from water;<sup>11</sup> solutions of chromic acid were standardized iodometrically. Mallinckrodt reagent grade 98 percent isopropyl alcohol was dried by refluxing over calcium oxide for 4 to 5 hours, quickly distilled, and again refluxed over fresh calcium oxide. The material thus treated was fractionated through a five plate distilling column; the fraction boiling at 82.0–82.1°,  $n_D^{20}=1.3775$ , was used in the experiments. Sodium perchlorate hydrate (G. F. Smith) was twice crystallized from water, dried, and weighed as the monohydrate. Manganous sulfate (General Chemical Company) was purified by crystallization from water slightly acidified with sulfuric acid; the salt was then dried, and analyzed for its manganese content by the bismuthate method.<sup>12</sup> All weighings of the dried manganous sulfate were made on the basis of the material thus analyzed. Perchloric acid (Mallinckrodt reagent grade 70–72 percent) was diluted to the approximate concentration required, and then standardized with carbonate-free base. In those experiments where  $\text{MnO}_2$  was suspended in the reaction mixture before the start of the reaction, Merck reagent grade  $\text{MnO}_2$ , washed several times with water, was used.

#### Measurement of Induction Factor

The procedure employed to measure the induction factor was to pipette the requisite amounts of chromic acid, perchloric acid, isopropyl alcohol, and manganous sulfate solutions into an Erlenmeyer flask, and to allow the reaction to proceed undisturbed at room temperature. After a time had elapsed sufficient for all the isopropyl alcohol to be completely oxidized,

<sup>10</sup> F. H. Westheimer and N. Nicolaides, in press.

<sup>11</sup> E. H. Archibald, *The Preparation of Pure Inorganic Substances* (John Wiley and Sons, Inc., New York, 1932), p. 279.

<sup>12</sup> W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis* (John Wiley and Sons, Inc., New York, 1929), p. 343.

TABLE V. Stability of  $\text{MnO}_2$  precipitate.

Time in hr.	Millieq. isopropyl alcohol oxidized	Millieq. chromic acid reduced	Millieq. $\text{Mn}^{++}$ oxidized (calc.)	Millieq. $\text{Mn}^{++}$ oxidized (anal)
48	0.202	0.287	0.085	0.081
69	0.202	0.287	0.085	0.079
91	0.202	0.289	0.087	0.080
139	0.202	0.277	0.075	0.066
69	0.505	0.678	0.173	
91	0.505	0.645	0.140	0.144
139	0.505	0.621	0.116	0.110
196	0.505	0.607	0.102	0.091

the  $\text{MnO}_2$  precipitate was filtered out on an asbestos mat and analyzed. The amount of chromic acid reduced during the reaction was determined by an iodometric titration of the filtrate against standard thiosulfate. The direct analysis of the  $\text{MnO}_2$  precipitate was carried out by washing the asbestos mat together with the  $\text{MnO}_2$  precipitate into a flask, digesting with a known excess of standard oxalate, and back titrating with standard permanganate.<sup>13</sup> The time required for the completion of the reaction varied from 40 hours to 80 hours, depending on the amounts of isopropyl alcohol oxidized.

Some experiments were also carried out at 40°, but here the amounts of  $\text{MnO}_2$  precipitated were smaller and the induction factors found were uniformly lower than in the corresponding experiments carried out at room temperature. When the acidity was reduced by one-half, a solution containing 25 cc 1.009*N*  $\text{HClO}_4$ , 25 cc 0.0999*N*  $\text{H}_2\text{CrO}_4$ , 10 cc 0.3*M*  $\text{MnSO}_4$ , and 1 cc 1.009*N* isopropyl alcohol gave 0.39 for the induction factor, again a value smaller than the limiting value noted in Table I.

TABLE VI. Induction factor.

Millieq. isopropyl alcohol oxidized	Millieq. chromic acid reduced	Millieq. $\text{Mn}^{++}$ oxidized (calc.)	Millieq. $\text{Mn}^{++}$ oxidized (anal)	Induction factor
1.009	1.080	0.071	0.079	0.07
0.909	1.039	0.130	0.126	0.14
0.808	0.961	0.153	0.146	0.19
0.707	0.896	0.189	0.182	0.26
0.606	0.784	0.178	0.174	0.29
0.505	0.676	0.171	0.177	0.34
0.404	0.566	0.163	0.164	0.40
0.303	0.430	0.127	0.131	0.43
0.202	0.301	0.099	0.091	0.47
0.101	0.153	0.052	0.048	0.50

<sup>13</sup> W. C. Pierce and E. L. Haenisch, *Quantitative Analysis* (John Wiley and Sons, Inc., New York, 1940), p. 195.

### Stability of Precipitated Manganese Dioxide

Precipitated  $\text{MnO}_2$  was suspended in 1.0*N* perchloric acid which contained an excess of chromic nitrate, and the mixture was allowed to stand for several days at room temperature. At the end of that time, most of the  $\text{MnO}_2$  had disappeared, and solution (which had initially been a clear green) had turned greenish-yellow. After the residual  $\text{MnO}_2$  had been removed by filtration, lead acetate solution was added to the filtrate, and a bright yellow precipitate of lead chromate was formed. Another sample of the filtrate, treated with  $\text{H}_2\text{O}_2$ , gave the blue color of perchromic acid.

The stability of the  $\text{MnO}_2$  precipitate formed in the induced oxidation was tested under various experimental conditions; some of the data obtained are shown in Table V.

The values of the induction factor found under a variety of experimental conditions are presented in Table VI. Low values for this factor are found under those experimental conditions where  $\text{MnO}_2$  is unstable.

### RATE MEASUREMENTS

The measurements were made at  $25^\circ \pm 0.01^\circ$  and an ionic strength of 0.600; the technique was that previously<sup>1</sup> used. In the calculation of the ionic strength, as well as in the computation of the rate constants, the acid chromate-dichromate equilibrium was taken into account; the "concentration" equilibrium constant was estimated as 0.015 mole/liter. The concentration of acid was computed as the sum of that of the chromic acid and that of the added perchloric acid.

When  $\text{MnO}_2$  precipitated in the reaction vessel, it was removed before the analyses by pipetting out samples through an attached tip packed with glass wool. Separate experiments were made to check the effect of acetone on the method of analysis, but the greatest amount of acetone likely to be formed in any of the experiments was found to be too small to affect the accuracy of the method.

The experiments in which a possible oxygen effect was sought were made by carrying out the reactions in thermostatted Drexel flasks into which either carbon dioxide or oxygen was bubbled. In order to minimize loss of isopropyl alcohol by evaporation, a train of two Drexel

flasks was set up for each experiment, and identical reactions were carried out in both flasks. Before the reactions were started, carbon dioxide (or oxygen) was bubbled through the flasks for an hour in order to remove dissolved oxygen (or to saturate the solutions with oxygen). The reaction was started in the usual manner, and the rate of reaction in the second flask of each train was followed.

The experiments in vacuum were carried out in a closed H-shaped double flask, in which the cross-bar was attached by a ground glass joint to a vacuum line. One compartment of the double flask was filled with measured volumes of chromic acid and perchloric acid solutions; the other was filled with a solution of isopropyl alcohol and sodium perchlorate. These solutions were such that the desired concentration of all reactants would be obtained when the solutions were mixed. Each compartment was frozen with dry ice-acetone and degassed three times. The double flask was then sealed off the vacuum line at a pressure of about  $10^{-5}$  mm of Hg, and thermostatted for several hours. The reaction was started by mixing together the solutions in the two arms of the flask. After the reaction had proceeded somewhat more than 50 percent, the flask was opened and the contents analyzed. All the experimental errors involved in this procedure (loss of water during degassing, distilling of isopropyl alcohol into the chromic acid compartment) tend to raise the observed reaction rate.

### Effect of Hydrogen Peroxide

Aqueous  $\text{H}_2\text{O}_2$  was added to solutions of chromic acid, perchloric acid, and isopropyl alcohol similar to those used in the kinetic experiments already recorded. The appearance of the blue perchromic acid was instantaneous; the color rapidly faded with evolution of oxygen. The amount of chromate consumed in the process was followed by titration. The initial loss of oxidizing power as a result of the reaction with  $\text{H}_2\text{O}_2$  was the same in the presence as in the absence of high concentrations (1.25 mole/liter) of isopropyl alcohol; the rate of decomposition of the perchromic acid was approximately the same in the presence as in the absence of isopropyl alcohol.