


**THE KINETICS OF THE CHROMIC ACID OXIDATION  
OF ACETALDEHYDE**

by

**Edward Raymond McCarthy**


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**APPROVED:**

  
\_\_\_\_\_  
**Director of Graduate Studies**

**APPROVED:**

  
\_\_\_\_\_  
**Head of Department**

  
\_\_\_\_\_  
**Dean of Applied Science and  
Business Administration**

  
\_\_\_\_\_  
**Supervisor**

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## I. INTRODUCTION

A kinetic study of the oxidation of acetaldehyde by  $\text{H}_2\text{CrO}_4$  in aqueous medium has been made in order to determine the order of the reaction with respect to the different reactants and the dependence of the rate upon  $(\text{HCrO}_4^-)$ . It was found that the reaction was first order with respect to  $\text{HCrO}_4^-$  and only approximately first order in  $\text{CrO}_3$ . It was also found that the reaction was first order in acetaldehyde and roughly second order in  $\text{H}^+$ .

Mechanisms have been postulated by other investigators for the  $\text{H}_2\text{CrO}_4$  oxidation of isopropyl alcohol in aqueous medium and the  $\text{H}_2\text{CrO}_4$  oxidation of organic compounds in acetic acid medium. In the kinetic study of the oxidation of isopropyl alcohol by  $\text{H}_2\text{CrO}_4$  in aqueous medium, it has been found that the reaction was first order in  $\text{HCrO}_4^-$ , first order in isopropyl alcohol and second order in  $\text{H}^+$ .

Because of the similarities of the two organic oxygen compounds, acetaldehyde and isopropyl alcohol, and because of the fact that both oxidations were carried out in aqueous medium, this agreement in the kinetics was expected.

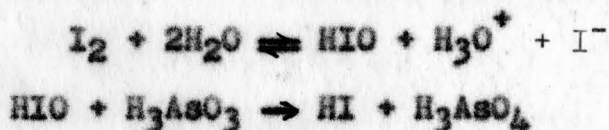
However, before a general mechanism for the oxidation of organic compounds by  $\text{H}_2\text{CrO}_4$  can be postulated, it will be necessary to study many different types of organic compounds in various media. A change in medium could result in a different mechanism.

### Mechanisms of Oxidation Reactions

Oxidation-reduction reactions may proceed by many possible mechanisms. These can be divided into two general classes: oxidation-reduction reactions that involve transfer of atoms and those that are brought about by an exchange of electrons.

One type of atom-exchange oxidation involves the transfer of a hydride ion from one molecule to the other. The molecule that loses the hydride ion is the one that has been oxidized. Such a transfer is postulated in the mechanism of the Cannizzaro reaction (7).

Many oxidation-reduction reactions proceed by means of an exchange of an oxygen atom. An example of this type of reaction is the oxidation of arsenite by iodine: (7)



Oxidation-reduction reactions that involve the transfer of electrons may proceed by means of a 1 electron or two electron transfer. (Three electron transfers are

considered very improbable.) The oxidation of organic molecules by one electron steps involves the formation of free radical intermediates.

Shaffer (15) has postulated that in order for an oxidation reduction reaction, involving the transfer of electrons, to take place it is necessary that the number of electrons which the reductant may lose or share must be the same as the number which the oxidant may gain or share.

In support of this hypothesis, Shaffer cited the following reaction:



This oxidation proceeds very slowly even at 100° though the reaction is thermodynamically possible. In terms of the Shaffer hypothesis the lack of appreciable reaction can be attributed to the fact that the oxidation of  $\text{Tl}^{+1}$  requires the loss of two electrons (divalent  $\text{Tl}^{+2}$  is unknown) while  $\text{Ce}^{+4}$  can accept only one. Westheimer (20) has suggested as an alternative that the lack of reaction may be explained by electrostatic repulsion between ceric and thallos ions.

Shaffer also pointed out that the addition of certain substances such as  $\text{MnSO}_4$  has a catalytic effect. To explain this effect of  $\text{Mn}^{+2}$  upon the reaction, Shaffer has used the following mechanism:



In the above mechanism the manganese acts as an intermediate in transferring two electrons from the thalious ion to the ceric ions.

Another case in point, as we shall describe later, is the oxidation of  $\text{Mn}^{+2}$  by chromic acid, which does not proceed in the absence of a catalyst or another substance being oxidized. Isopropyl alcohol induces the oxidation of  $\text{Mn}^{+2}$  by  $\text{H}_2\text{CrO}_4$ . This suggests that an intermediate compound of chromium is required which can exchange an equal number of electrons with  $\text{Mn}^{+2}$ .

#### Nature of Chromic Acid Solutions

A detailed mechanism to explain the way in which chromium oxidizes organic compounds may involve both stable chromium compounds and various transitory intermediates. Every step of such a mechanism must be consistent with the known behavior of chromium. It therefore seems desirable at this point to review the behavior of chromium in its various valence states.

The valence state of +3 is the most stable for chromium (17). Thus, when its valence state is +6 it is a strong oxidizing agent and is reduced to  $\text{Cr}^{+3}$  by many

organic and inorganic compounds (17).  $\text{Cr}^4$  and  $\text{Cr}^5$  are less stable than  $\text{Cr}^3$  and  $\text{Cr}^6$  and may have only transitory existence (17,20), (but must be taken into account in postulating any oxidation mechanism by chromic acid).\*

The usual ability of  $\text{Cr}^3$  to form complexes (17) perhaps explains its special stability. This complex forming ability of  $\text{Cr}^3$  extends to many kinds of addenda but is especially strong with amines and some other nitrogen compounds (17).

The aquo compounds of  $\text{Cr}^3$  are another important series of coordination complexes although not as numerous as the amine derivatives (17). The extreme form of the aquo complex is  $(\text{Cr}(\text{H}_2\text{O})_6)^{+3}$ . This species exists in solution of all simple chromic salts and in many of their crystals (17).

Chloride ion also exhibits the property of coordinating with  $\text{Cr}^3$  as shown from the existence of such ionic species as  $(\text{Cr}(\text{H}_2\text{O})_5\text{Cl})^{+2}$  and  $(\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2)^{+1}$  (5).

Chromic acid can be considered as a compound formally analogous to the hydrated chromic ion  $(\text{Cr}(\text{H}_2\text{O})_6)^{+3}$  or more strictly to  $\text{Cr}(\text{OH})_3$ .

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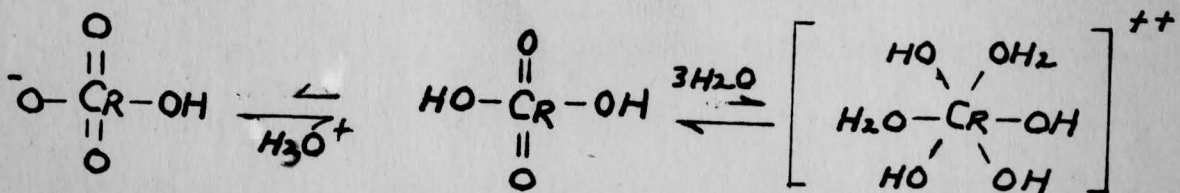
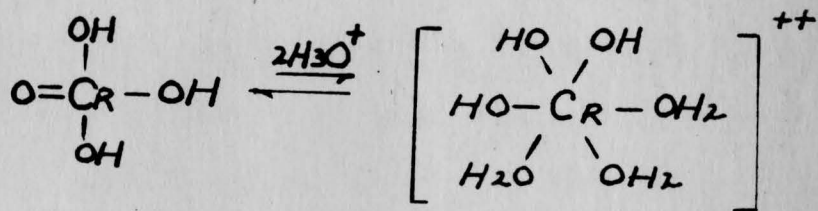
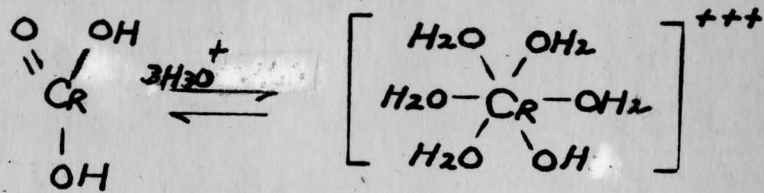
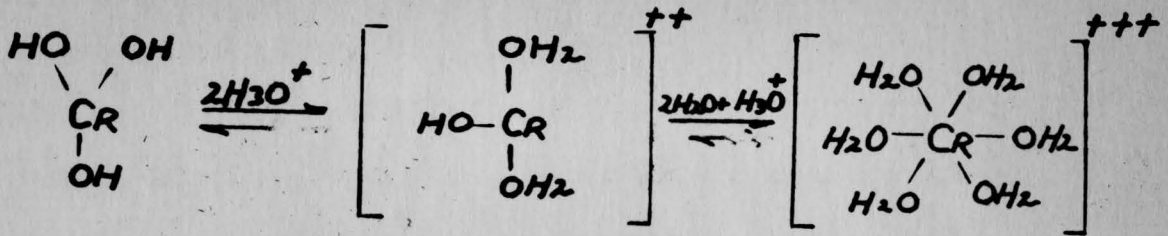
\* Symbols such as  $\text{Cr}^4$ ,  $\text{Cr}^5$  will be used to designate the total chromium in the indicated valence state without implying what ionic or molecular species are present.

In both of these structures the chromium is linked directly to oxygen and the protons attached to oxygen have acidic properties.

Chromic hydroxide is amphoteric. It acts as a proton acceptor, forming salts with acids, which are highly hydrolyzed in water. It also can act as a proton donor by forming salts with alkalis, the chromites, which are likewise highly hydrolyzed (17). Chromic acid functions as a proton donor. Its ability to accept protons is slight because of the high positive charge of +6 on the chromium atom. This results in a large electrostatic force of repulsion between chromium and the hydrogen attached to the oxygen which makes this hydrogen acidic and prevents approach of a second proton to the chromic acid molecule.

This series can be illustrated as on page 9.





In view of this tendency of chromium in all valences to form covalent complexes, it seems reasonable to conclude that the compounds oxidized by  $\text{CrO}_3$  are involved in some sort of complex. Westheimer (20) has postulated the existence of an unstable ester intermediate in the oxidation of isopropyl alcohol by chromic acid. To prove the presence of such an intermediate ester, a chromic acid ester corresponding to two moles of alcohol for each mole of chromic acid was isolated in benzene solution (21).

Westheimer (22) observed that the presence of  $\text{Cl}^-$  decreased the rate of oxidation of isopropyl alcohol with chromic acid by 30 percent. This very reasonably could be attributed to the formation of a compound such as  $\text{HCrO}_3\text{Cl}$ .

Since there is much evidence to suggest that solutions of hexavalent chromium contain several different ionic species and since most oxidations by  $\text{Cr}^6$  depend strongly on the acid concentrations, it seems reasonable to expect that not all of these ions are effective oxidizing agents.

A few experimental facts can be cited to demonstrate the existence of several ionic species in solutions of hexavalent chromium. If a solution of  $\text{K}_2\text{CrO}_4$  is acidified, it is possible to crystallize out the salt  $\text{K}_2\text{Cr}_2\text{O}_7$  which the acid salt  $\text{KHCrO}_4$  does not form (6). If a large excess of acid is added the anhydride  $\text{CrO}_3$  can be crystallized out (18). In the oxy-acids  $\text{Cr}^6$  shows a strong tendency to

to condense, not only to the dichromates but also to the tri- and even tetra- chromates. The molybdates and tungstates below chromium in group VI-B go much further, forming the highly condensed polyacids and hetero-polyacids (17). Solutions of chromic acid may therefore contain  $\text{CrO}_4^{2-}$ ,  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$  and some undissociated  $\text{H}_2\text{CrO}_4$ . It is also possible that in addition to these three ions other species such as  $\text{HCr}_2\text{O}_7^-$  and  $\text{H}_2\text{Cr}_2\text{O}_7$  are also present.

The equilibria involving  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{HCrO}_4^-$  and undissociated chromic acid can be represented as follows:

1.  $\text{H}_2\text{CrO}_4 \rightleftharpoons \text{HCrO}_4^- + \text{H}^+$
2.  $\text{HCrO}_4^- \rightleftharpoons \text{H}^+ + \text{CrO}_4^{2-}$
3.  $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4^-$
4.  $\text{HCr}_2\text{O}_7^- \rightleftharpoons \text{H}^+ + \text{Cr}_2\text{O}_7^{2-}$

Even though these ions are regarded as the only ones present, it is difficult to determine their relative concentrations. For example, their absorptions are very similar as shown by the fact that chromic acid solutions deviate only slightly from Beer's Law.

Sherrill (16) has attempted to evaluate  $K_3$  for the  $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4^-$  equilibrium. His work was based on the fact that the depressions in freezing points of solutions of  $\text{K}_2\text{Cr}_2\text{O}_7$  are greater than would be expected if

$K^+$  and  $Cr_2O_7^{2-}$  were the only ions present in solution. However, these determinations were made before the idea of activity coefficients was introduced. As a result, his findings are subject to error.

Neuss and Rieman (12) have made the most accurate determination of the value of  $K_3$ . This determination was made by taking into account equilibria 2 and 3. By means of glass electrodes they measured the e.m.f of different  $K_2CrO_4 - K_2Cr_2O_7$  solutions of varying concentrations. From these e.m.f values the pHs of different solutions were calculated. By means of these  $H^+$  activities, the values of  $K_2$  and  $K_3$  for different ionic strength levels can be calculated. The best value of  $K_3$  at  $25^\circ$  was found to be .023 while the value of  $K_2$  was found to be  $3.20 \times 10^{-7}$ . The same authors have calculated the value of  $K_1$  to be  $0.18 \pm 0.04$ .

Using the data of Neuss and Rieman the concentrations of the various ions can be determined. By means of  $K_3$  a graph of  $HCrO_4^-$  concentration can be plotted against concentration  $Cr^{6+}$ . (See page 13.) In this way the amount of  $HCrO_4^-$  present at any concentration of  $Cr^{6+}$  can be directly found.

#### Oxidation of Isopropyl Alcohol

A very detailed study of the mechanism and kinetics of the chromic acid oxidation of isopropyl alcohol has been

FIGURE- 1-A

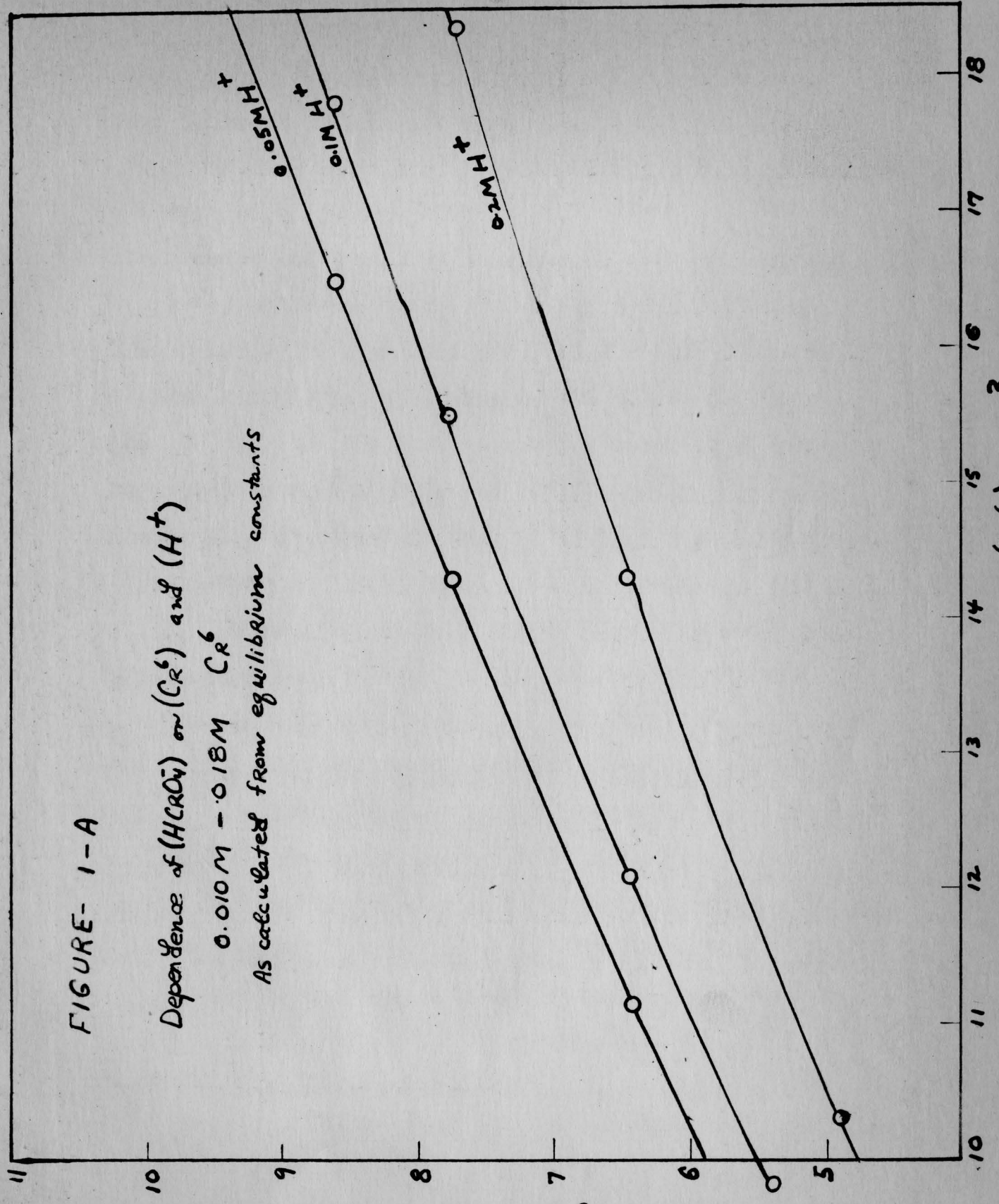
Dependence of  $(\text{HCrO}_4^-)$  on  $(\text{Cr}^6)$  and  $(\text{H}^+)$

0.010M - 0.18M  $\text{Cr}^6$

As calculated from equilibrium constants

$(\text{HCrO}_4^-) \times 10^{-3}$

$(\text{Cr}^6) \times 10^3$



made by Westheimer and his students. In these investigations isopropyl alcohol was used as the reductant because it is water soluble and is cleanly oxidized to a product, acetone, which is stable under the experimental conditions involved.

In this work, Westheimer (22) took into account the equilibrium  $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4^-$  which had not been quantitatively considered by previous investigators. He was able to show that the reaction was first order in  $\text{HCrO}_4^-$ . Thus it seems that this ion is the principal oxidizing agent in this reaction and that the ions  $\text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$  are much less reactive.

A number of mechanisms were considered in an attempt to formulate the manner in which the oxidation proceeds. After eliminating many mechanisms, it was finally decided that a mechanism which involves the transitory existence of  $\text{Cr}^4$ ,  $\text{Cr}^5$  and  $\text{Cr}^2$  agreed best with the experimental results.

The rate studies showed that the reaction was first order with respect to isopropyl alcohol and approximately second order with respect to  $\text{H}^+$ . When the concentration of  $\text{Cr}^6$  was not varied over too wide a range, the reaction appeared to be first order with respect to  $\text{Cr}^6$ . However, when the chromic acid concentration was varied eighty fold, from .0005316M to .04316M, there was a slight but significant

decrease in  $k$  with increasing concentration. This decrease is explained at least qualitatively if the reaction occurs principally between  $\text{HCrO}_4^-$  and isopropyl alcohol.

On the assumption that  $\text{HCrO}_4^-$  is the active oxidizing agent, the rate of reaction can be written as

$$\frac{d(\text{CrO}_3)}{dt} = k(\text{HCrO}_4^-)((\text{CH}_3)_2\text{CHOH})(\text{H}^+)^2$$

or when integrated

$$kt = \int_{(\text{CrO}_3)_0}^{(\text{CrO}_3)_t} \frac{d(\text{CrO}_3)}{(\text{HCrO}_4^-)((\text{CH}_3)_2\text{CHOH})(\text{H}^+)^2}$$

The concentrations of  $\text{HCrO}_4^-$  can be determined from the equilibrium constants discussed in the previous section. The principal equilibrium involved is



The concentrations of  $\text{HCrO}_4^-$  corresponding to the various concentrations of  $\text{Cr}^6$  were calculated and substituted in the above equation. The integral was then evaluated graphically for each particular time interval. When these values were plotted against time, it was found that the points of all the experiments fell on essentially the same straight line, demonstrating quantitatively the dependence on  $\text{HCrO}_4^-$ . The slope of this line gave the fourth order rate constant for the reaction.

During this series of runs the ionic strength was maintained at 0.4 by the addition of  $\text{NaClO}_4$ . The temperature was  $40^\circ$ . In most of the runs the isopropyl alcohol and  $\text{H}^+$  were present in large excess. The dependence upon  $\text{H}^+$  concentration was determined by a series of runs in which the concentrations of  $\text{CrO}_3$  and isopropyl alcohol remained constant while the  $\text{H}^+$  concentration was varied. To study the dependence upon isopropyl alcohol, the  $\text{H}^+$  concentration and chromic acid concentration were held constant while the isopropyl alcohol concentrations were varied.

As was pointed out earlier,  $\text{Mn}^+$  alone is not oxidized by chromic acid, unless certain other substances are oxidized at the same time. Westheimer (23) has investigated this fact in detail in an attempt to shed some light on the mechanism of the oxidation of isopropyl alcohol by chromic acid.  $\text{Mn}^{+2}$  in the presence of isopropyl alcohol is oxidized by chromic acid. There are thus two competing reactions. How well  $\text{Mn}^{+2}$  competes for  $\text{Cr}^6$  is measured by the ratio of moles of  $\text{MnO}_2$  produced to moles alcohol oxidized. (Westheimer calls this ratio the induction factor.)

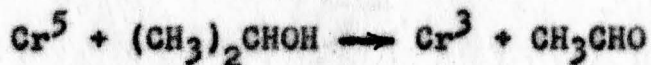
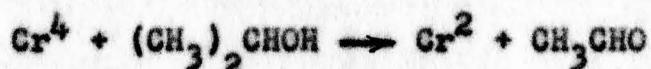
This induction factor was found to approach a maximum value of 0.5. This fact is of considerable significance. Westheimer also found that the rate at which isopropyl



alcohol is oxidized by chromic acid is lowered by 50 percent by the presence of  $Mn^{+2}$ .

In the light of these two facts and the kinetic data, many possible mechanisms were considered. Two mechanisms which satisfactorily explain this behavior have been postulated by Westheimer. The first accounts for the oxidation of isopropyl alcohol in the absence of  $Mn^{+2}$  and the second describes the oxidation in the presence of  $Mn^{+2}$ .

(1) In the absence of  $Mn^{+2}$ :



(2)  $Mn^{+2}$  requires the existence of  $Cr^4$ :



#### Other Studies of Oxidations by Chromic Acid

Waters (19) has attributed the fact that oxygen is absorbed during chromic acid oxidation of various organic compounds in acetic acid solution to the presence of organic free radicals. This oxygen absorption has been observed with hydrocarbons, alcohols, ethers and ketones. The formation of the free radical would result from the abstraction

of a hydrogen atom by the  $\text{CrO}_3$  from the organic compound. Westheimer (20) has pointed out that oxygen is absorbed not only in chromic acid oxidations of organic substances but also when chromic acid is used to oxidize inorganic substances. From this fact it is possible that the observed absorption of oxygen can be attributed to one of the intermediate valence states of chromium. Westheimer found no effect of oxygen on the oxidation of isopropyl alcohol in aqueous solution.

Mosher (10) has postulated that the chromic acid oxidations of various alcohols proceed by way of an intermediate formed by the abstraction of a hydride ion from the hydroxyl group of the alcohol. Westheimer's experiments (24) with deuterated alcohol rule out such a possibility. In these studies Westheimer found that the rate of oxidation of the 2-deutero-2 propanol is only one-sixth as fast as the undeuterated isopropyl alcohol. This indicates that the oxidation involves the removal of the secondary hydrogen.

Pudovik and Sinaiskii (13) have investigated the oxidation of various organic compounds by  $\text{K}_2\text{Cr}_2\text{O}_7$ . In the case of acetaldehyde it was found that oxidation was slight at low concentrations of  $\text{H}_2\text{SO}_4$  but increased with quantity of acid. Oxidation to acetic acid is complete when 15 to 47 percent  $\text{H}_2\text{SO}_4$  is present.

Lucchi (8) has found that the oxidation of aldehydes with chromic acid in acetic acid-sulphuric acid medium is of the second order. The reaction is strongly affected by acetic acid as solvent.

The present study was undertaken to extend our understanding of mechanisms of oxidation of organic compounds by  $\text{H}_2\text{CrO}_4$ . As we have already pointed out, the most detailed study made of an oxidation by chromic acid was of isopropyl alcohol in aqueous medium. The reaction with acetaldehyde was chosen for study since acetaldehyde is similar to isopropyl alcohol and it would be of interest to establish whether or not the reactions proceed in the same way. Other advantages are that acetaldehyde is water soluble and is oxidized to a compound, acetic acid, which is stable under the experimental conditions. In particular we will be interested in finding whether  $\text{HCrO}_4^-$  is the principal oxidizing agent for this oxidation as it is in the oxidation of isopropyl alcohol by chromic acid.

## II. KINETICS OF THE OXIDATION OF ACETALDEHYDE

### Experimental Approach

The first point to establish is the dependence of the rate of oxidation of  $\text{AcH}^*$  on its concentration. If this reaction is similar to the oxidation of isopropyl alcohol, it is to be expected that the oxidation will be first order with respect to acetaldehyde.

It is known that the chromic acid oxidation of  $\text{CH}_3\text{CHO}$  depends strongly on  $\text{H}^+$  (13). It will therefore be necessary to vary the  $(\text{H}^+)$  to determine to what power its concentration will be raised in the rate expression.

In this study, perchloric acid was used as a source of hydrogen ions. Westheimer (22) has found that when perchloric acid or benzenesulfonic acids were used the rates of oxidation of isopropyl alcohol by  $\text{Cr}^6$  were identical, but that with  $\text{HCl}$ , a 30 percent lower rate was obtained.

The order with respect to chromic acid must next be determined. In order to reveal whether the oxidation depends on  $\text{HCrO}_4^-$  the concentration of  $\text{Cr}^6$  must be varied over as wide a range as feasible. The data thus obtained should provide knowledge which will aid in the formulation of a mechanism.

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\*  $\text{AcH}$  designates acetaldehyde.

Since the rate of a chemical reaction is affected by the ionic strength of the solution, it is necessary to maintain the ionic strength at some constant value during the course of the reaction. This can be done by adding some inert salt. In the oxidation of acetaldehyde by chromic acid the ionic strength was maintained at a value of 0.3 by the addition of varying amounts of  $\text{NaClO}_4$ .

The velocity of a chemical reaction is also a function of the temperature. During the study of the rate of oxidation of chromic acid by acetaldehyde, the temperature was kept at  $25^\circ \pm 0.1$ . It was found that when the temperature was raised from  $25^\circ$  to  $40^\circ$  there is only a slight change in rate constant; the temperature coefficient having been found equal to -1.5 percent.

To follow the progress of the oxidations, the different amounts of chromic acid present at various times were determined by means of a Model DU Beckman Quartz Spectrophotometer except in a few preliminary runs. The absorption was measured at a wave length of 350 m $\mu$ , which is near the maximum of the absorption spectrum, using a calibration curve in which the optical densities were plotted against a range of chromic acid concentrations. The concentrations corresponding to these absorptions were read directly from the calibration curve, even though  $\text{Cr}^6$

solutions obey Beer's Law.

From preliminary studies of the rate of oxidation of acetaldehyde, it was found that the reaction proceeded very slowly if the concentrations of chromic acid were very low (i.e. about  $10^{-4}M$ ). This was unfortunate because it would have been more opportune to carry out the reaction at these low concentrations, because at low concentrations the change in an original ionic strength of 0.3 during the course of the reaction is not as appreciable as it is at higher concentrations. The same holds true for the  $H^+$  concentrations since  $H^+$  may be present in relatively large excess.

#### Experimental Details

To start a run, a stock solution of acetaldehyde was pipeted into the calibrated volumetric flask first, and then solutions of the  $NaClO_4$  and  $HClO_4$ . The acetaldehyde and  $HClO_4$  were added from calibrated delivery pipets. The acetaldehyde was added first to the flask in order to keep this reactant as close to the bottom of the flask as possible. These three substances were then diluted to the neck of the flask, with as little mixing as possible, with distilled water. The flask was then placed in a bath to allow the mixture to come to the bath temperature.

After the mixture had come to temperature the chromic acid solution was added from a 1-ml calibrated delivery

pipet, securely clamped in position which could be read to .005 ml. The pipet was equipped with a capillary tip so that the solution could be layered over that in the flask with only slight mixing. By means of this delivery pipet the chromic acid solution was prevented from diffusing into the lower acetaldehyde layer. The height of the pipet was regulated so that the tip was only a short distance from the mixture. After the addition of the chromic acid solution, the flask was returned to the bath for about five minutes to allow the reactants to come to temperature. The reaction was then begun by vigorously shaking the flask.

Aliquot portions of the reaction mixture were removed after various times by means of a calibrated delivery pipet. This volume was then pipeted directly into the quenching medium. The time was recorded when one-half of the sample had run out of the pipet. All the flasks and pipets used in the runs were calibrated to deliver their rated volumes.

The quenching medium used in the main runs was a  $1.8 \times 10^{-5} M$   $H^+$  buffered solution prepared by mixing equimolecular amounts of acetic acid and sodium acetate. This particular solution was used because it was found that the oxidation did not proceed at such a low  $H^+$  concentration.

In preliminary runs a boric acid-sodium hydroxide buffered solution of pH 8 was used (4). However, reproducible results were not obtained when this buffer was used as the quenching medium. The possibility of using a .1M NaOH solution for quenching was considered. However, a continual increase was observed in the optical density of a quenched chromic acid solution upon standing. This increase was probably due to the polymerization of acetaldehyde.

Since the wave length 350 m $\mu$  occurs in the vicinity of an absorption maximum for Cr<sup>6</sup> solutions, it was decided to employ this wave length in the analysis of the chromic acid samples.

Because Cr<sup>6</sup> solutions obey Beer's Law, the concentration range to which the aliquot portions of the reaction mixture were to be diluted could be determined from the molecular extinction coefficient of a K<sub>2</sub>CrO<sub>4</sub> solution at 350 m $\mu$ .

A calibration curve was then constructed in which a range of Cr<sup>6</sup> concentrations were plotted against the corresponding optical densities. The aliquot samples of the reaction mixture which were removed at various times were diluted to this range by pipeting the samples into calibrated volumetric flasks containing the quenching medium.



The optical densities of these solutions were then read on the spectrophotometer at the wave length 350 m $\mu$  with a slit width of .32. However, during the course of the experiments the tungsten light source burned out and was replaced with a new bulb. This necessitated the use of a new slit width of .200. Since a wave length of 350 m $\mu$  was used in the analysis, a red-purple filter was employed.

#### Reagents and Stock Solutions

Baker and Adamson chromium trioxide was recrystallized three times from distilled water according to the method outlined by Archibald (2) except that porcelain crucibles were used rather than platinum. The mother liquor from the last recrystallization was then tested for the presence of halogens and sulfates and was found to meet A. C. S. specifications of less than .005 percent Cl<sup>-</sup> and not more than .005 percent SO<sub>4</sub><sup>==</sup> (1). The chromic acid solution prepared from this was standardized iodometrically against sodium thiosulfate according to the procedure outlined in Willard and Furman (25).

Eastman Kodak best grade acetaldehyde was distilled under nitrogen through a 40 cm. column packed with glass beads. Only middle fractions were used. The distillate was collected in weighed vials and sealed.

To guard against loss of acetaldehyde in preparing the stock solution, the acetaldehyde in the vials was dissolved in the following manner: a funnel was connected to a short length of rubber tubing and a glass tube leading into the volumetric flask. The vial of acetaldehyde was placed in the tubing and broken by tightening a screw clamp. Water over the vial washed the contents into the flask, and the solution was then diluted to the mark.

To prevent escape of acetaldehyde upon standing, the volumetric flask was capped with an inverted vial which was fitted on to the flask by means of a rubber stopper.

Despite these precautions taken in preparing the stock solution, it was realized that possibly some acetaldehyde was lost in this process. Therefore immediately after the stock solutions were prepared a U. V. was taken of the solution to determine its concentration.

From a graph of wave length vs. optical density of an acetaldehyde solution it was seen that the absorption maximum occurs at 276 m $\mu$ .

From a stock solution of acetaldehyde prepared without any apparent loss of acetaldehyde, the concentration, based on the weight of acetaldehyde dissolved was calculated to be .0290M. The optical density of this solution at 276 m $\mu$  was .215. Substituting these values in the

Beer-Lambert equation,  $\epsilon$ , the molecular extinction coefficient can be determined

$$\epsilon = \frac{1}{M} \log_{10} \frac{I_0}{I}$$

$$\epsilon = \frac{.215}{.0290} = 7.42.$$

This value of  $\epsilon$  was used in all subsequent determinations. Knowing  $\epsilon$  and taking the optical density, the concentration of any acetaldehyde solution can be found. U. V. readings were taken of the acetaldehyde stock solutions immediately after they were prepared and after they had been standing for a time. Of the different stock solutions used, the maximum difference in readings of any one solution was 12 parts per 1000.

G. F. Smith 60 percent C. P.  $\text{HClO}_4$  was used to prepare the  $\text{HClO}_4$  stock solutions. This stock solution was then standardized against carbonate free NaOH.

The  $\text{NaClO}_4$  solution was prepared by adding slightly more than an equivalent amount of standard NaOH to a portion of the  $\text{HClO}_4$  solution. This was brought to exact neutrality by adding .1980  $\text{HClO}_4$ , the required amount being determined by titrating a 50 ml. sample of the  $\text{NaClO}_4$  solution against the .1980 M  $\text{HClO}_4$ . The resulting solution when analyzed on a pH meter showed a pH of exactly 7.0.

To prepare the standard solutions of sodium hydroxide and perchloric acid, boiled, distilled water was used.

To maintain the initial ionic strength at 0.3, the contributions to the ionic strength from  $H^+$ ,  $ClO_4^-$ ,  $Cr_2O_7^{2-}$  and  $HCrO_4^-$  were determined from the formula  $\frac{1}{2}\sum c_i z_i^2$ . This value was then subtracted from 0.3. The difference represents the ionic strength that must be made up in the form of  $NaClO_4$  to bring the ionic strength to the value 0.3.

This can be illustrated by the following example. If the initial concentrations of chromic acid and  $HClO_4$  were .012 M and .2287 M respectively, the total  $H^+$  would be .2287 M + .012 M or .2299 M. This assumes that for each mole of  $Cr^{6+}$  dissolved, one mole of  $H^+$  is formed. At a pH 1, a solution .012 M with respect to  $Cr^{6+}$  would contain .001 M  $Cr_2O_7^{2-}$  and .001 M  $HCrO_4^-$ . If these values are substituted in the following equation the values of  $\mu$  before the addition of  $NaClO_4$  can be found.

$$\mu = \frac{1}{2}\sum c_i z_i^2$$

$$\mu = \frac{1}{2} (H^+) + (ClO_4^-) + 4(Cr_2O_7^{2-}) + (HCrO_4^-)$$

$$\mu, \text{ (before addition of } NaClO_4) = .2518$$

$$\text{contribution from } NaClO_4 = .3000 - .2518 =$$

$$.0482$$

### The General Kinetic Equation

The general rate equation for the oxidation of acetaldehyde by chromic acid in the presence of perchloric acid can be represented as follows

$$-\frac{d(\text{Cr}^6)}{dt} = k_0 (\text{Cr}^6)^m (\text{AcH})^n (\text{H}^+)^p$$

where  $\text{Cr}^6$  in the above expression represents the total amount of chromium in the valence state +6.

In this study the concentrations of acetaldehyde and  $\text{H}^+$  were always in at least 2-fold excess of the concentration of  $\text{Cr}^6$ . In each run the initial concentrations of AcH and  $\text{H}^+$  will therefore remain constant while the  $\text{Cr}^6$  is changing. A new constant,  $k^1$ , can then be defined.

$$-\frac{d(\text{Cr}^6)}{dt} = k^1 (\text{Cr}^6)^m$$

$$\text{where } k^1 = k_0 (\text{AcH})^n (\text{H}^+)^p$$

The order observed for this new rate equation will be the order with respect to decrease in  $\text{Cr}^6$ .

The reaction at least over a limited concentration range was found to be first order in  $\text{Cr}^6$ .

### Order with Respect to Acetaldehyde

To determine the order with respect to acetaldehyde a set of runs was performed in which the acetaldehyde, always present in excess, was varied over a five-fold range,

from .1713 M to .0342 M. In these runs the initial concentrations of  $H^+$  and  $Cr^6$  were maintained at .1155 M and .01980 M respectively. For each run the Ach is in excess of  $Cr^6$ . The highest (Ach) of .1713 M represents a 9-fold excess over ( $Cr^6$ ) while the .0342 M is only a 2-fold excess. The data are plotted according to a first order equation,

$\log \frac{(Cr^6)_0}{(Cr^6)_t}$  vs.  $t$  in figures 1, 2 and 3. In Table 1 (see

page 31) the constant  $k$  has been evaluated for each run and was found to be independent of the acetaldehyde concentration raised to the first power. From this it was concluded that the reaction was first order in acetaldehyde.

Preliminary runs were attempted in which the reactants were present at lower concentrations. It was found that the reaction was inappreciable at these lower concentrations. This made it necessary to use concentrations in the range  $10^{-2}$  M. If the reaction had been more rapid, the lower concentration would have allowed more freedom in variation of hydrogen ion and chromic acid, for the same ionic strength.

Curves 4 through 10 (figures 1, 2, and 3) do not pass through the origin and thus appear to have a high initial rate. This may have resulted, however, from some reaction taking place while the reactants were coming to

Table 1. Order with Respect to Acetaldehyde  
 $(Cr^{6+}) = .01980 M, H^+ = .1155 M, p = 0.3$

Curve	$CH_3CHO \frac{M}{I}$	$k'$ (=slope x 2.303)	$k \left( \frac{k'}{(CH_3CHO)} \right)$
1	.1713	$6.62 \times 10^{-5}$	$3.86 \times 10^{-4}$
2	.1370	$5.38 \times 10^{-5}$	$3.92 \times 10^{-4}$
3	.1142	$4.53 \times 10^{-5}$	$3.96 \times 10^{-4}$
4	.1096	$4.07 \times 10^{-5}$	$3.71 \times 10^{-4}$
5	.08768	$3.07 \times 10^{-5}$	$3.50 \times 10^{-4}$
6	.07990	$2.76 \times 10^{-5}$	$3.46 \times 10^{-4}$
7	.06576	$2.19 \times 10^{-5}$	$3.34 \times 10^{-4}$
8	.05710	$2.07 \times 10^{-5}$	$3.63 \times 10^{-4}$
9	.04384	$1.57 \times 10^{-5}$	$3.59 \times 10^{-4}$
10	.03507	$1.31 \times 10^{-5}$	$3.55 \times 10^{-4}$
11	.03420	$1.19 \times 10^{-5}$	$3.48 \times 10^{-4}$

FIGURE 1 -

DEPENDENCE ON  
ACETALDEHYDE

$$\text{LOG} \left( \frac{C_0}{C} \right) \times 10^3$$

SEC X 10<sup>-3</sup>

.01980M Cr <sup>6+</sup>	.1155MH <sup>+</sup>
	(CH <sub>3</sub> CHO)
1	.1713 M
3	.1142 M
8	.05710 M
11	.03420 M

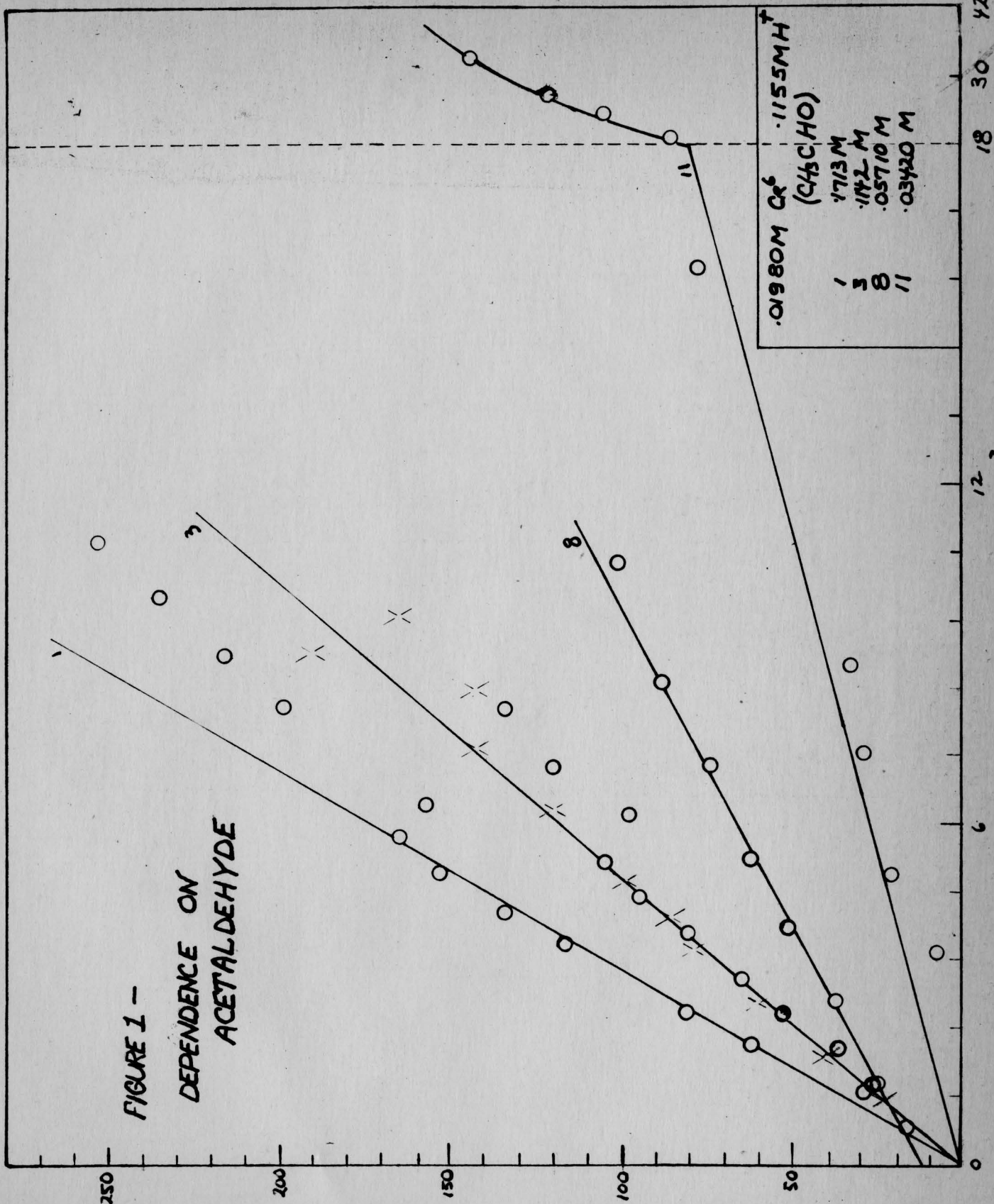




FIGURE 2 - DEPENDENCE UPON ACETALDEHYDE

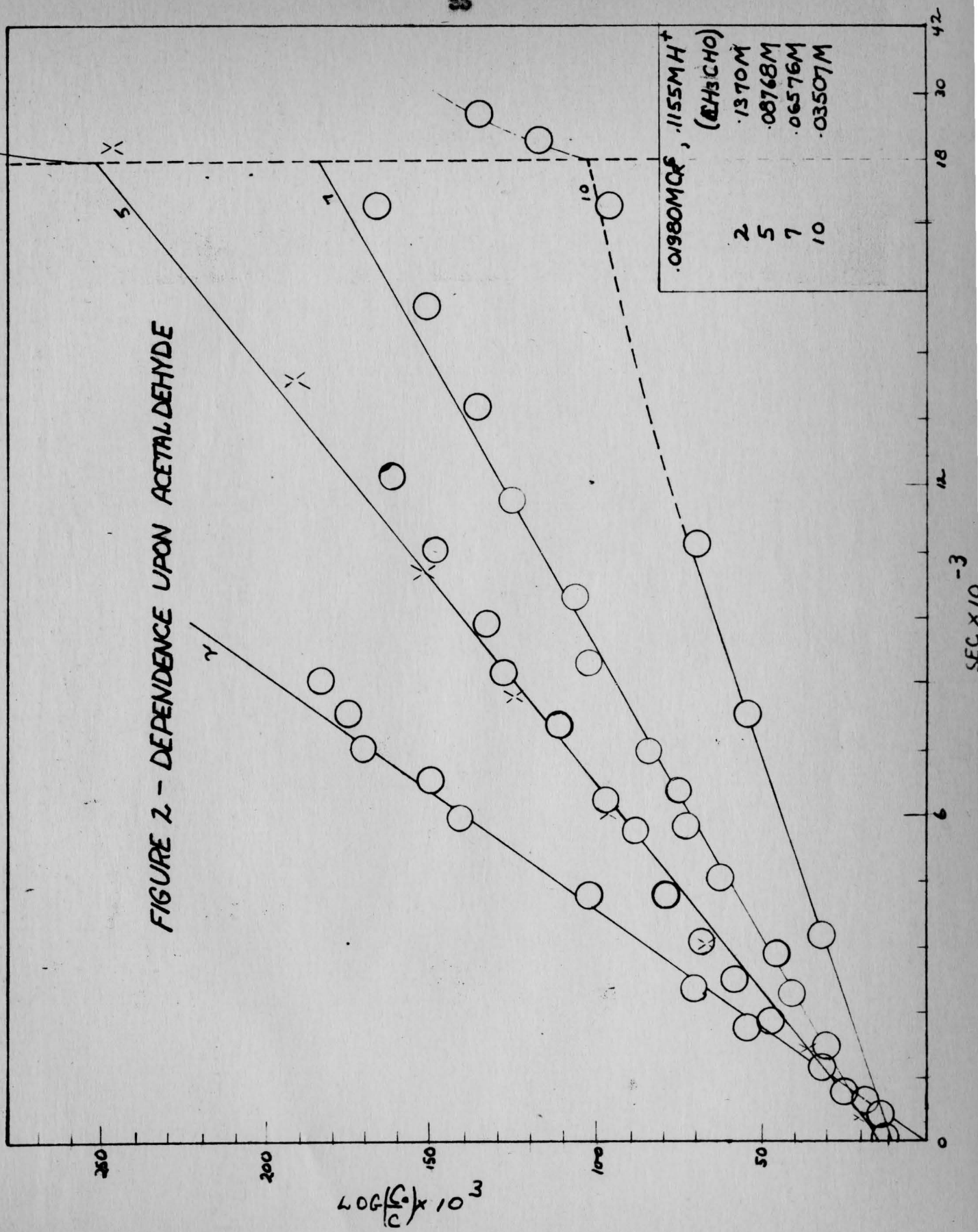
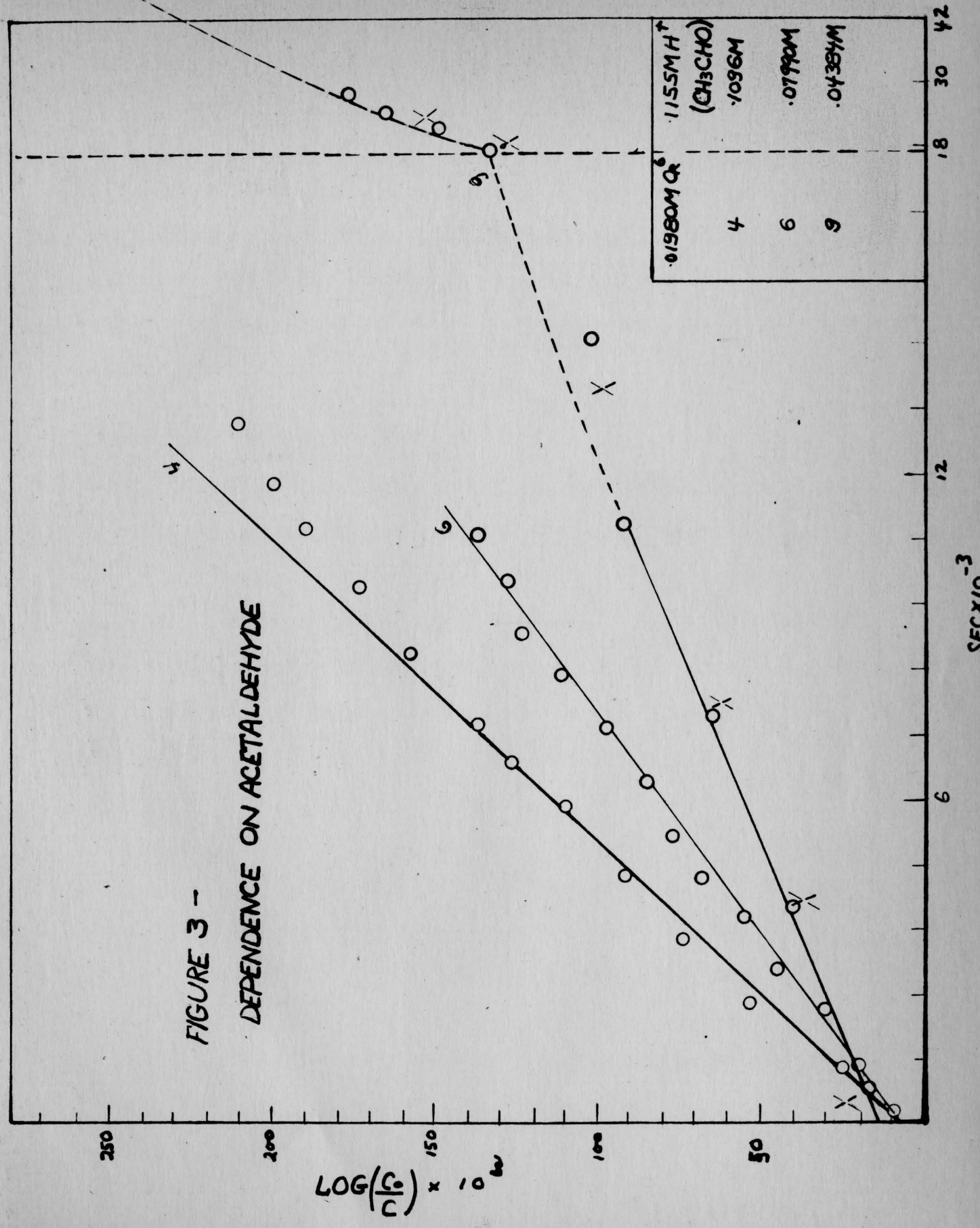


FIGURE 3 -  
DEPENDENCE ON ACETALDEHYDE



the temperature of the bath.

In curves 1 and 3 values of  $\log \frac{C_0}{C}$  corresponding to use of a 1-ml pipet to withdraw samples of reaction mixture are out of line with the other points and therefore were not considered in evaluating the rate constants. It would seem that some error had been made in the calibration of the 1-ml pipet, but the cause of the discrepancy was not finally traced down.

#### Order with Respect to $\text{HCrO}_4^-$

From the data presented thus far it can be concluded that the reaction is approximately first order with respect to  $\text{Cr}^6$ .  $\log (\text{Cr}^6)_0 / (\text{Cr}^6)_t$  was plotted against time in accordance with a first order equation. Over a limited concentration range a straight line is obtained. However, after an extended time a gradual decrease in the slope of the line can be seen. This suggests that the reaction is not precisely first order with respect to  $\text{Cr}^6$ .

Westheimer (22) has noticed a similar dependence of rate upon  $(\text{Cr}^6)$  in his studies of the oxidation of isopropyl alcohol by chromic acid and has shown that the active oxidizing species in that reaction is  $\text{HCrO}_4^-$ . (cf p. 3)

In order to show the dependence of the rate upon  $(\text{HCrO}_4^-)$  it is necessary to vary the  $(\text{Cr}^6)$  over a wide range.

Here a 50-fold variation of  $(\text{Cr}^6)$ , from .04952 M to .000990 M was employed. When the data were evaluated in terms of  $(\text{Cr}^6)$  and  $\log \frac{(\text{Cr}^6)_0}{(\text{Cr}^6)_t}$  plotted against time, a wide range of the rate constant was obtained (see figures 4 and 5). This is shown in table 2.

Table 2. Dependence upon  $\text{Cr}^6$

Curve	$(\text{Cr}^6) \frac{1}{M}$	$k^*$ (=slope x 2.303)	$k$ ( $= \frac{k^*}{(\text{CH}_3\text{CHO})}$ )
1	.04952M	$2.76 \times 10^{-5}$	$2.11 \times 10^{-4}$
2	.02971M	$4.78 \times 10^{-5}$	$3.66 \times 10^{-4}$
3	.01980M	$5.12 \times 10^{-5}$	$3.94 \times 10^{-4}$
4	.00505M	$8.06 \times 10^{-5}$	$6.16 \times 10^{-4}$
5	.000990M	$1.02 \times 10^{-4}$	$7.81 \times 10^{-4}$

If  $\text{HCrO}_4^-$  is the active oxidizing species, the rate equation can be written as follows:

$$\frac{d(\text{Cr}^3)}{dt} = k_0 (\text{CH}_3\text{CHO}) (\text{HCrO}_4^-) (\text{H}^+)^n$$

or

$$k_0 t = \int \frac{d(\text{Cr}^3)}{(\text{CH}_3\text{CHO}) (\text{HCrO}_4^-) (\text{H}^+)^n}$$

To evaluate the above integral the concentrations of  $\text{H}^+$ ,  $\text{CH}_3\text{CHO}$ , and  $\text{HCrO}_4^-$  must be known after various intervals

FIGURE 4 - DEPENDENCE ON  $CR^6$

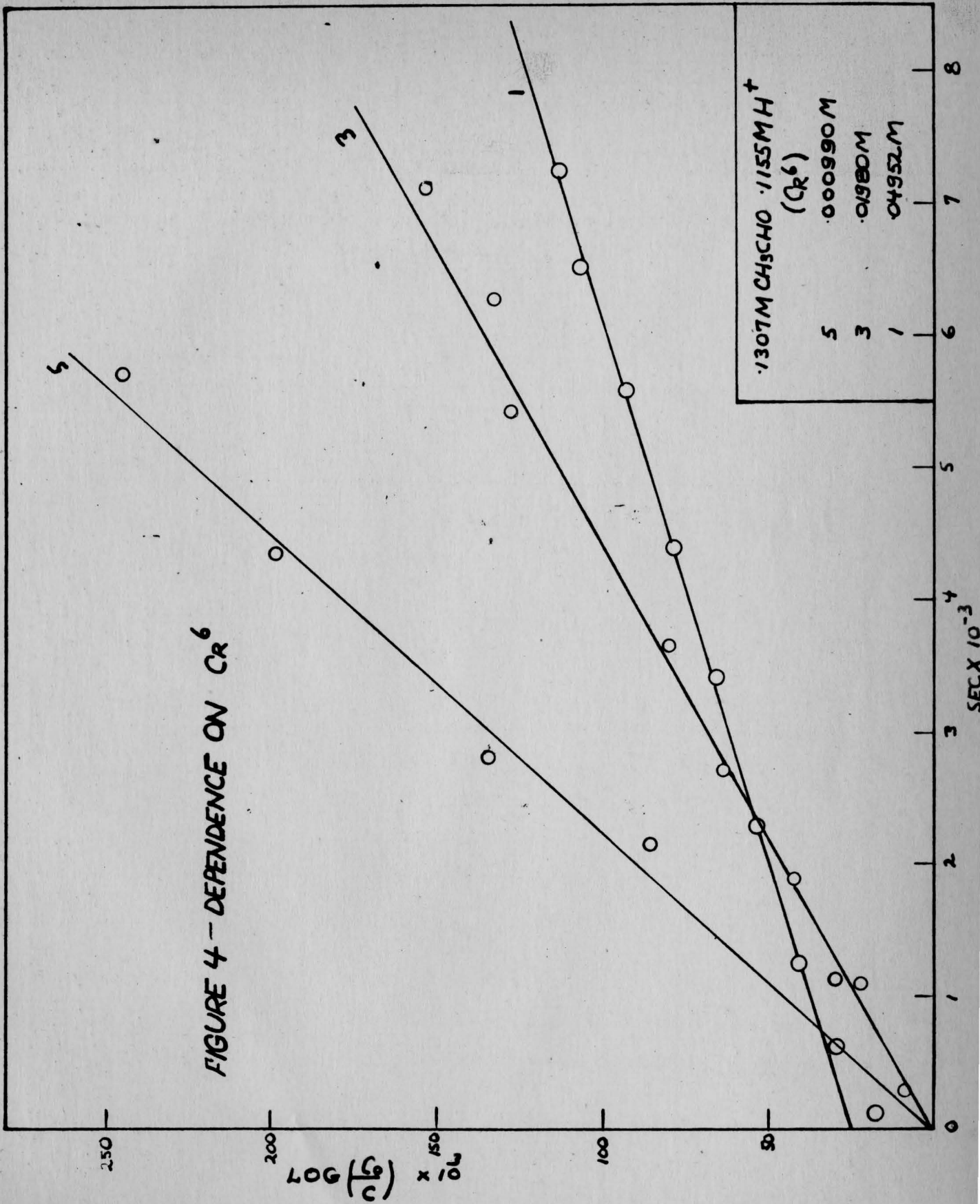
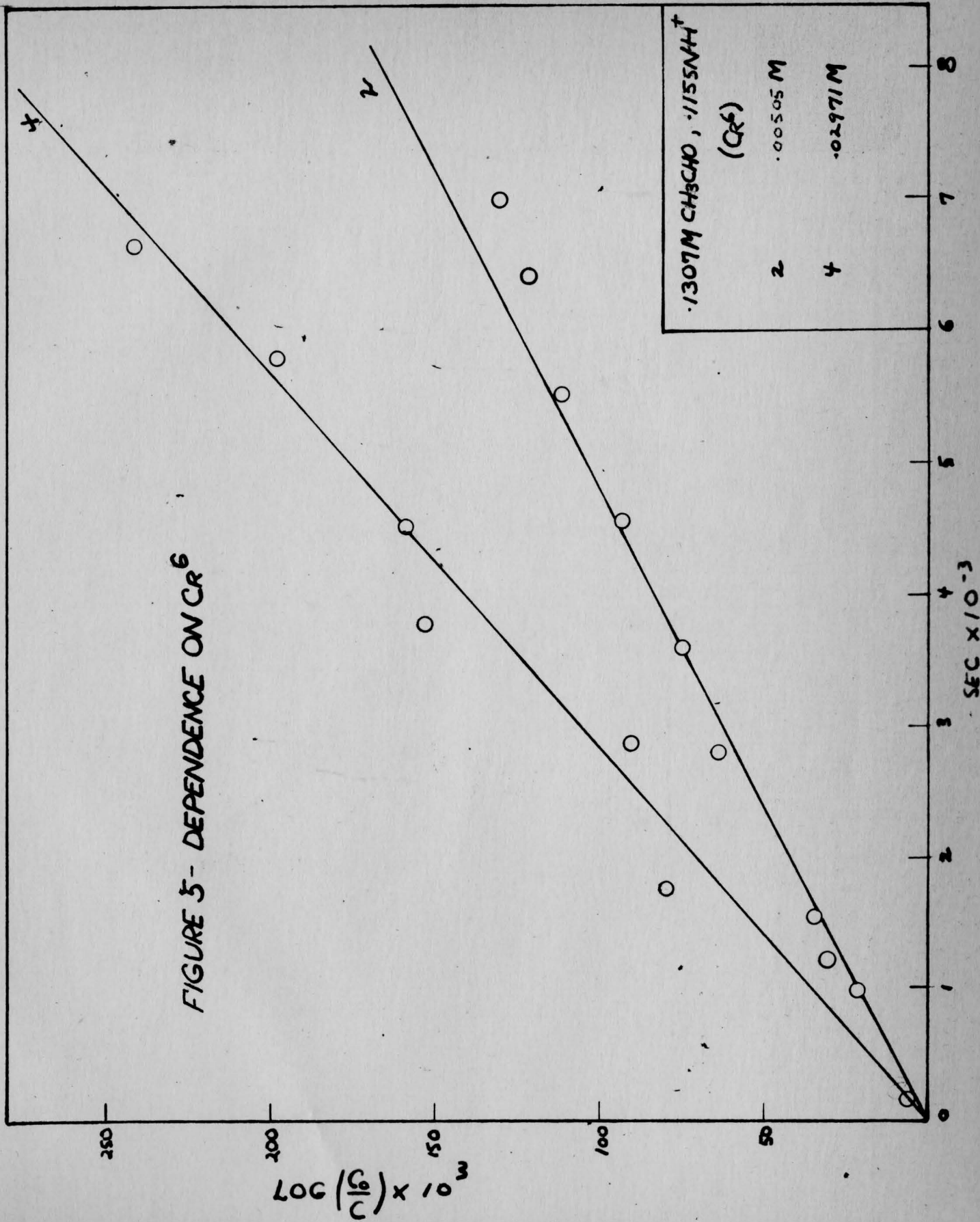


FIGURE 5- DEPENDENCE ON CR<sup>6</sup>



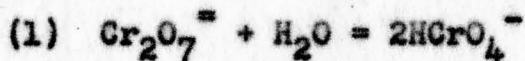
have elapsed.

The concentrations of  $H^+$  and  $CH_3CHO$  can be determined with the aid of the stoichiometric equation, knowing the concentration of  $Cr^{6+}$



From this equation it can be seen that for each mole of  $Cr^{6+}$  consumed,  $3/2$  mole of  $AcH$  and 3 moles of  $H^+$  are used up.

The concentration of  $HCrO_4^-$  corresponding to various concentrations of  $Cr^{6+}$  is dependent on the  $H^+$  and total  $Cr^{6+}$  present. It can be determined with the aid of the following equilibria



The value of the equilibrium constant  $K_1$  has been determined by Neuss and Rieman (12) at  $25^\circ$  where  $K_1$  is defined as the thermodynamic equilibrium constant

$$K = \frac{(HCrO_4^-)^2 \gamma_{HCrO_4^-}^2}{(Cr_2O_7^{2-}) \gamma_{Cr_2O_7^{2-}}} = .23$$

A value of .0115 for  $K_1^i = \frac{(\text{HCrO}_4^-)^2}{(\text{Cr}_2\text{O}_7^{2-})}$  has been used in

the following calculations. This is in terms of concentrations and involves an estimate of the effect of ionic strength.

The same authors have evaluated  $K_2$  as

$$K_2 = \frac{(\text{H}^+)(\text{CrO}_4^{2-})\gamma_{\text{CrO}_4^{2-}}}{(\text{HCrO}_4^-)\gamma_{\text{HCrO}_4^-}} = 3.2 \times 10^{-7}$$

At an ionic strength of .16,  $K_2^i$  is equal to approximately  $10^{-6}$ . Neuss and Rieman estimated  $K_3$  as 0.18. A value of 0.3 for  $K_3^i$  has been used here.

With the aid of  $K_2^i$  a value of  $(\text{Cr}_2\text{O}_7^{2-})$  can be found.

$$(\text{Cr}_2\text{O}_7^{2-}) = (\text{H}_2\text{CrO}_4) - (1 + 10^6 \text{H}) (\text{CrO}_4^{2-})$$

Using the value  $K_1^i$  and the expression given above,  $(\text{CrO}_4^{2-})$  can be determined.

$$(\text{CrO}_4^{2-}) = \frac{-\frac{(1+10^{16}\text{H} \times 1.15)}{10^{14}\text{H}^2} + \sqrt{\frac{1.5(1+10^{16}\text{H})^2 + 4.60}{10^{28}\text{H}^4} (\text{Cr}^6 - \text{H}_2\text{CrO}_4)}}{2}$$

For a given  $(\text{H}^+)$  and value of  $(\text{Cr}^6) - (\text{H}_2\text{CrO}_4)$  the values of  $(\text{CrO}_4^{2-})$  and  $(\text{Cr}_2\text{O}_7^{2-})$  can be determined. Then the value of  $(\text{HCrO}_4^-)$  can be found.



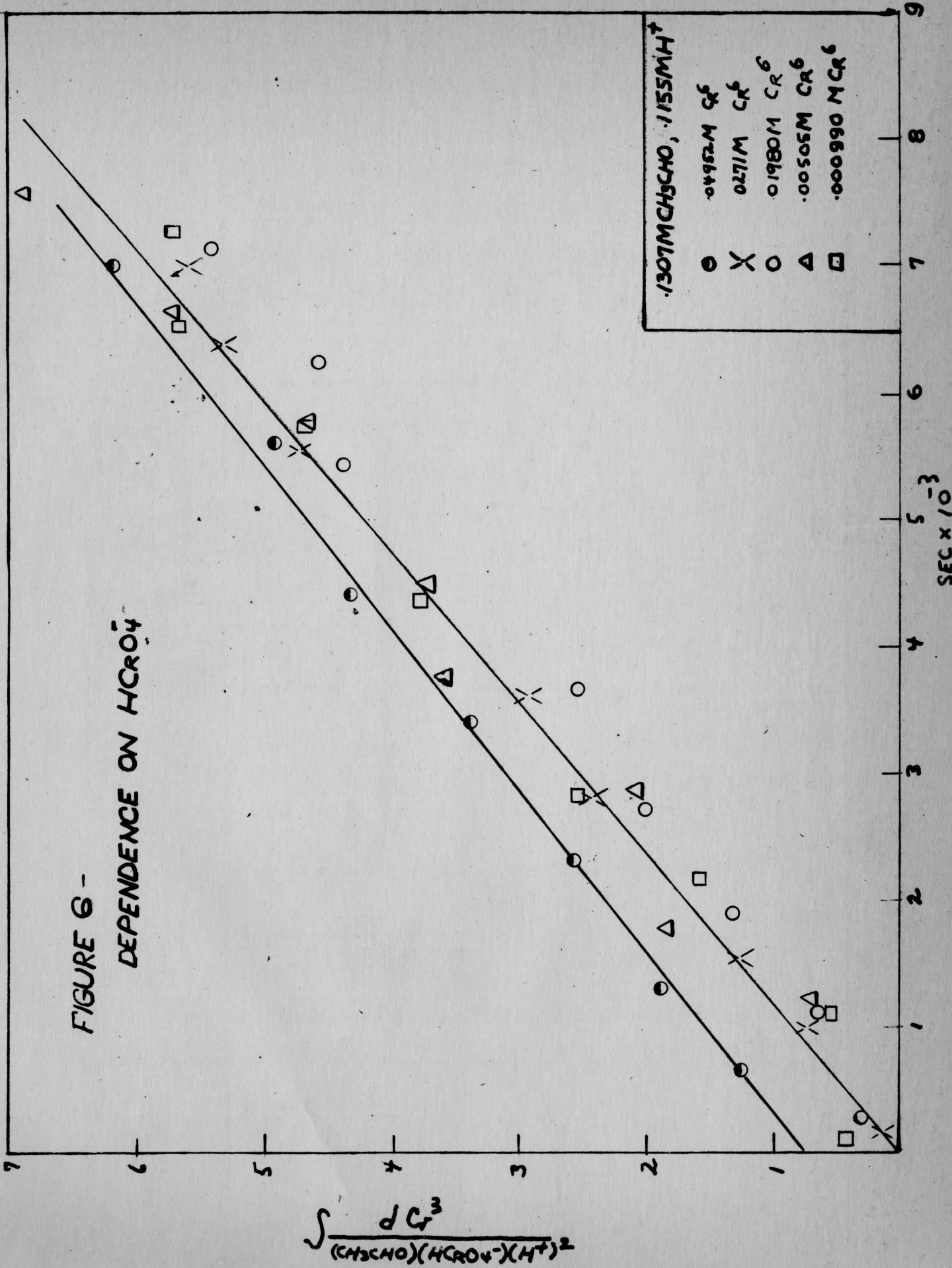
For each concentration of  $H^+$ , the values of  $CrO_4^{=}$  thus obtained are plotted against the corresponding values of  $(HCrO_4^-)$ . A graph, as illustrated in figure 1-A, is obtained in which the values of  $(HCrO_4^-)$  can be read directly.

That  $(H^+)$  must be raised to the second power in the rate expression was determined from two runs in which the initial concentrations of acetaldehyde and  $Cr^6$  were .1307 M and .01980 M respectively in both runs. However, in one run the initial  $(H^+)$  was .1155 M (c.f. figure 4, curve 3,  $Cr^6$  series) and in the second, initial  $(H^+)$  was .3013. It is not certain that the reaction is second order with respect to  $H^+$  (see page 46). However, since  $H^+$  is in excess, the dependence on  $(H^+)$  will only change the numerical value of the rate constant but will not alter the conclusion as to whether the reaction is first order with respect to  $(HCrO_4^-)$ .

The expression  $\int \frac{1}{(CH_3CHO)(HCrO_4^-)(H^+)^2} d(Cr^3)$  is of the form  $\int_a^b F(x)dx$ . If values of  $F(x)$  are plotted against corresponding values of  $x$ , the value of the integral will be the area bounded by the curve and the ordinate  $a$  and  $b$ .

From figure 6 (see page 42) it can be seen that when the value of the evaluated integral is plotted against time,

FIGURE 6 -  
DEPENDENCE ON  $HCrO_4^-$



all the points of the runs corresponding to concentrations of .02710 M, .01980 M, .00505 M, .000990 M,  $\text{Cr}^6$  fall on essentially the same straight line. The slope of this line was evaluated by the method of least squares and found to be .087. The slope corresponding to .04952 M  $\text{Cr}^6$ , where the initial value of the integral was not 0, was calculated to be .077.

This independence of the rate constant upon  $(\text{Cr}^6)_0$  indicates that the order with respect to  $\text{HCrO}_4^-$  is one, and  $(\text{HCrO}_4^-)$  is the active oxidizing species.

#### Order with Respect to $\text{H}^+$

From the discussion presented thus far, the initial rate for the reaction can be written as

$$r_i = - \left( \frac{d\text{Cr}^6}{dt} \right) = k_0 (\text{AcH})_i (\text{H}^+)_i^n (\text{Cr}^6)_i$$

where the order with respect to  $\text{H}^+$  is yet to be determined.

If the initial rate is divided by the initial concentrations of acetaldehyde and  $\text{Cr}^6$  a new constant is obtained which depends only on the initial  $(\text{H}^+)$

$$k = \frac{r_i}{(\text{AcH})_i (\text{Cr}^6)_i} = k_0 (\text{H}^+)_i^n$$

Since the reaction is strictly first order in  $\text{HCrO}_4^-$ , the concentration of  $\text{HCrO}_4^-$  should be substituted for  $\text{Cr}^6$  concentrations.

A series of runs was performed in which the initial concentrations of  $H^+$  was .0200 M. The acetaldehyde was .06576 M and the  $Cr^6$  was varied from .00742 M to .002970 M.

Figure 7, page 47, shows the results of this series and the values of  $k$  are given in table 3.

Table 3. Determination of  $k_{AV}$ .

Curve	$(Cr^6)_1$	initial rate	$\frac{r_1}{(HCrO_4)_1(CH_3CHO)_1}$
1	.00742M	$2.02 \times 10^{-8}$	$6.25 \times 10^{-5}$
2	.00594M	$1.42 \times 10^{-8}$	$5.25 \times 10^{-5}$
3	.00505M	$1.62 \times 10^{-8}$	$6.70 \times 10^{-5}$
4	.00297M	$0.86 \times 10^{-8}$	$5.80 \times 10^{-5}$
			$k_{AV} = 6.00 \times 10^{-5}$

A second series of runs is provided by the determination of the order with respect to  $Cr^6$ .  $k$  given in table 2 (page 36) was obtained on the assumption that the reaction is first order in  $Cr^6$ . We must therefore multiply by  $\frac{(Cr^6)}{(HCrO_4^-)}$  for a comparison with table 3.

The values of  $k$  for the five runs of the  $Cr^6$  series were calculated and the mean determined in table 4.

Table 4. Determination of  $k_{AV}$  for  $Cr^6$  Series

$(Cr^6)_i$	$(HCrO_4)_i$	$k \times \frac{(Cr^6)}{(HCrO_4)}$
.0495M	.0173M	$6.04 \times 10^{-4}$
.02971M	.0123M	$8.84 \times 10^{-4}$
.01980M	.00925M	$8.43 \times 10^{-4}$
.00505M	.00308M	$10.10 \times 10^{-4}$
.000990M	.000770M	$11.04 \times 10^{-4}$
		$K_{AV} = 8.89 \times 10^{-4}$

If an average initial rate expression is obtained for two sets of runs at two different initial  $(H^+)$  and these expressions divided by one another and logarithms taken of the quotient, an expression relating  $k$  to the order can be obtained.

$$\frac{r_A}{r_B} = \frac{k_o (H^+)_A^p}{k_o (H^+)_B^p}$$

or

$$p = \frac{\log \frac{r_A}{r_B}}{\log \frac{(H^+)_A}{(H^+)_B}}$$

From the two different values of  $k$  obtained at the two different  $(H^+)_i$ , the value of  $p$  can be found.

$$p = \frac{\log \frac{r_A}{r_B}}{\log \frac{(H^+)_A}{(H^+)_B}} = \frac{\log \frac{8.89 \times 10^{-4}}{6.00 \times 10^{-5}}}{\log \frac{.1155}{.0200}} = 1.53$$

The determination of  $p = 1.53$  for the order of  $H^+$  in the rate expression is tentative and additional data should be obtained. The dependence of the rate upon  $H^+$  had previously been estimated to be of the second order. This had been concluded from two runs in which two different  $(H^+)$  had been used (see page 41). However in the second of these runs the initial ionic strength had exceeded 0.3.

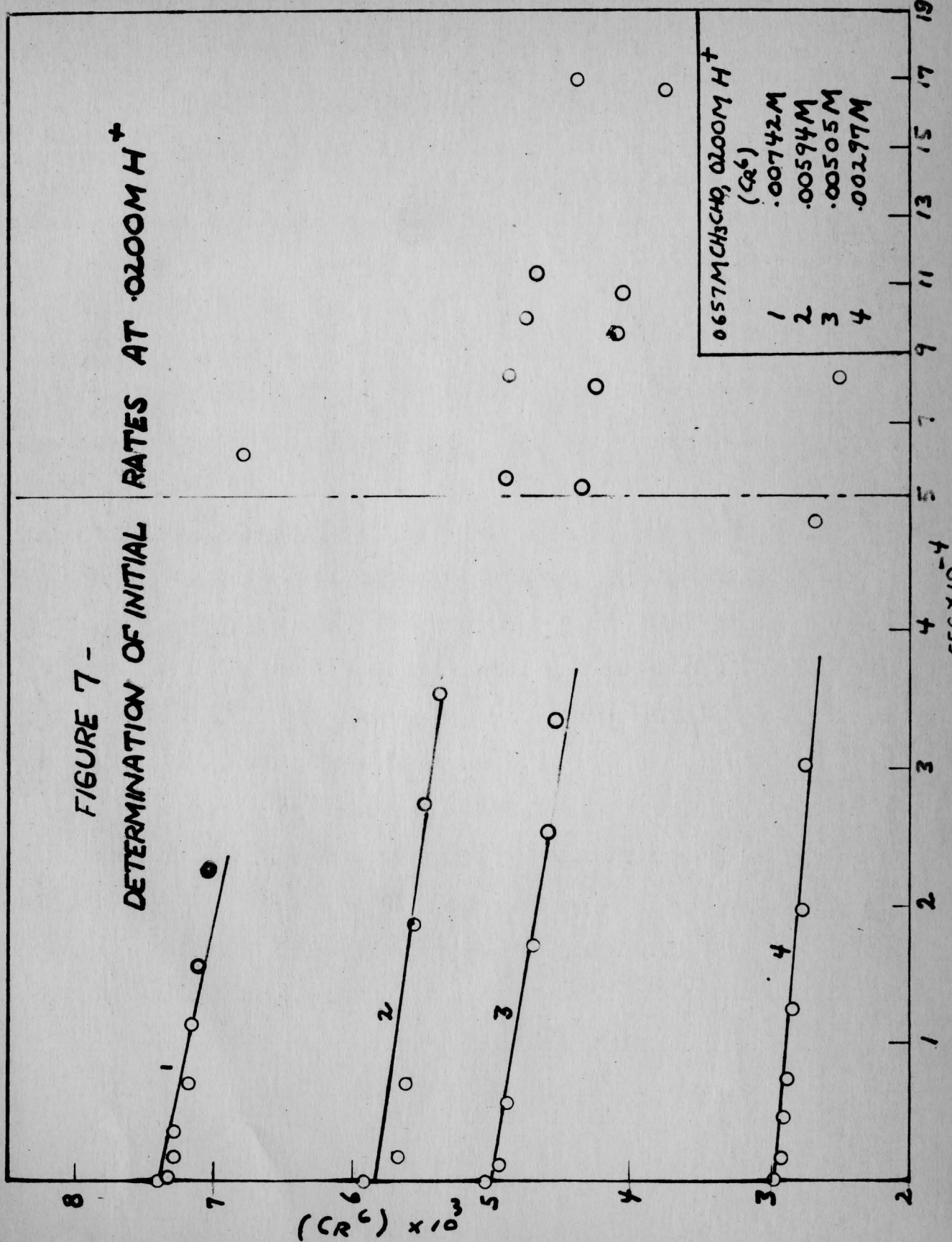
#### Effect of $Mn^{+2}$ Upon Rate

As was mentioned in the introduction, Westheimer has found in his study of the induction of the oxidation of manganous salts by  $Cr^6$  in the presence of isopropyl alcohol, that the rate at which isopropyl alcohol is oxidized by  $Cr^6$  is decreased in the presence of  $Mn^{+2}$ .

An exploratory experiment was run in order to determine whether the presence of  $Mn^{+2}$  had a similar inhibitory affect upon the oxidation of  $CH_3CHO$  by  $Cr^6$ . A run similar to curve 7 of the Ach series was performed in the presence of .00945 M  $MnSO_4$ .

The results of these two runs are compared in table 5. The initial concentrations of  $Cr^6$ ,  $CH_3CHO$ , and  $H^+$

FIGURE 7 -  
DETERMINATION OF INITIAL  
RATES AT  $0.200M H^+$



are .01980 M, .06576 M and .1155 M respectively and are the same for both runs.

Table 5. Effect of  $Mn^{+2}$  upon Rate

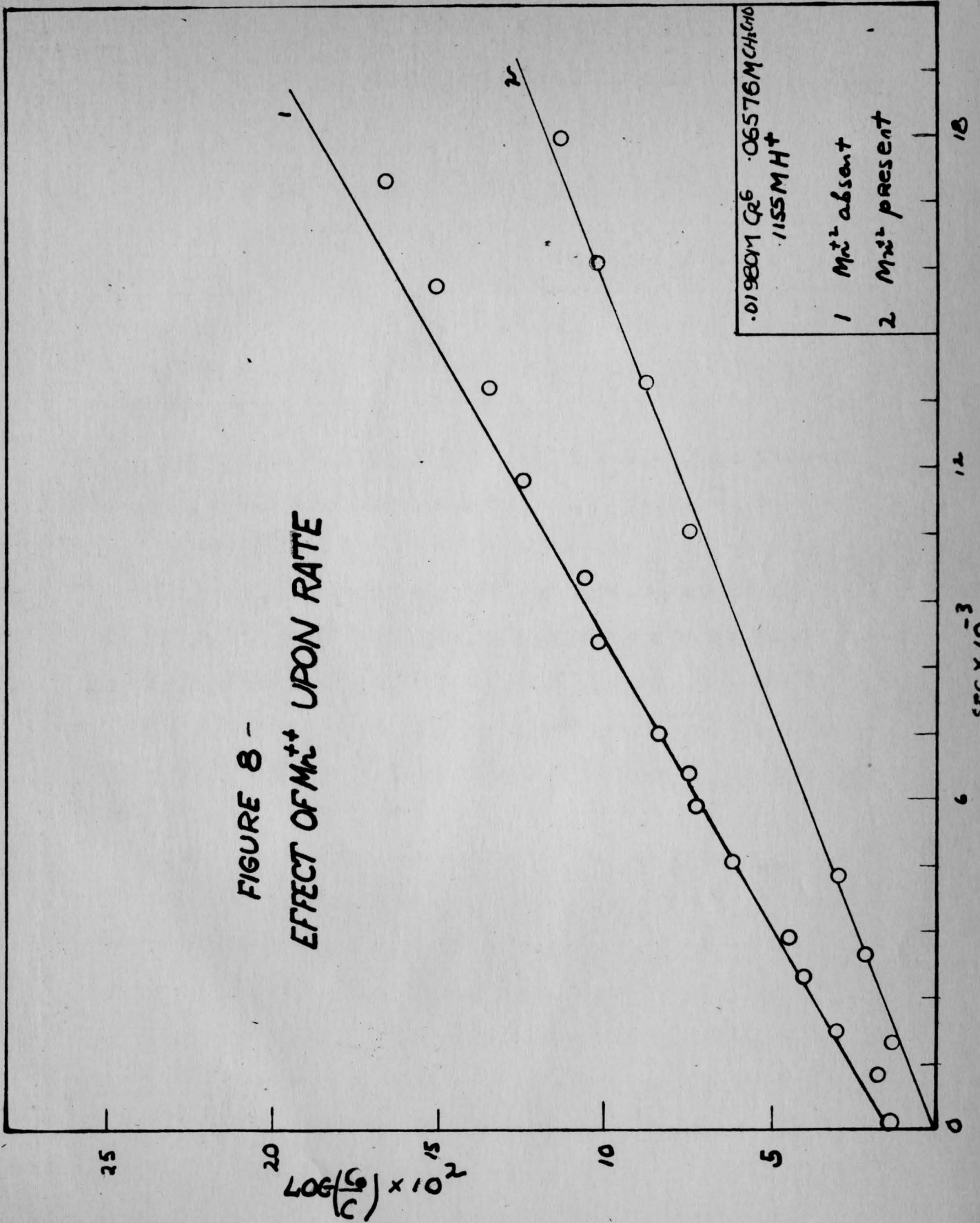
Curve	$k'$ (slope x 2.303)
1. (no $Mn^{+2}$ )	$2.19 \times 10^{-5}$
2. (.00945 M $Mn^{+2}$ )	$1.49 \times 10^{-5}$

The presence of  $Mn^{+2}$  thus does inhibit the rate of reaction, a 32 percent decrease in rate resulting from the addition of  $Mn^{+2}$ .

In the run in which  $Mn^{+2}$  was present the contribution of  $Mn^{+2}$  and  $So_4^{=}$  to the initial ionic strength has been taken into account.



FIGURE 8 -  
EFFECT OF  $Mn^{++}$  UPON RATE



### III. DISCUSSION

#### Conclusions from Experimental Work

The chief conclusion to be drawn from the previous section is that the oxidation of acetaldehyde by  $\text{Cr}^6$  closely resembles the oxidation of isopropyl alcohol under the same conditions. In view of this similarity, one might reasonably expect that the detailed mechanism outlined by Westheimer should fit the oxidation of acetaldehyde also.

The similarities in the oxidations will be evident from the following comparison:

(A) The oxidation of acetaldehyde is first order in the aldehyde. This was concluded from the constancy of the rate constants obtained on the assumption that the reaction was first order in acetaldehyde, when the concentrations of the aldehyde were varied over a 5-fold range. Westheimer has demonstrated that the oxidation of isopropyl alcohol is first order in alcohol.

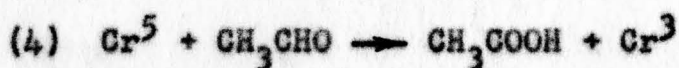
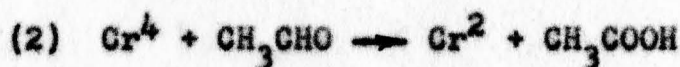
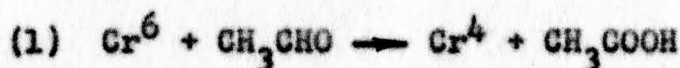
(B) The rate of oxidation of acetaldehyde has been found to be only approximately first order in  $\text{Cr}^6$ . However, when the various equilibria in chromic acid solutions are taken into account, the oxidation is found to be first order in  $\text{HCrO}_4^-$  over a wide range of concentrations. This dependence upon  $\text{HCrO}_4^-$  was one of the important conclusions of Westheimer's study of the oxidation of isopropyl alcohol.

(C) The oxidation of acetaldehyde by  $\text{Cr}^6$  is roughly second order in  $\text{H}^+$ . This dependence, however, must be studied in greater detail. The oxidation of isopropyl alcohol has been found to be second order in  $\text{H}^+$ .

(D) In one experiment, the oxidation of  $\text{Mn}^{+2}$  to  $\text{MnO}_2$  was induced by the presence of acetaldehyde and the rate of disappearance of  $\text{Cr}^6$  was decreased 32 percent. The analogous behavior with isopropyl alcohol was of considerable importance in postulating a mechanism.

#### Mechanism of the Oxidation

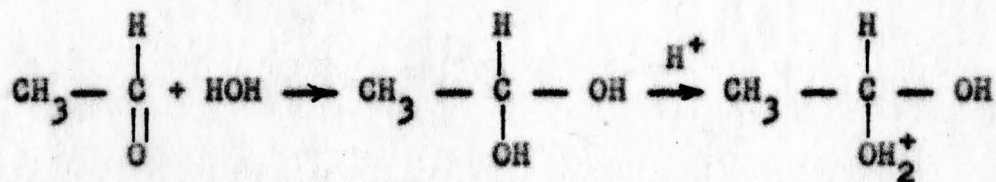
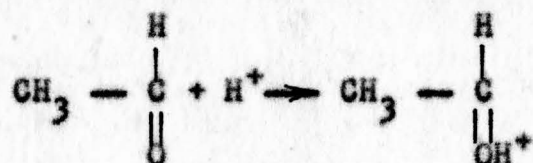
The mechanism favored for the oxidation of isopropyl alcohol by  $\text{Cr}^6$  has been outlined in the introduction. If this mechanism applies to the oxidation of acetaldehyde, the reaction may be said to proceed in the following manner:



It will be noticed that acetaldehyde is oxidized in a succession of 2-electron steps. This means that no organic free radicals are formed.

$Mn^{+2}$  is considered to be oxidized by  $Cr^{+4}$  in 1-electron steps. (see page 17) If  $Mn^{+2}$  is present in large enough concentration, a 50 percent decrease in the rate of the oxidation will result because reaction (3) no longer occurs. In addition, when  $Mn^{+2}$  is in excess, 2 equivalents of acetaldehyde are oxidized for every mole of  $Mn^{+2}$  oxidized. It would be well to examine in detail how reaction (1) might occur.

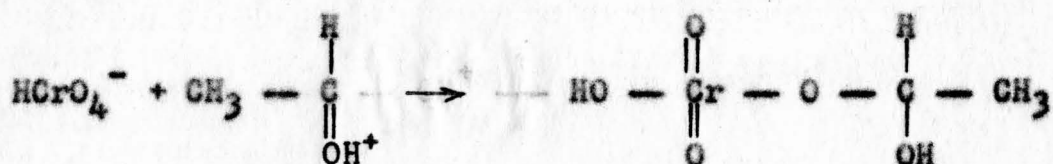
In aqueous solution at  $25^{\circ}$ , acetaldehyde is about 54 percent hydrated (3). This equilibrium is catalyzed by acids and bases. In view of these facts, the following forms will be expected in acid solutions of acetaldehyde



Because the reaction is first order in  $HCrO_4^-$  one may suppose that the initial step of the reaction involves  $HCrO_4^-$  with one of the above forms of acetaldehyde. Any one of these forms of acetaldehyde could react with  $HCrO_4^-$

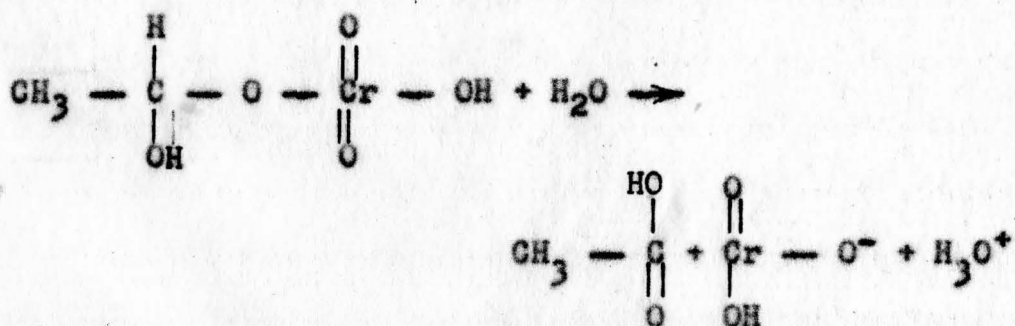
but the form  $\text{CH}_3 - \overset{\text{H}}{\underset{\text{OH}^+}{\text{C}}} \text{---}$  will be employed because it accounts

for part of the dependence of oxidation on  $(\text{H}^+)$ . This would react with  $\text{HCrO}_4^-$  to form an intermediate containing an ester linkage



Westheimer has given evidence for the existence of an analogous ester intermediate in the chromic acid oxidation of isopropyl alcohol, as we have described on page 10.

The chromic acid ester of acetaldehyde could be split up by the base, water. This would abstract a proton from the acetaldehyde portion of the molecule to give acetic acid and an ion of  $\text{Cr}^4$ , analogous to  $\text{HCrO}_4^-$ .



Steps (2) and (4) will proceed in a similar manner since  $\text{Cr}^4$  and  $\text{Cr}^5$  are strong oxidizing agents.

### Suggestions for Further Work

To complete the study of the mechanism of the oxidation of acetaldehyde, the dependence of the rate upon ( $H^+$ ) should be studied further. A second order dependence has been found but this is not conclusive. Additional knowledge concerning the induced oxidation of  $Mn^{+2}$  would be of interest in discussing the detailed mechanism of the reaction.

Other substances, besides  $Mn^{+2}$ , may have a similar inhibitory effect upon the rate and their study might throw further light on the mechanism. If  $O_2$  were absorbed during the course of a reaction this would suggest the presence of an organic free radical. The effect of light upon the reaction could be examined also.

A transitory intermediate containing an ester linkage and decomposed by the base water is involved in the mechanism discussed for acetaldehyde. It would be of interest to see if further evidence for such an intermediate could be found, as was done for the analogous ester in the study of the oxidation of isopropyl alcohol.

The mechanism of the oxidation may depend on the medium in which the oxidation is carried out. There is evidence for a free radical mechanism for oxidations by  $CrO_3$  in acetic acid, and it would be of very great interest to study the kinetics of the oxidation of acetaldehyde and

other substances in this medium.

The chromic acid oxidation of other substances, such as lactic acid or malic acid, in which the kinetics of reaction are extremely complex, could also be examined. In the oxidation of lactic acid by chromic acid, oxidation takes place at the carboxyl group rather than at the hydroxyl group.

## IV. SUMMARY

The kinetics for the reaction of the oxidation of acetaldehyde by chromic acid in aqueous medium has been studied in an attempt to extend the present knowledge of oxidation by chromic acid. In particular, these experiments were undertaken in order to see if there are any similarities between this reaction and the oxidation of isopropyl alcohol in aqueous medium, which other investigators have studied.

The main runs were carried out at 25°, at an ionic strength of 0.3. The reaction was followed by the decrease in chromic acid concentration as determined with the Beckman Spectrophotometer. In all of the runs, the concentrations of acetaldehyde and  $H^+$  were in excess of the chromic acid concentrations.

It was found that the oxidation of acetaldehyde is first order in acetaldehyde and first order in  $HCrO_4^-$ , (but not strictly first order in total chromic acid). The reaction is roughly second order in  $H^+$ .  $Mn^{+2}$  has an inhibitory effect upon the rate, as has been found in the isopropyl alcohol oxidation.

Because of the similarity in kinetic behavior between acetaldehyde and isopropyl alcohol, the mechanisms are



probably very similar. This mechanism for acetaldehyde oxidation has been discussed in some detail.

## V. ACKNOWLEDGMENTS

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