# Kinetic Studies of the Oxidation of Fatty Acids

Thesis Submitted For the Degree of
DOCTOR OF PHILOSOPHY
In Chemistry

SHAKOOR MOHAMMAD KHAN

Department of Chemistry
Aligarh Muslim University, Aligarh
December 1968

# T H E S I S

Submitted in fulfilment
of the requirements for the degree of
DOCTOR OF PHILOSOPHY
IN CHEMISTRY

By

Shakoor Mohd. Khan

Chemical Laboratories
Aligarh Muslim University
Aligarh.

December, 1968.

# ABSTRACT

The oxidation of fatty acids is of fundamental importance in many processes such as the utilization of fats in the animal body; drying oil industry and in the investigation of structure of fatty acids. Besides, the outstanding difference between chemical and biochemical oxidation processes is best exemplified by reference to carboxylic acids which can easily be oxidized to carbon dioxide by living cells, but are inert to chemical oxidizing agents in neutral aqueous solution.

Chromic acid is an extremely important oxidant in both organic and inorganic chemistry. It has occupied an equally important position in the study of oxidation mechanisms. It reacts almost all types of oxidizable groups. The reactions often may be controlled to yield largely one product, and this makes chromic acid oxidation a useful synthetic tool. Although the knowledge of the mechanisms of chromic acid oxidation of organic compounds is fragmentary, yet as a result of pioneering work of Westheimer, Rocek, Wiberg and Waters, the mechanism of some of the reactions is fairly well understood. The present work was carried out to elucidate the mechanism of oxidation of lower fatty acids by this oxidant.

The reaction rate was measured as a function of concentrations of chromic acid, substrates and hydrogen ions. In all the experiments the oxidant concentration was kept so low relative to those of substrates and hydrogen ions that the latter remained essentially constant throughout any single run. Even under these conditions, the first order rate constants vary with changing chromic acid concentration.

The order of the reaction with respect to each fatty acid was determined by varying the fatty acid concentration and observing the effect on the rate keeping chromic acid and sulphuric acid concentrations constant. The plots of rate constants against substrate concentrations yielded straight lines passing through the origin. It indicates that the order of the reaction with reference to substrate is unity, and the self decomposition of chromic acid is negligible under our experimental conditions.

The dependence of rate constant on the hydrogen ion concentration was studied in the same way. The oxidant and substrate concentration were kept constant and concentration of hydrogen ions was varied maintaining the ionic strength constant by using sodium hydrogen sulphate.

The quotients obtained by dividing pseudo first order rate constants by hydrogen ion concentration varied from run to run. But the quotients obtained by dividing first order rate constants by the square of hydrogen ion concentration remained reasonably constant showing second order dependence on acidity.

The effect of ionic strength on the oxidation rate was observed by varying the ionic strength by using sodium perchlorate. An overall acceleration with increasing ionic strength was observed. Temperature dependence of the reaction rate was studied and thermodynamic parameters were calculated. The effect of acetic acid, the final oxidation product, on the rate of oxidation was measured by adding various amounts of acetic acid to the reaction mixture. The rate constants were found to increase with increasing acetic acid concentration.

Chromic acid oxidation of fatty acids was also studied in the presence of manganous and cerous ions. It was found that the amount of chromic acid consumed in the absence of $Mn^{++}$ or $Ce^{+++}$ was more than in the presence of these ions.

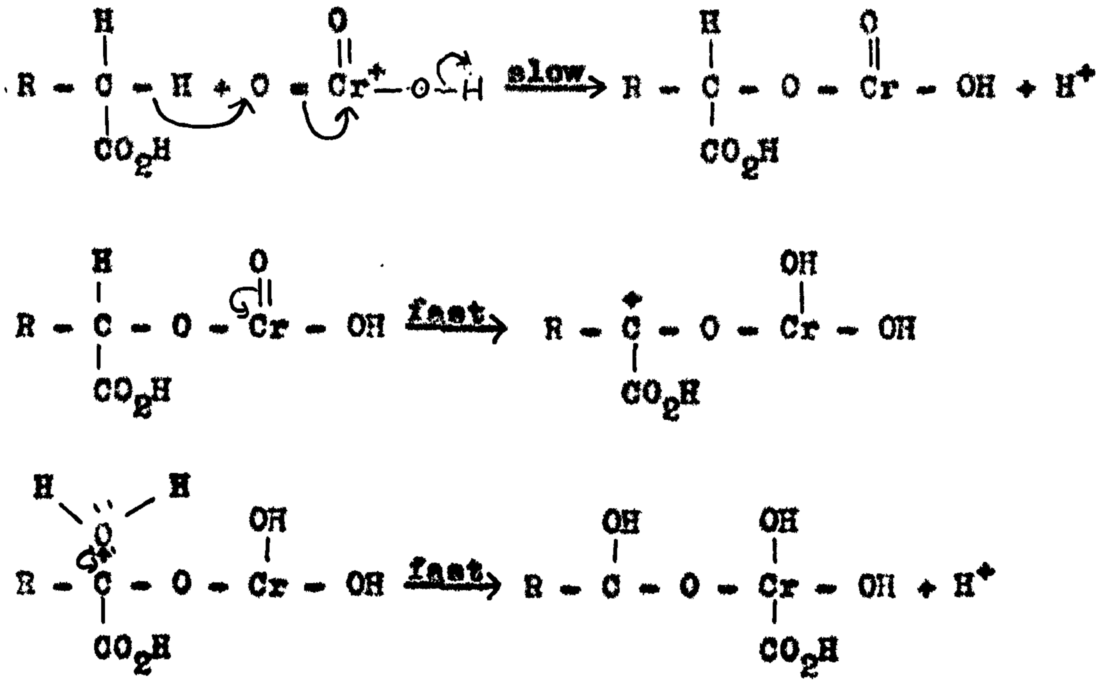
The influence of chain length on the oxidation rate of fatty acids was investigated. The observed order or reactivity followed the sequence propionic < butyric < valeric. The effect of branching was also studied and it was found that isobutyric and isovaleric acids were more rapidly oxidised than propionic and butyric acids. Pivalic acid was unaffected. To determine the effect of phenyl group on the oxidation rate, benzoic and phenylacetic acids were studied. Benzoic acid was not oxidised but the rate of oxidation of phenylacetic acid was much higher than that of propionic acid.

On the basis of above results the following rate law was obtained.

$$-\frac{d(Cr^{VI})}{dt} = k[\text{Fatty acid}][Cr^{VI}][H^+]^2.$$

The mechanism which is consistant with the above rate law may be written as:

(1) $HCrO_4^- + 2H^+ \xrightleftharpoons{\text{fast}} \overset{+}{HCrO_3} + H_2O$

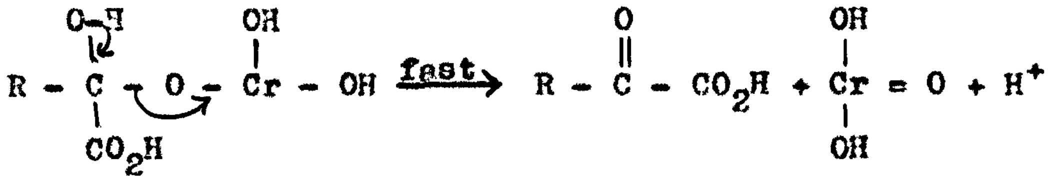


(2) $R-\overset{\overset{H}{|}}{\underset{\underset{CO_2H}{|}}{C}}-H + O=\overset{\overset{O}{\|}}{Cr^+}-O-H \xrightarrow{\text{slow}} R-\overset{\overset{H}{|}}{\underset{\underset{CO_2H}{|}}{C}}-O-\overset{\overset{O}{\|}}{Cr}-OH + H^+$

(3) $R-\overset{\overset{H}{|}}{\underset{\underset{CO_2H}{|}}{C}}-O-\overset{\overset{O}{\|}}{Cr}-OH \xrightarrow{\text{fast}} R-\overset{+}{\underset{\underset{CO_2H}{|}}{C}}-O-\overset{\overset{OH}{|}}{Cr}-OH$

(4) $R-\overset{\overset{H\quad H}{\overset{+}{O}}}{\underset{\underset{CO_2H}{|}}{C}}-O-\overset{\overset{OH}{|}}{Cr}-OH \xrightarrow{\text{fast}} R-\overset{\overset{OH}{|}}{C}-O-\overset{\overset{OH}{|}}{\underset{\underset{CO_2H}{|}}{Cr}}-OH + H^+$

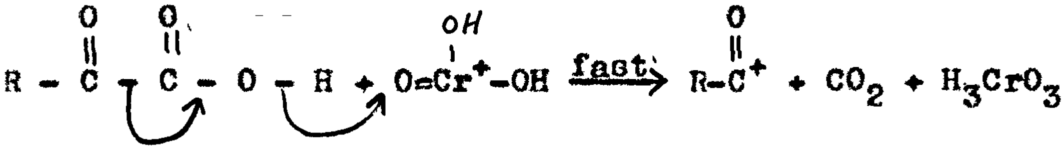
(5)



$$R-\overset{O-H}{\underset{CO_2H}{C}}-O-\overset{OH}{Cr}-OH \xrightarrow{fast} R-\overset{O}{\overset{\|}{C}}-CO_2H + \overset{OH}{\underset{OH}{Cr}}=O + H^+$$

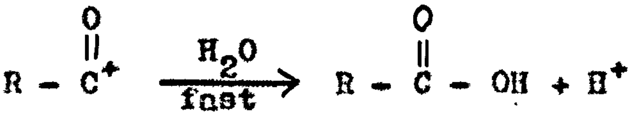
(6) $H_2CrO_3 + H\overset{+}{Cr}O_3 + H^+ \xrightleftharpoons{fast} 2\ H_2\overset{+}{Cr}O_3$

(7)



$$R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-O-H + O=\overset{OH}{Cr^+}-OH \xrightarrow{fast} R-\overset{O}{\overset{\|}{C^+}} + CO_2 + H_3CrO_3$$

(8)



$$R-\overset{O}{\overset{\|}{C^+}} \xrightarrow[fast]{H_2O} R-\overset{O}{\overset{\|}{C}}-OH + H^+$$

This is to certify that the thesis entitled "Kinetic studies of the oxidation of fatty acids", is the original work of Mr. Shakoor Mohd. Khan and is suitable for submission for the degree of Ph.D.

A. Aziz Khan

Dr. A. Aziz Khan

# ACKNOWLEDGEMENT

I wish to express my gratitude to Dr. A. Aziz Khan for his supervision and also to Dr. M.A. Beg for the valuable suggestions regarding the selection of the problem. I am thankful to Prof. A.R. Kidwai and Dr. S.M. Fazlur Rahman for providing necessary facilities. Thanks are also due to Dr. W. Rahman and Dr. M.S. Ahmad for their helpful suggestions during writing of the thesis. The help of Dr. Firoz Ahmad and other members of Physical Section is acknowledged gratefully.

Shakoor Mohd Khan
Shakoor Mohd. Khan

# CONTENTS

# CHAPTER I

## GENERAL INTRODUCTION

# GENERAL INTRODUCTION

The oxidation of fatty acids is one of the important reactions in chemistry of fats and oils. This is of fundamental importance in many processes such as utilization of fats in the animal body; in the drying of films; in the manufacture of various products of drying oil industry and in the investigations of the structure of fatty acids and their derivatives.

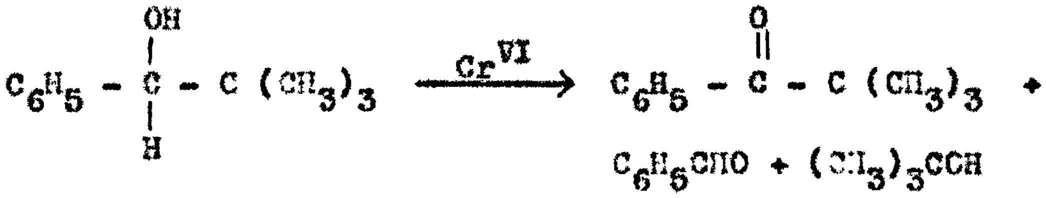
As would be expected, the saturated fatty acids are most resistant to chemical oxidation. Only the oxidants which can attack saturated paraffins are able to oxidise fatty acids. The end products are numerous and diverse depending upon the oxidant and the conditions of oxidation such as temperature, concentration, solvent, period of oxidation and catalyst. The oxidation may pass through a series of intermediates or may directly be converted to specific end products. In many instances the initial oxidation products are so transitory that their formation is only a matter of speculation. Similar other complications may arise and the investigation of oxidation mechanism is, therefore, fraught with various difficulties.

Inspite of the above facts, some investigators have attempted to study the mechanism, the nature of the intermediates and the end products of oxidation of fatty acids by different oxidizing agents.

Some oxidants are highly specific in their reactivity while others are quite general in both reactivity and application. Thus, potassium permanganate, ozone, and organic peracids are widely used in investigating the structure of unsaturated fatty acids, whereas lead tetraacetate and periodic acid are restricted to the cleavage of polyhydroxylated or other partially oxidised fatty acids of certain structural types. A number of oxidants do not possess any special merit in the investigation of fatty acids and consequently, they have not come into general use. A few oxidants like sulphuric and nitric acids which are of some value in certain industrial processes, are now largely of historical interest in the elucidation of the structure of fatty acids.

Chromic acid is one of the few strong oxidants which has been widely used and reacts with almost all types of oxidisable groups. It has regularly been used for well over a century both in volumetric analysis and in synthetic and degradative organic chemistry. Although the knowledge of mechanism of chromic acid oxidation of organic compounds is only fragmentary, yet as a result of pioneering work of Westheimer, Rocek and Stewart the mechanism of some of the reactions is fairly well understood. A review of the literature on the chromic acid oxidation of various functional groups is given below.

The Chromic acid oxidation of alcohols has been studied extensively because of its major use in synthetic chemistry. Primary alcohols give aldehydes and acids in quantitative yields while ketones are obtained from secondary alcohols. The reaction is less satisfactory in presence of easily oxidisable functional groups. The difficulty encountered is due to the possibility of the cleavage reaction. Phenyl tert-butyl carbinol, for example, gives benzaldehyde and tert-butyl alcohol as cleavage products accompanied by a smaller quantity of the expected ketone.



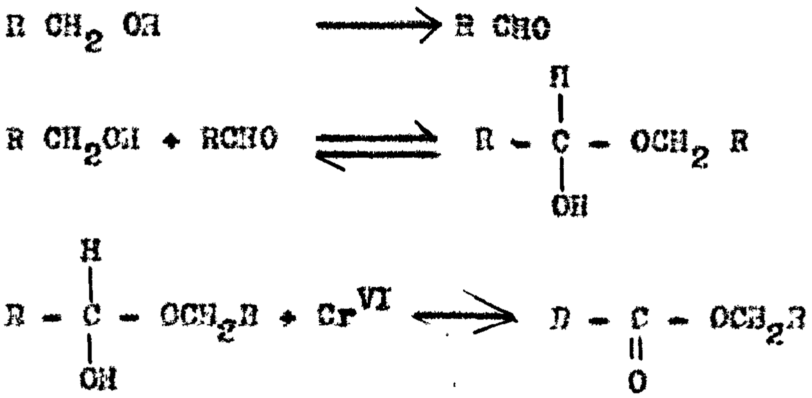
$$C_6H_5 - \underset{H}{\overset{OH}{C}} - C(CH_3)_3 \xrightarrow{Cr^{VI}} C_6H_5 - \overset{O}{\overset{\|}{C}} - C(CH_3)_3 + C_6H_5CHO + (CH_3)_3COH$$

Phenylalkyl carbinols give generally large amounts of cleavage products. Westheimer and co-workers[1,2] obtained 6% cleavage with phenyl isopropyl carbinol and 60% cleavage with phenyl tert-butyl carbinol. Such types of cleavage reactions are known to occur in many other carbinols[3,4].

The cleavage reaction can be eliminated by addition of manganous ions.

Bowden and co-workers[5] found that the oxidation of secondary alcohols in acetone medium proceeded more rapidly than in acetic acid. One of the advantages was that because of the large excess of acetone in the former case the ketone produced was protected against further oxidation. Later on, Bowman et al.[6] found that potassium dichromate and chromium trioxide in acetic acid were the effective reagents for the oxidation of secondary alcohols. Fieser[7] oxidized cholestanol to cholestanone in good yield using dichromate in acetic acid. The difficulty encountered in the oxidation of primary and secondary alcohols was overcome by Sarett[8] who visualized that pyridine-chromium trioxide complex might not oxidise the other functional groups. The reagent has been used successfully in the oxidation of a group of steroidal alcohols. Holum[9] explored the utility of this reagent for the oxidation of a large number of alcohols.

Primary alcohols are oxidized by chromic acid to aldehydes which are further oxidized to the corresponding carboxylic acids. The poor yield of aldehyde have been attributed to the side reaction between aldehyde and unreacted alcohol to give hemiacetal which may further be oxidized to ester[10].



$$R\,CH_2\,OH \longrightarrow R\,CHO$$

$$R\,CH_2OH + RCHO \rightleftharpoons R-\overset{H}{\underset{OH}{C}}-OCH_2\,R$$

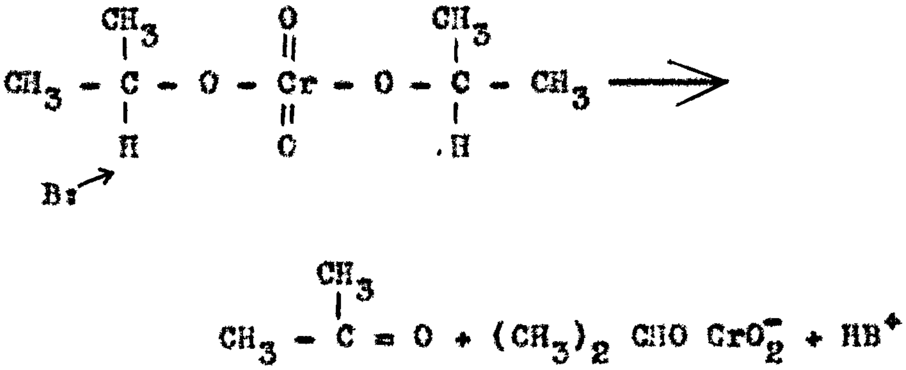
$$R-\overset{H}{\underset{OH}{C}}-OCH_2R + Cr^{VI} \longrightarrow R-\underset{O}{\overset{}{\underset{\|}{C}}}-OCH_2R$$

Ester formation is diminished by sweeping off aldehyde out of the reaction mixture with a strain of carbon dioxide or nitrogen. Oppenauer and Oberrauch[11] reported for the first time that tert-butyl chromate in petroleum ether was a remarkable oxidant for the oxidation of primary alcohols to aldehydes in excellent yields. Hexadecanol, for example, was converted to hexadecanal in 80-85% yield; geraniol to geranial in 85% yield and benzyl alcohol to benzaldehyde in 94% yield[11]. It was shown that this reagent reacted by a rapid trans-esterification with primary and secondary alcohols. This esterification and its reverse usually involved electronpair displacements at the chromium atom i.e. acyl-oxygen bond fission.

As a result of extensive studies on the chromic acid oxidation of alcohols, Westheimer[15] proposed a rate *law*

$$v = k_a[HCrO_4^-][R_2CHOH][H^+] + k_b[HCrO_4^-][R_2CHOH][H^+]^2$$

which was found to be applicable to all the primary and secondary alcohols studied[15-22] so far. Krauss[23] observed that it was possible to prepare esters of chromic acid with primary and secondary alcohols and these were decomposed by pyridine to give the corresponding carbonyl compounds according to the following scheme:



$$B: \quad CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-O-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH_3 \longrightarrow$$

$$CH_3-\overset{\overset{CH_3}{|}}{C}=O+(CH_3)_2\ CHO\ CrO_2^- + HB^+$$

On this basis Westheimer proposed that the oxidation of primary and secondary alcohols proceeded via the acid chromate ester.

$$R_2CHOH + HCrO_4^- + H^+ \longrightarrow R_2CHO\ CrO_3H + H_2O$$

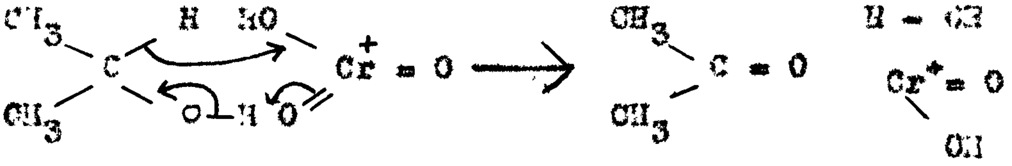
$$R_2CHO\ CrO_3H + H^+ \longrightarrow R_2CHO\ CrO_3H_2^+$$

$$R_2CHO\ CrO_3H \xrightarrow{k_1} R_2C=O + Cr^{IV}$$

$$R_2CHO\ CrO_3H_2^+ \xrightarrow{k_2} R_2C=O + Cr^{IV}$$

The data on the kinetics and isotope effect for isopropyl alcohol oxidation could be explained satisfactorily by the above reaction sequence. Klaning[24] also demonstrated the formation of acid chromate ester in the reaction solution. Later on, the intermediacy of the chromic acid ester was confirmed by an investigation of the oxidation of sterically hindered alcohol 3β-28-diacetoxy-6β-hydroxy-18β-, 12-oleanen[25]. Although the formation of ester as an intermediate has been confirmed but its conversion to products is still an unsettled problem. General base catalysis by pyridine, as supposed originally, was confuted later on[26,27].

Rocek and Krupicka[26] showed that the logarithm of the rate constant is linearly dependant upon the Hammett's acidity function $H_o$. They suggested that the oxidation proceeded by a molecular cyclic electron switch, involving molecular $H_2CrO_4$ at low acidities, and a protonated species $H_3CrO_4^+$ or $HCrO_3^+$ at higher acidities.



This cyclic mechanism may provides a more satisfactory explanation of the relative rates of oxidation of para-substituted 1-phenylethanols; the order of reactivity being

MeO > MeC- > Me- > H- > Cl- > $NO_2$-.

Electron-donating substituents favoured oxidation[28]. Graham and Westheimer[29] also concede that in very strong acid a cyclic mechanism such as above may operate.

Chromic acid oxidation of large number of organic compounds seems to proceed by the scheme,

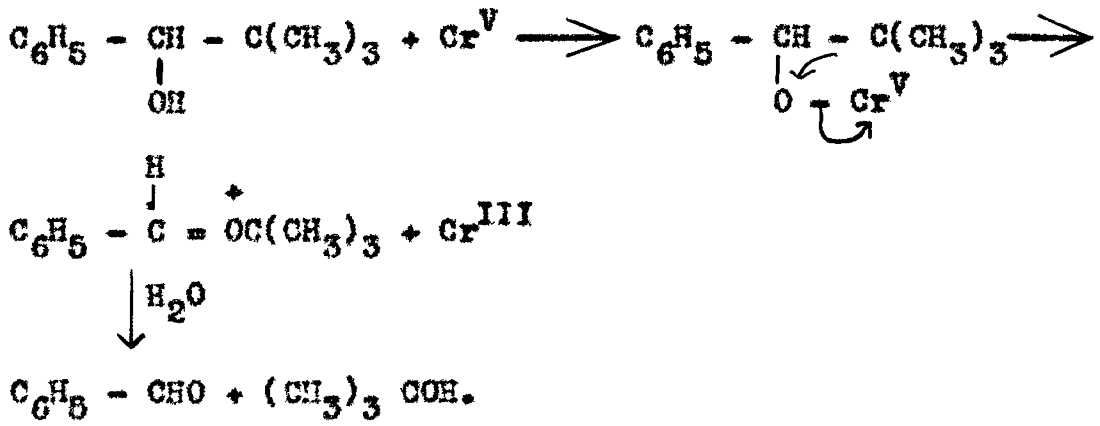
$$\mathrm{Cr}^{(VI)} + \mathrm{S} \longrightarrow \mathrm{Cr(IV)} + \mathrm{P}$$

$$\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \longrightarrow 2\ \mathrm{Cr(V)}$$

$$2\mathrm{Cr(V)} + 2\mathrm{S} \longrightarrow 2\mathrm{Cr(III)} + 2\mathrm{P}.$$

Hence, the oxidation with chromic acid is in fact an oxidation by Cr(V). This was concluded from the fact that 67% of cleavage products (benzaldehyde and tert-butyl alcohol) were obtained from the chromic acid oxidation of phenyl-tert-butyl carbinol and the remainder was the expected ketone. The degree of cleavage was suppressed by addition of cerous and manganous ions, indicating that cleavage was affected by Cr(IV) or Cr(V) and not by Cr(VI). The cleavage reaction does not involve the hydrogen attached to the reaction centre as is indicated by the lack of isotopic fractionation in the competitive oxidation of labelled and unlabelled alcohols. The data suggest two possible mechanisms[30].

1.

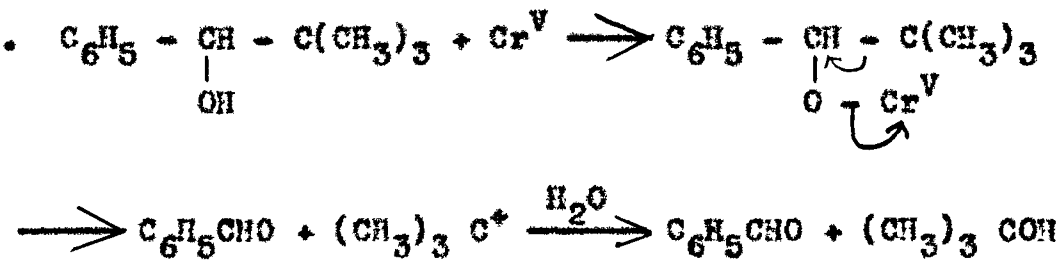


$$C_6H_5-\underset{OH}{CH}-C(CH_3)_3 + Cr^{V} \longrightarrow C_6H_5-\underset{O-Cr^{V}}{CH}-C(CH_3)_3 \longrightarrow$$

$$C_6H_5-\overset{H}{C}=\overset{+}{O}C(CH_3)_3 + Cr^{III}$$

$$\xrightarrow{H_2O} C_6H_5-CHO + (CH_3)_3\,COH.$$

2.



$$C_6H_5-\underset{OH}{CH}-C(CH_3)_3 + Cr^{V} \longrightarrow C_6H_5-\underset{O-Cr^{V}}{CH}-C(CH_3)_3$$

$$\longrightarrow C_6H_5CHO + (CH_3)_3\,C^{+} \xrightarrow{H_2O} C_6H_5CHO + (CH_3)_3\,COH$$

Lack of oxygen-18 in the tert-butyl alcohol formed in the cleavage of the lebelled alcohol indicates the unlikelyhood of mechanism(1). Mechanism (2) was supported by the observation that phenyl aprocamphyl carbinol was oxidized without cleavage[31].

Oxidation of tertiary alcohols is more difficult than that of primary or secondary alcohols, but can be affected in the presence of sulphuric acid. The studies of Sager[32] and Rocek[33] on the mechanism of oxidation of tertiary alcohols showed that the reaction is first order with respect to alcohol but independent of the concentration of the oxidant. It indicated that an olefin was formed slowly which was then rapidly oxidized to a ketone.

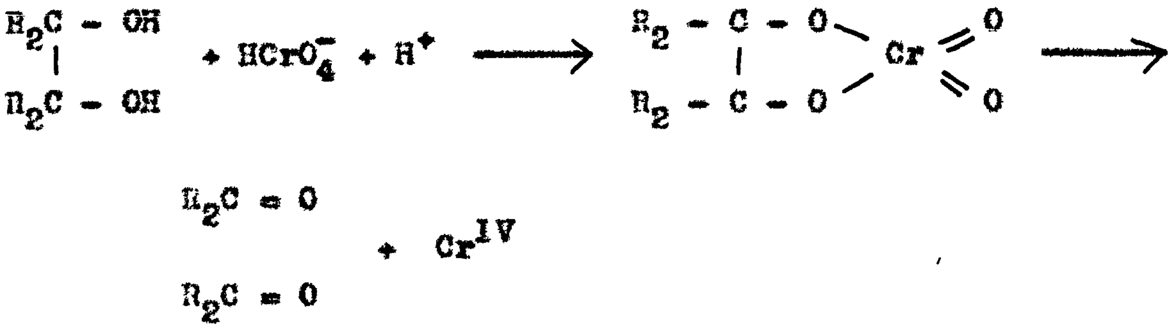
Slack and Waters[34] for the first time investigated the chromic acid oxidation of diols. They observed that the cleavage of 2,3-butylene glycol (20-30%) was more than that of ethylene glycol (1.2%). Chatterjee and Mukherjee[35] carried out a detailed investigation and postulated kinetic rate laws for different glycols, namely for ethylene glycol and pinacol the rate laws were as under:

$$v = k_1[\text{diol}][\text{HCrO}_4^-][\text{H}^+] + k_2[\text{diol}][\text{HCrO}_4^-][\text{H}^+]^2$$

$$v = k[\text{diol}][\text{HCrO}_4^-][\text{H}^+].$$

It seems that two reaction courses are possible. In the first case normal oxidation occurs giving an α-hydroxy-carbonyl compound, which may be further oxidised. In the second, cleavage of carbon-carbon bond occurs.

Chang and Westheimer[36] also studied the chromic acid oxidation of pinacol and found a solvent isotope effect $k_{D_2O}/k_{H_2O} = 2.7$. They observed that monomethyl ether of pinacol was oxidised very slowly. It indicates that oxygen-hydrogen bond cleavage does not occur in the rate determining step and cyclic chromate ester is probably the intermediate. This ester is decomposed to the observed products in a manner similar to that suggested for lead tetraacetate[37] and periodic acid[38].



Cyclic chromate formation mechanism was further supported by the observation that cis-1,2-dimethyl-1,2-cyclopentanediol was oxidised 17,000 times faster than its trans isomer[39]. The large difference in the rate of oxidation could not be explained by a non-cyclic mechanism. The rate of increase of cleavage with the methyl substitution was explained on the assumption that alkyl substitution stabilized the activated complex for the decomposition of the cyclic chromate ester.

Although considerable work has been done on the chromic acid oxidation of diols yet the reason for a change in mechanism with increasing methyl substitution is not yet clear. Also the ability of chromic acid to effect both normal oxidation and cleavage is not well understood.

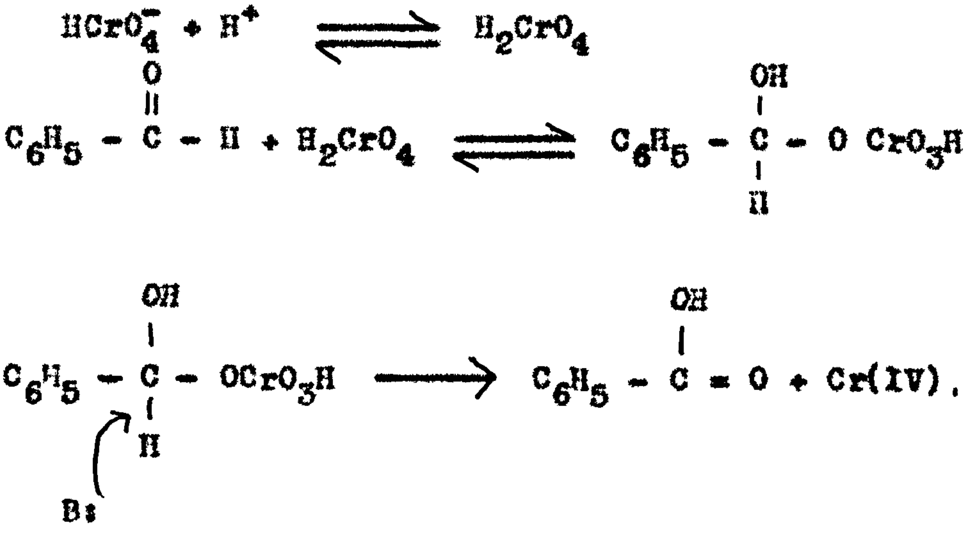
Aldehydes are the intermediate products in chromic acid oxidation of primary alcohols to the corresponding carboxylic acids. Lucchi[40], for the first time studied the oxidation of aromatic aldehydes in acetic acid-sulphuric acid medium. He showed that the reaction was first order in aldehyde and in Cr(VI) and that the electron withdrawing groups facilitated the reaction. He, however, did not study the effect of sulphuric acid on the rate of the reaction. Wiberg and Mill[41] carried out a detailed kinetic study of oxidation of benzaldehyde and formulated a rate law as

$$v = k_1[\mathrm{RCHO}][\mathrm{HCrO_4^-}][\mathrm{H^+}] + k_2[\mathrm{RCHO}][\mathrm{HCrO_4^-}][\mathrm{H^+}]^2$$

(in aqueous solution),

and $v = k[\mathrm{RCHO}][\mathrm{HCrO_4^-}]\,h_0$ (in acetic acid).

On the basis of the similarity in rate law and isotope effect in the oxidation of benzaldehyde by permanganate[42] and by chromic acid, they suggested the following mechanism:



$$\mathrm{HCrO_4^-} + \mathrm{H^+} \rightleftharpoons \mathrm{H_2CrO_4}$$

$$\mathrm{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-H} + \mathrm{H_2CrO_4} \rightleftharpoons \mathrm{C_6H_5-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-O\,CrO_3H}$$

$$\mathrm{C_6H_5-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-OCrO_3H} \longrightarrow \mathrm{C_6H_5-\overset{\overset{\displaystyle OH}{|}}{C}=O} + \mathrm{Cr(IV)}.$$

The mechanism is similar to that proposed by Westheimer for the isopropyl alcohol[16].

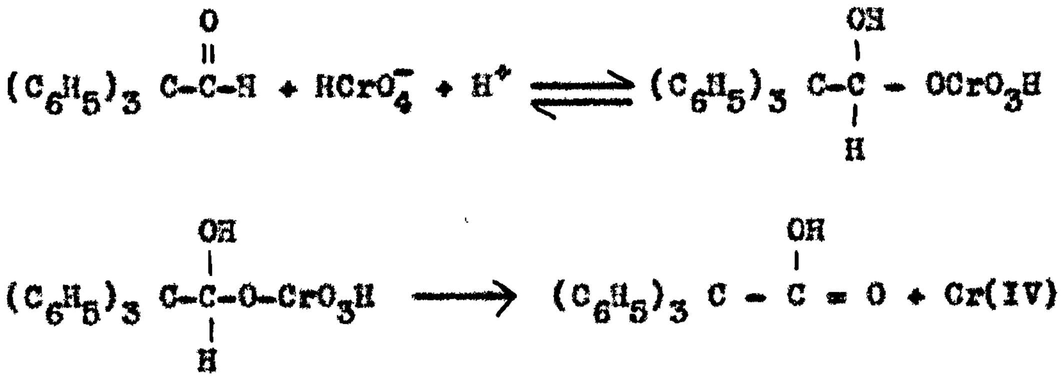
Oxidation of aliphatic aldehydes[43] has not received much attention. However, the rate laws found in some cases are quite similar to those obtained for the aromatic aldehydes. The rate law for formaldehyde[44,45] has been shown to be

$$v = k[HCHO][HCrO_4^-][H^+]^2 / 1 + a[H^+]$$

Kemp and Waters[4] found that kinetic isotope effect and energy of activation decreased in the solutions of high acidity. They suggested that it was due to the effect of acid concentration on the reactions of Cr(IV) and Cr(V). At higher acidities the ratio Cr(IV)/Cr(VI) increased more rapidly, and the oxidation was effected mainly either by Cr(IV) or Cr(V). Chaterjee[49] determined the induction factor as 0.5 which indicated that Cr(IV) was the product in the oxidations by Cr(VI).

A number of stable hydrates of aldehydes are known[46-48]. It was reported by Merz and Waters[49] that in the oxidation of formaldehyde, the hydrated form of aldehyde was the reacting species. The value of $\rho$, for aromatic aldehydes is + 1.02[41] and that for aliphatic aldehyde is -1.2. The difference between the reaction constants for the two types of aldehydes is approximately the reaction constant for the hydration equilibrium for the aromatic aldehydes. Thus, if the aromatic aldehydes are assumed to react in the hydrated form, the $\rho$ value for the reaction would be about -1, corresponding to the value obtained in the oxidation of aliphatic aldehydes & alcohols. The assumption that the reaction involves the hydrate of the aldehyde is in agreement with the result obtained by varying the water content of the acetic acid - water mixtures.

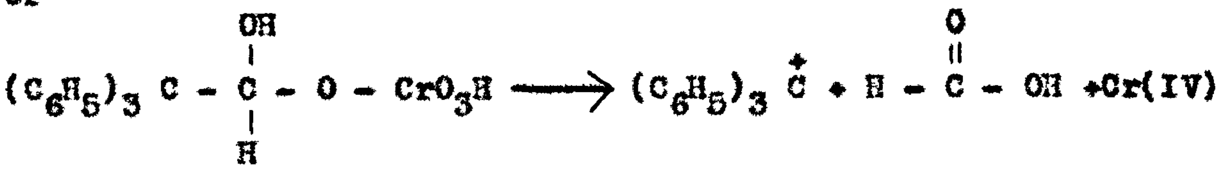
The main problem in the oxidation of aldehydes by chromic acid is to determine whether it is a one electron or a two electron process. Westheimer used induced oxidation as a diagnostic tool to solve the problem. Wiberg and Richardson[50] reported a very interesting non-kinetic example to determine whether Cr(IV) or Cr(V) was the active intermediate. They observed that triphenylacetaldehyde was oxidized by chromic acid to give approximately one third triphenylacetic acid and two thirds triphenylcarbinol and carbon monoxide. The ester mechanism might be expected to give either triphenylacetic acid or triphenylcarbinol and formic acid.



$$(C_6H_5)_3\,C-\overset{O}{\overset{\|}{C}}-H + HCrO_4^- + H^+ \rightleftharpoons (C_6H_5)_3\,C-\underset{H}{\overset{OH}{C}}-OCrO_3H$$

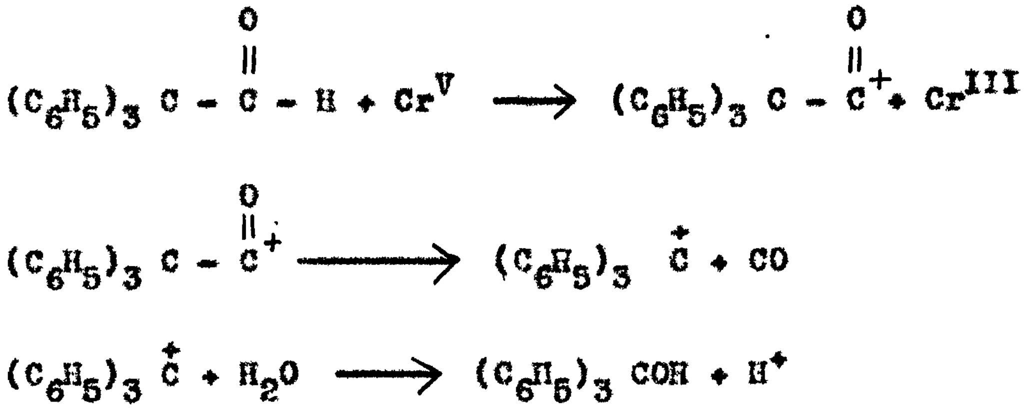
$$(C_6H_5)_3\,C-\underset{H}{\overset{OH}{C}}-O-CrO_3H \longrightarrow (C_6H_5)_3\,C-\overset{OH}{C}=O + Cr(IV)$$

Or



$$(C_6H_5)_3\,C-\underset{H}{\overset{OH}{C}}-O-CrO_3H \longrightarrow (C_6H_5)_3\,\overset{+}{C} + H-\overset{O}{\overset{\|}{C}}-OH + Cr(IV)$$

Hydride or hydrogen atom abstraction, however, might lead to triphenylcarbinol and carbon monoxide.

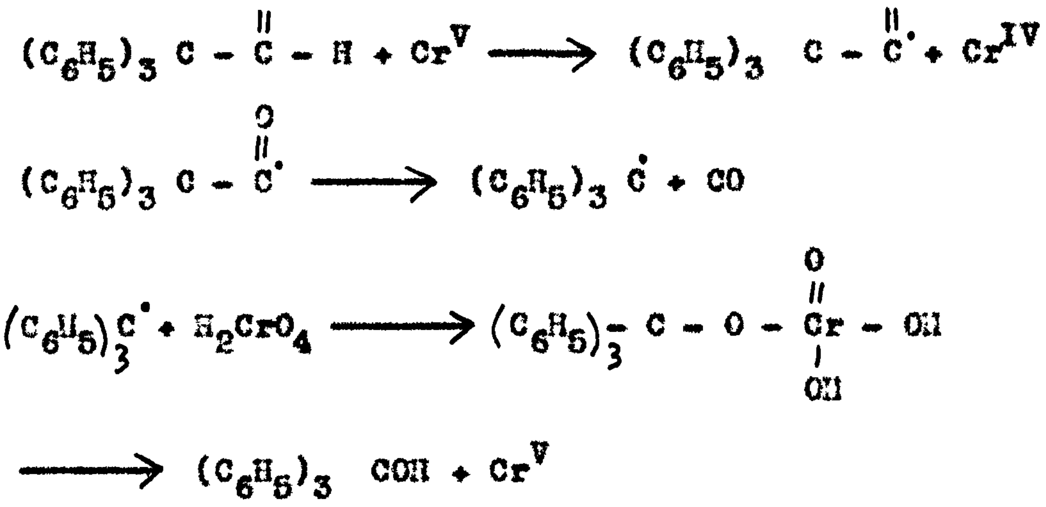


$$(C_6H_5)_3\,C-\overset{O}{\overset{\|}{C}}-H + Cr^V \longrightarrow (C_6H_5)_3\,C-\overset{O}{\overset{\|}{C}}{}^{+} + Cr^{III}$$

$$(C_6H_5)_3\,C-\overset{O}{\overset{\|}{C}}{}^{+} \longrightarrow (C_6H_5)_3\,\overset{+}{C} + CO$$

$$(C_6H_5)_3\,\overset{+}{C} + H_2O \longrightarrow (C_6H_5)_3\,COH + H^+$$

Or



$$(C_6H_5)_3\,C-\overset{O}{\overset{\|}{C}}-H + Cr^V \longrightarrow (C_6H_5)_3\,C-\overset{O}{\overset{\|}{C}}{}^{\bullet} + Cr^{IV}$$

$$(C_6H_5)_3\,C-\overset{O}{\overset{\|}{C}}{}^{\bullet} \longrightarrow (C_6H_5)_3\,\overset{\bullet}{C} + CO$$

$$(C_6H_5)_3C^{\bullet} + H_2CrO_4 \longrightarrow (C_6H_5)_3\,C-O-\underset{OH}{\overset{O}{\overset{\|}{Cr}}}-OH$$

$$\longrightarrow (C_6H_5)_3\,COH + Cr^V$$

The product study suggests that one third of the reaction proceeds via the ester mechanism and two thirds via either hydride abstraction or hydrogen atom abstraction mechanism. This clearly indicates that Cr(V) is the main reacting species in the oxidation of aldehydes, but in part the reaction proceeds with Cr(IV).

The oxidation of ketones by chromic acid was first studied by Petit[61]. He found that the oxidation rate increased with increasing chain length from acetone to heptyl methyl ketone, and the reaction took place through an enolisation mechanism. Uceda and Tarama[62] carried out the oxidation of cyclohexanone in presence of HCl, $H_2SO_4$ and $HClO_4$ and suggested a mechanism which involved the enolisation of cyclohexanone, addition of two molecules of $HCrO_4^-$, the fission of the double bond and oxidation to adipic acid of the resulting aldehyde. Littler and Waters[63] studied the kinetics of oxidation of cyclohexanone by three electron, two electron and one electron oxidants and concluded that two electron oxidant attacked the enol form while one electron oxidant attacked the keto form of the substrate. But the attack of chromic acid (3 electron oxidant) on the cyclohexanone remained undecided. The rate controlling step could be the attack of chromic acid on the double bond of enol form or it could be the decomposition of the chromic acid ester of the enol form. But as the rate of oxidation of cyclohexanone was slower than its rate of enolization at the same acidity it could not be concluded whether the keto or enol form was attacked. It merely indicated that the transition state of the rate determining process involved a ketone molecule and a chromic acid molecule.

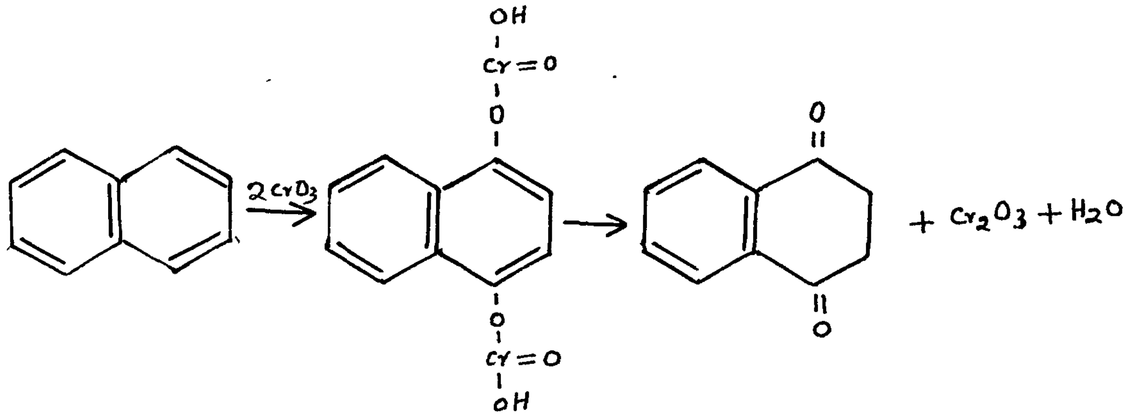
Wiberg and Gatzke[54] suggested the possibility of the free radical mechanism for the oxidation of deoxybenzoin by chromic acid on the basis of their observation that 6% bidesyl was obtained along with the expected benzil. Rocek[55] also visualized the formation of some free radicals in the oxidation of cyclohexanone.

The oxidation of aryl alkanes is particularly useful from synthetic point of view because of the formation of aryl carboxylic acids and aromatic aldehydes. It is also helpful in determining the orientation of alkyl groups attached to the aromatic nucleus. Benzene[56] is resistant to oxidation but aromatic polycyclic and heterocyclic hydrocarbons[57-59] are easily oxidized to quinones. The order of the reactivity of these compounds depends upon their electron availability and is wholly consistant with the attack by a cation $\mathrm{H\overset{+}{Cr}O_3}$. Electron donating groups have been found to assist the ring destruction.

The alkyl group of an alkyl benzene, regardless of its length, is finally oxidized to carboxyl group with the formation of an aromatic carboxylic acid. Thus, toluene gives benzoic acid and m & p-xylenes give the corresponding dicarboxylic acids[61]. With longer chains the initial attack is at the $\alpha$-position to the aromatic ring. Thus, from the products obtained in the oxidation, the nature of the alkyl groups attached to the ring can be determined. Polynuclear hydrocarbons are oxidized in the same manner. Waters[62] obtained benzophenone in good yields from the chromic acid oxidation of diphenylmethane. The oxidation of anthracene and fluorene and their nitrohomologues was studied by Ogata and Akimoto[63] who found that electron withdrawing groups (nitro) retarded the reaction. It was noted that triaryl substituted methanes gave the corresponding tertiary alcohols which under vigorous conditions led to the breakdown of one aryl group with the formation of diaryl ketones.

Brandenberger and co-workers[64] reported that ring oxidation was competitive with the side chain oxidation in the chromic acid oxidation of alkyl benzenes under Kuhn-Roth conditions and that the amount of ring oxidation increased with increasing acid concentration. In order to suppress the attack on the aromatic nucleus and to effect the oxidation of side chain only, the use of potassium dichromate in water at elevated temperature was noteworthy. Friedman et al.[65] used this reagent to obtain a number of aromatic mono and polycarboxylic acids from alkyl amine oxidation.

The first detailed study of the oxidation of aryl alkanes with chromic acid was reported by Slack and Waters[62]. They studied the oxidation of diphenylmethane and triphenylmethane in glacial acetic acid. It was observed that the order of the reaction with respect to chromium trioxide in the oxidation of diphenylmethane and triphenylmethane was two and one respectively, while the order with respect to hydrocarbons was one in both the cases. They also reported that chromium acetochromate $[Cr^{III}(HCrO_4)(OOCCH_3)_2]$ formed in the reaction retarded the rate. In the oxidation of toluenes and ring substituted toluenes[63], the order with respect to the substrate was one but two with respect to chromium trioxide. Later on, these studies were extended to naphthalene and fluorenes. The observed rates satisfied the previous rate equation. It was, therefore, concluded that the same mechanism was operating in these oxidations, i.e. the attack of two molecules of chromium trioxide on one molecule of the substrate.

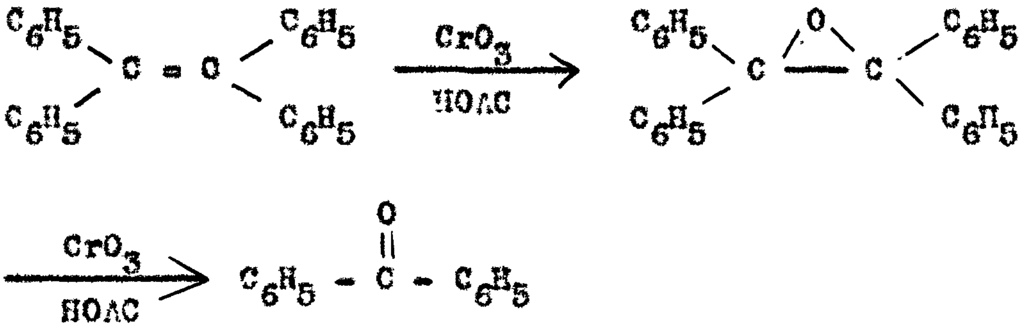


Evans[66] studied the oxidation of diphenylmethane and other compounds in 95% acetic acid using mineral acid as catalyst. Product analysis showed the presence of $Ph_2CH_2$ and $Ph_2CO$. The proposed rate equation was

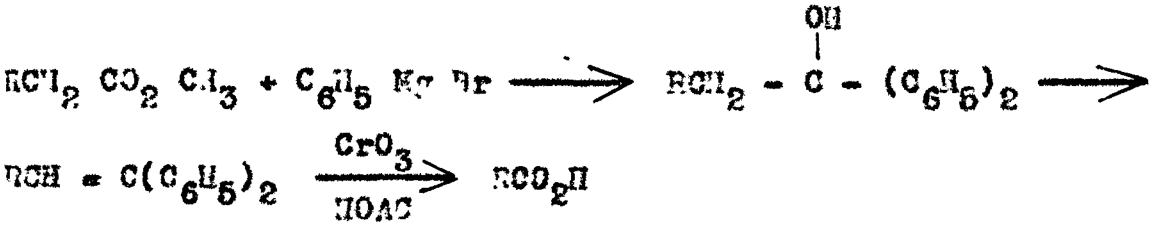
$$v = k\,[Ph_2CH_2][CrO_3]\,h_o.$$

where $h_o$ is the Hammett acidity function[67]. The value of the kinetic isotope effect ($k_H/k_D$) was found to be 6.4 at 30°C and it was noted that the electron releasing groups facilitated the reaction moderately. On the basis of these data it was concluded that the initial step was the abstraction of hydrogen atom with the formation of $Ph_2CH^{\bullet}$ radical which was further oxidised to Ph CO Me.

Chromic acid oxidation of alkenes leads to carbon-carbon bond fission at the olefinic link with the formation of a variety of products. The reaction is employed in Barbier-Wieland degradation and in the oxidation of tetraphenylethylenes. Tetraphenylethylenes[68-70] with smaller amounts of chromic acid give the corresponding epoxides while benzophenone is obtained with larger amounts.



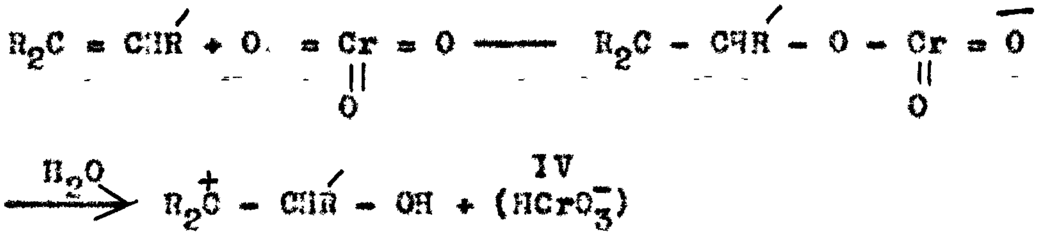
The study of oxidation of many steroidal double bonds suggests that the initial compounds formed in the reaction with chromic acid (whatever its structure) decompose to give the epoxide and the ketol in the two separate reactions; and at least part of ketol is formed directly and not via the epoxide. Barbier-Wieland degradation[71,72] is of great importance in the degradation and modification of steroids.



$$RCH_2CO_2CH_3 + C_6H_5MgBr \longrightarrow RCH_2-\overset{OH}{\overset{|}{C}}-(C_6H_5)_2 \longrightarrow RCH=C(C_6H_5)_2 \xrightarrow[HOAC]{CrO_3} RCO_2H$$

The oxidation of alkenes by chromic acid in sulphuric acid is different from that in acetic acid medium. The initial reaction may be the same in the two cases but the ultimate products are different. Rearrangement is possible in the former solvent[73]. Hickinbottom and Wood[74,75] suggested that an epoxide might be an intermediate in these reactions and the formation of the rearrangement products could be accounted for by assuming an acid catalyzed pinacolic type rearrangements of the intermediate epoxide. Further, Hickinbottom and co-workers[76] suggested that the initial step involved an electrophilic addition of $H_2CrO_4$ to the double bond forming an intermediate which might decompose to epoxide by loss of Cr(IV), or it might lead directly to the rearrangement products without involving the epoxide. The hypothesis was however, discarded by Zeiss and Zwanzig[77] who found that in the oxidation of 1-methyl fenchene with chromic acid the rearrangement product fenchone was obtained in very little amount (6%).

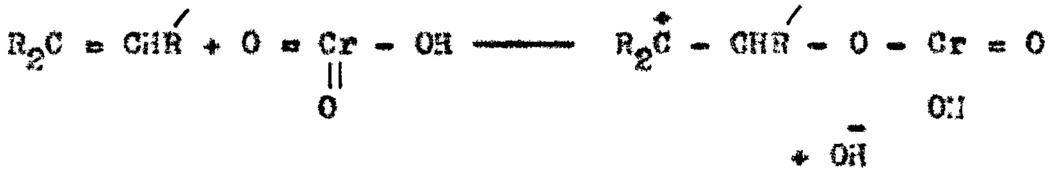
It appears from Hickinbottom's[78] studies that an electron pair is donated by the olefin to $O = Cr$ bond producing an intermediate which rapidly reacts with water to yield the conjugated acid of an epoxide.



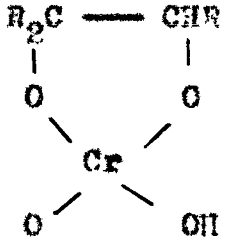
$$R_2C=CHR' + O=\underset{\overset{\|}{O}}{Cr}=O \longrightarrow R_2C-CHR'-O-\underset{\overset{\|}{O}}{Cr}=\overline{O}$$

$$\xrightarrow{H_2O} R_2\overset{+}{C}-CHR'-OH + (H\overset{IV}{Cr}O_3^-)$$

1:2 Diol formation is certainly a secondary reaction as epoxides can be isolated in high yields from olefins by use of chromium trioxide in acetic anhydride diluted with carbon disulphide. Zeiss and Zwanzig[77] determined that the oxidation of olefins by chromic acid was of first order with respect to both olefin and chromic acid. They proposed that carbonium ion formation provided a more satisfactory explanation than the cyclic intermediate.



$$R_2C=CHR' + O=\underset{\overset{\|}{O}}{Cr}-OH \longrightarrow R_2\overset{+}{C}-CHR'-O-\underset{OH}{Cr}=O \quad + \overline{OH}$$



The above mechanism can be applied to the oxidation of conjugated dienes which easily yield ketols[79].

A detailed study of oxidation of hydrocarbons by chromic acid has been carried out by Rocek and co-workers.[80-82] They determined the relative rates of oxidation of primary, secondary and tertiary carbon-hydrogen bonds as 1:110:7000. It is seen that methyl group is seldom oxidised. The oxidation of secondary carbon-hydrogen bond yields ketones which are rapidly oxidized by chromic acid. The yield of the ketone, therefore, depends upon the relative rates of oxidation of ketone and hydrocarbon and upon the ability of the worker to check the reaction at the point of maximum yield of ketone. In some cases,[83,85] a reasonable yield of ketone is obtained where its enolisation becomes difficult. Tertiary carbon-hydrogen bond is oxidised to corresponding tertiary alcohol. 3-Ethyl-3-pentanol (50% yield) is obtained from the chromic acid oxidation of 3-ethylpentane.[86,87] Rocek[83] also showed that 1-methylcyclohexanol was a major intermediate in the oxidation of methylcyclohexane.

The influence of structure on the rate of oxidation of hydrocarbons was also studied by Rocek and co-workers.[80-82] They showed that an increase in the chain length caused a small increase in the oxidation rate. Steric hindrance was found to effect the reaction rate in highly branched chain hydrocarbons. Phenyl substitution at the reaction site augmented the oxidation rate.

A considerable number of data on the mechanism of oxidation of alkanes by chromic acid in aqueous acetic acid and reasonably large kinetic isotope effect indicate that the rate determining step is the cleavage of carbon-hydrogen bond. The kinetic rate law has been shown[80-83] to be $v = k\,[\text{alkane}][CrO_3]\,h_o$, and the hydride abstraction mechanism,

$$R_3-C-H + O=CrO_3H_2 \longrightarrow R_3C\ HOCrO_3H_2 \xrightarrow{H_2O} R_3COH,$$

has been postulated. But Wiberg and Eisenthal[89] put forward arguments against the above mechanism and suggested the possibility of hydrogen atom abstraction-mechanism.

$$R_3C-H + H_2CrO_4 \longrightarrow [R_3C^{\cdot}\ H_3CrO_4]$$

$$[R_3C^{\cdot}\ H_3CrO_4] \longrightarrow R_3-C-O-Cr(IV)$$

$$R_3-C-O-Cr(IV) \xrightarrow{H_2O} R_3COH + Cr(IV).$$

In order to explain the rearrangement in the oxidation of neohexane, the formation of organic azide in the presence of azide ion and enormous reactivity of the tertiary hydrogens, Rocek[90] suggested that the solvent-cage trapped-radical formed in the initial step should be written as resonance hybrid of the structures

$$[R_3C^{\cdot}\ Cr^{V}] \longleftrightarrow [R_3\overset{+}{C}\ Cr^{IV}]$$

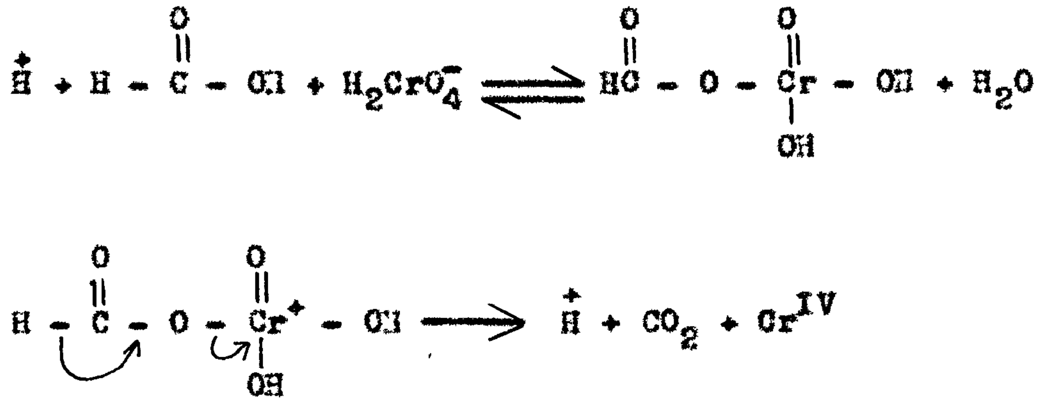
The resonance hybrid could either decompose to the carbonium ion or undergo combination to give the Cr(IV) ester which is now generally regarded as the reaction intermediate leading to alcohol formation. The carbonium ion may be formed by the electron transfer process or by a cleavage reaction of Cr(IV) ester with carbon oxygen bond. It is difficult to decide between the two possibilities.

Chromic acid has been used in the oxidation of saturated, unsaturated, hydroxy, keto and other types of acids to produce a variety of oxidation products depending upon the reaction conditions and the nature of substrates. Most of the published work describes the use of this oxidant for analytical purposes in the cleavage of fatty acid chain. It has also been applied to the disruptive oxidation of unsaturated acids and to the further oxidation of partially oxidized products such as hydroxy and keto acids. However, little work has been done on the controlled and stepwise oxidation of unsaturated fatty acids with chromic acid. The difficulties encountered in this kind of study are that the large number of competitive reactions take place and the intermediate oxidation products are more readily oxidized than the starting material. The major reaction of saturated fatty acids is an oxidative degradation. The oxidation takes place initially at $\alpha$-carbon atom. This is evidenced by the large amount of shorter chain acids which have been found among the oxidation products.

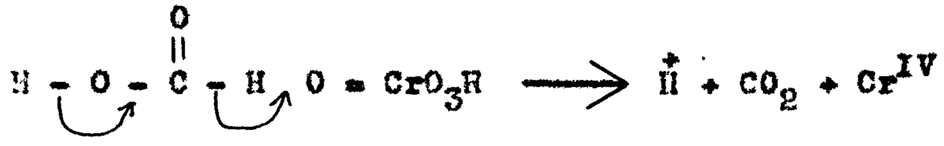
Snethlage[91] studied the oxidation of oxalic acid by chromic acid in concentrated sulphuric acid medium. He observed that the order of the reaction with respect to chromic acid varied between 1 - 1.5 while that of oxalic acid between 1-2. Maximum rate was found at 70% sulphuric acid concentration. Later on, Asnaree and Baga[92] found that only 50% of oxalic acid was oxidized in all cases. Some chromic acid remained unchanged when the reaction stopped even at the boiling point. They postulated that a heat stable complex $[Cr(C_2O_4)(H_2O)_4]^+$ was formed as an intermediate which was converted to $[Cr(C_2O_4)_2(H_2O)_2]^-$. A series of dicarboxylic acids were studied by Rocek and Mares[93] who calculated the retardation factor of carboxyl group. The oxidation rate constant per methylene group has been determined to be $5.2 \times 10^{-3}$ mole$^{-1}$ sec$^{-1}$ which agrees well with the value $5.73 \times 10^{-3}$ l-mole$^{-1}$ sec$^{-1}$ established in the series of n-paraffins.

A detailed study of the oxidation of formic acid in sulphuric acid medium has been carried out by several investigators[94-98]. The reaction is found to be approximately first order with respect to formic acid and Cr(VI). But it depends upon the square of the acid concentration at low acidity, and follows $h_0$, the Hammett acidity function at higher concentrations. Waters[98] determined the isotope effect ( $k_H/k_D = 7.2$) and solvent isotope effect ($k_{D_2O}/k_{H_2O} = 5.7$) which indicated that the reaction involved two protons in the rate determining step. On the basis of above results two mechanisms were proposed.

(A)



(B)

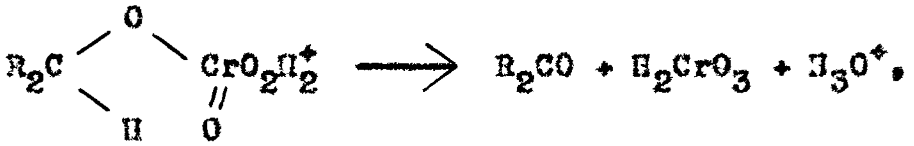


Westheimer[99] pointed out that the chromic acid oxidation of hydroxy acids was extremely complex on account of the wide differences in reaction products.

For example lactic acid was oxidized not at the hydroxyl but at the carboxyl group[100].

$$8\overset{+}{H} + 2HCrO_4^- + 3CH_3CHOH\,COOH \longrightarrow 3CH_3CHO + 3CO_2 + 2Cr^{III} + 8H_2O$$

The above reaction does not involve an oxidation of lactic acid to pyruvic acid as an intermediate for pyruvic acid, under the experimental conditions in question, undergoes further oxidation[101] much more rapidly than it undergoes decarboxylation[102]. Bakore and Shyam Narain[103] also studied the oxidation of lactic, malic and mandelic acids by chromic acid in perchloric acid medium. They suggested that the mechanism



$$R_2C(H)\text{-}O\text{-}Cr(=O)O_2H_2^+ \longrightarrow R_2CO + H_2CrO_3 + H_3O^+,$$

proposed by Kwart and Francis[104] for the oxidation of cyclic secondary alcohols was also applicable to this reaction.

From the above review of the literature regarding the oxidation of organic compounds by chromic acid, it may be concluded that although large amount of work has been done on the use of this oxident but only scant references are available on the oxidation of saturated fatty acids. The few references[105-107] which are reported are only of qualitative nature and no systematic work has been done on the kinetics and mechanism of oxidation of saturated fatty acids by chromic acid. The work described in this thesis has been carried out with a view to study the kinetics under various experimental conditions and to throw light on the mechanism of oxidation of fatty acids.

# CHAPTER II

# KINETICS OF OXIDATION OF NORMAL CHAIN FATTY ACIDS

## INTRODUCTION

Saturated fatty acids are quite resistent to chemical oxidation. They are oxidized only by those oxidants which attack paraffins. Dakin[107,108] reported a series of pioneering studies of oxidation of fatty acids by a mild oxidizing agent, hydrogen peroxide. Later on, he repeated experiments with a view to determine the nature of ketonic oxidation products[109]. He showed that there was a close resemblance between the oxidative processes in organisms and the oxidation reactions affected by hydrogen peroxide. It was shown that each acid from butyric to stearic yielded a methyl--ketone ($R.CO.CH_3$), having one carbon atom less than the parent acid. The first step presumed by him was the formation of a ketonic acid which underwent decarboxylation according to the following scheme,

$$R\ CH_2CH_2\ COOH \longrightarrow R\ CO\ CH_2\ COOH \longrightarrow R\ COCH_3 + CO_2.$$

Chutterbuck and Raper[110] carried out the oxidation of ammonium salts of higher fatty acids by hydrogen peroxide and arrived at the same conclusion that the first step in the oxidation of saturated fatty acids was the production of a series of keto rather than the hydroxy acids.

Allen and Witzemann[111] found that certain buffered oxidation systems were useful for the oxidation of saturated fatty acids by hydrogen peroxide. They used three different catalytic systems ($Na_2HPO_4$ - $H_2O_2$ system, $NH_3$ - $H_2O_2$ system and $(NH_4)_2$ $HPO_4$ - $H_2O_2$ system), and obtained carbon dioxide as the major product (50-80%). Acetic acid and acetone were also obtained in significant yields. The authors interpreted the catalytic effect of the buffers as the intensification of the feeble oxidizing power of hydrogen peroxide by these substances. It was assumed that they promoted the reduction of hydrogen peroxide by supplying hydrogen from the organic acid used. The final oxidation of the substrate to carbon dioxide was a secondary reaction depending on the addition of water and was not due primarily to the peroxide itself.

The acid catalyzed formation of peracids from aliphatic acids and hydrogen peroxide has been studied kinetically by Ogata and Sawaki[112]. They observed that the rate of peracid formation together with equilibrium constants increased with increasing concentrations of sulphuric acid and was correlated with the acidity of medium.

Some further work on the oxidation of carboxylic acids by hydrogen peroxide is reported in the literature. Hatcher[113] studied the oxidation of propionic, normal and isobutyric acids and suggested that they reacted in the molecular form, giving peracids as intermediates. After the formation of peracids, hydroxylation occurred at the $\alpha$-carbon atom and keto acids were formed.

Berezin[114] made a kinetic study of reactions of hydrogen peroxide with carboxylic acids. It was shown that the decomposition of hydrogen peroxide in presence of propionic acid was a first order reaction with the rate constant equal to that of the decomposition of aqueous hydrogen peroxide. They also observed that the evolution of carbon dioxide was a first order reaction. The amount of carbon dioxide formed at 110-150°C was a linear function of the degree of hydrogen peroxide decomposition. The results were interpreted by an ion-radical mechanism.

Osmium tetroxide[115] is a remarkable catalyst for the oxidation processes because of its stability in acid, basic and neutral media. $H_2O_2$ - Os $O_4$ system oxidizes acetic and propionic acids to carbon dioxide quantitatively. Foster and Pyne[116] found a relation between the oxidizing action and catalytic decomposition of concentrated hydrogen peroxide by osmium tetroxide. Their method made possible the simultaneous determination of the extent of oxidation, (indicated by the amount of carbon dioxide formed) and the extent of decomposition of peroxide (indicated by the evolution of oxygen). $\beta$-oxidation of propionic acid by hydrogen peroxide has been reported on the basis of product study[117].

Other oxidants have also been used for the oxidation of fatty acids. Dimitrov and Natan[118] studied the oxidation of fatty monocarboxylic acids by potassium permanganate in various media. Paper chromatographic analysis of the products indicated that $\beta$-oxidation occurred in alkaline and acid media while both $\alpha$- and $\beta$-oxidations took place simultaneously in neutral solutions. The occurrence of $\beta$-oxidation of fatty acids by potassium permanganate in basic medium was also shown by Neunhoeffer and Paths[119].

Deupre[120] obtained pyruvic acid on oxidizing propionic acid by selenium dioxide. Periodic acid[121] was however, shown to be incapable of oxidizing propionic acid even at 100°C in a sealed tube. The oxidizing action of quinquevalent vanadium on some oxygenated compounds of acylic series was determined by Moretto and Gaudefroy[122]. At high concentration of vanadium in 9N sulphuric acid, acetic, propionic, valeric, palmitic and stearic acids were unattacked at temperatures upto 100°C, but isobutyric and oleic acids reacted slowly.

Waters[123] presented the evidence to prove that the oxidation of carboxylic acids by Co(III) took place by inner sphere mechanism. It involved the rapid reversible formation of a cobaltic complex breaking down slowly with liberation of free alkyl radicals which underwent further reaction. The following mechanism was proposed for the reaction.

1. $R.CO_2H + CO(H_2O)_6^{3+} \overset{k_1}{\rightleftharpoons} [R.CO_2Co(H_2O)_5]^{2+} + H^+ + H_2O.$
2. $[R.CO_2Co(H_2O)]^{2+} \xrightarrow{k_2} R^{\cdot} + CO_2 + Co^{2+} + 5H_2O$
3. $R^{\cdot} + Co^{3+} \longrightarrow R^+ + Co^{2+}$
4. $R^+ + H_2O \longrightarrow ROH + H^+$

Chromic acid oxidation of carboxylic acids has been reported by several authors, but none of them has carried out the systematic kinetic investigation of these reactions. Michael Polonovski[124] reported that a strong sulfochromic mixture rapidly oxidized the lower fatty acids, but with weak mixture no reaction was found to take place. These[105,106] acids are oxidized to acetic acid which remains unattacked under the experimental conditions. Petit[51] studied the oxidizability of a number of organic compounds resistant to oxidation. In the oxidation of aliphatic acids he showed that oxidizability increased with increasing chain length.

## EXPERIMENTAL

<u>Materials.</u>

Sulphuric acid: Sulphuric acid A.R. (B.D.H.) was diluted with double distilled water & standardized with 1N sodium hydroxide.

Chromic acid: Stock solutions of chromic acid were prepared by dissolving weighed amount of AnalaR (B.D.H) potassium dichromate in definite volumes of double distilled water. Chromium trioxide solutions decomposed slowly because of the slight amount of the acid present and hence were abandoned in favour of dichromate.

Acetic acid: Acetic acid (E. Merck) was used. The solutions were prepared by dissolving measured volumes of the acid in conductivity water.

Sodium thiosulphate: Thiosulphate solutions were made up by dissolving the requisite amounts of the solid reagent followed by standardization with potassium dichromate. The solution was always freshly prepared and its concentration checked before use.

Sodium perchlorate: Sodium hydrogen sulphate and all other reagents used were either of B.D.H. AnalaR or E.Merck. G.R. quality. The solutions were made up by dissolving weighed amounts of the reagents in double distilled water.

Organic acids: Propionic and butyric (E. Merck) valeric (Light), isobutyric and isovaleric acids (Riedel) were used as supplied. Phenylacetic acid (Bush) was used after recrystallisation.

## Measurements

Experiments were conducted in oil thermostat held to within 0.1°C of the indicated temperature. Solutions of the desired concentrations for any particular experiment were made up from stock solutions. The following sequence was adopted for combining the reactants: water (to make up the volume 125 ml), sulphuric acid, substrate and chromic acid. The reaction vessel containing water, sulphuric acid and substrate and a flask containing dichromate solution of required concentration were immersed in the thermostat for 15-20 minutes to attain the steady temperature. The oxidation was commenced by adding the dichromate solution to the reaction vessel. The time of half addition of the oxidant solution was taken as the zero time of the reaction. The reaction vessel was vigorously shaken to ensure the thorough mixing of the reactants.

The progress of the reaction was followed iodometrically. 10 ml aliquots of the reaction mixture were withdrawn at suitable intervals of time usually 10 minutes. This aliquot was then discharged into 100 ml conical flask containing 10 ml of boiled and cooled double distilled water, 10 ml of 5% potassium iodide and a catalyst for dichromate-iodide reaction.*

The flask was covered with paper and kept in the dark for 10 minutes. It was diluted with 20 ml of water and titrated with standard sodium thiosulphate solution using freshly prepared starch as an indicator. The thiosulphate solution was restandardized frequently during the analysis due to the instability of the dilute solutions (0.01N). Every run was followed till at least 50% of the reaction was complete.

---

* B.D. Sully[126] has reported that copper is a very powerful catalyst for the reaction between potassium dichromate and potassium iodide. He showed that 1 ml of N/1000 copper sulphate liberated 90% of iodide in 4 minutes and 10 ml of the same solution afforded 90% of the iodine in 45 seconds without a catalyst this degree of reaction requires 30 minutes.

The error introduced by air oxidation of iodide ion under these experimental conditions was negligible. The concentration of dichromate solution did not change appreciably in 5M sulphuric acid at the reaction temperature. Hence, no corrections due to these factors were applied. Several identical sets were run simultaneously in different vessels to check the reproducibility of the results. It was observed that readings were accurate to 0.5%.

Waters has reported the uptake of atmospheric oxygen during chromic acid oxidations of organic compounds. In order to study the effect of atmospheric oxygen, three identical reaction mixtures were taken and oxygen, carbon dioxide and nitrogen gases were bubbled through them. Rate constants were found to approximate to the same value in all these cases. The oxidation, therefore, was studied in open vessels.

The concentrations of unreacted Cr(VI) in moles per litre were calculated from the volume of thiosulphate used for each titration and have been reported in the tables. Determination of the specific rate constant (k) was accomplished by plotting log $[Cr^{VI}]$ vs. time which in each case yielded very good straight lines, whose slopes measured the first order rate constants.

## Identification of oxidation products.

Acetic acid and carbon dioxide were the main products of oxidation of the fatty acids studied. They were confirmed in the following manner.

The organic acids, sulphuric acid and an excess of potassium dichromate were taken in the reaction vessel.

After the completion of oxidation (24 hrs.), the reaction mixture was transferred to a 200 ml distillation flask with a side arm for the introduction of steam. The flask was heated on a mantle. The temperature of the distillation flask and the rate of steam input were regulated so that a reasonable rate of distillation was obtained with a constant liquid level in the distillation flask. The efficiency of the method was demonstrated by distillation of a sample of acetic acid from an aqueous sulphuric acid - chromic acid mixture without entrainment of sulphuric acid. All distillates were tested with barium chloride to establish the absence of sulphuric acid.

The identification of acetic acid was accomplished by the lanthanum iodine test[127].

A drop of the test solution was mixed on a spot plate with a drop of 5% solution of lanthanum nitrate and a drop of 0.01N iodine solution. A drop of ammonia (1N) was added and in few minutes (in the presence of acetate) a blue ring developed around the drop of ammonia.

Benzoic acid was obtained in the oxidation of phenylacetic acid. It was detected by its usual test[127].

The lime water test gave positive indication of carbon dioxide formation.

# STUDIES WITH PROPIONIC ACID

## Order in Chromic acid

The rate of oxidation of propionic acid by chromic acid was determined by following the progress of the reaction iodometrically. It was found that first order equation with respect to chromic acid fits well in the date. A slight increase in the rate constant was observed when chromic acid concentration was decreased. Observations showing the influence of chromic acid concentration on the rate constant are recorded in the following tables.

FIG. 1

DEPENDENCE OF RATE CONSTANT ON CHROMIC ACID CONCENTRATION

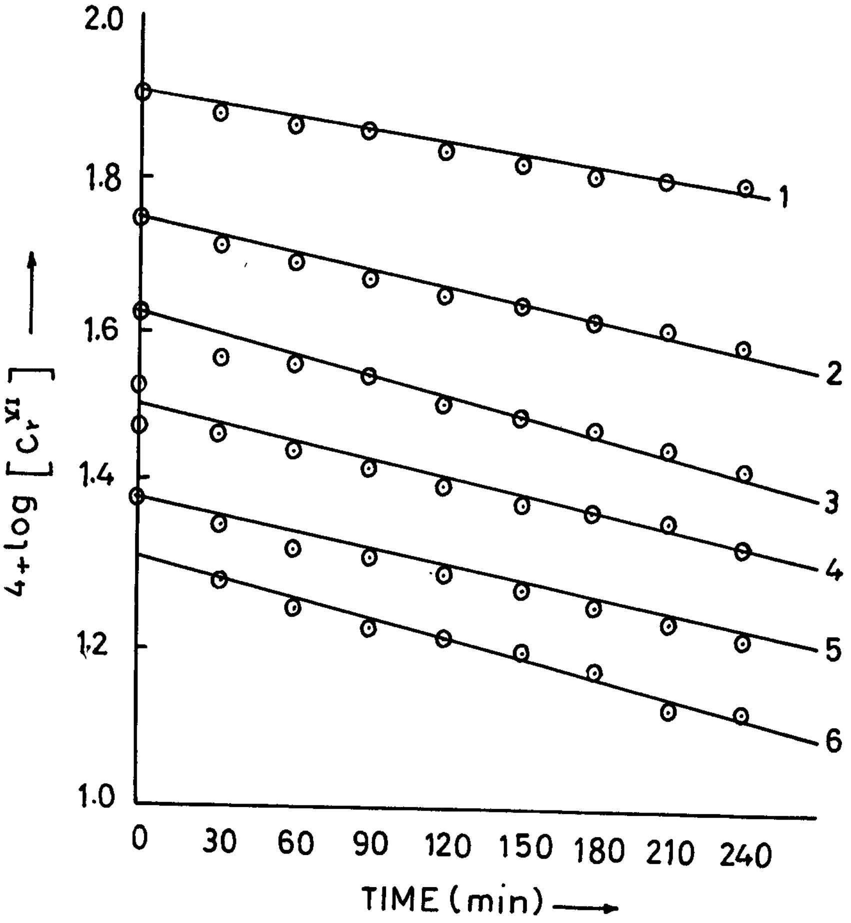


Table - I.

Dependence of rate constant on chromic acid concentration.

Temp. $75 \pm .1^{\circ}C$; $[H_2SO_4] = 5.0M$; [Propionic acid] = 2.0M.

| [Chromic acid] | $166.55 \times 10^{-4}M$ | | $83.32 \times 10^{-4}M$ | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}](M)$ | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}](M)$ | $4+\log[Cr^{VI}]$ |
| 0 | 166.65 | 2.221 | 83.32 | 1.920 |
| 30 | 163.92 | 2.214 | 79.43 | 1.899 |
| 60 | 157.30 | 2.196 | 75.35 | 1.877 |
| 90 | 150.25 | 2.176 | 74.12 | 1.869 |
| 120 | 143.20 | 2.155 | 69.50 | 1.841 |
| 150 | 138.68 | 2.141 | 68.23 | 1.833 |
| 180 | 132.62 | 2.122 | 65.94 | 1.819 |
| 210 | 127.53 | 2.105 | 65.05 | 1.812 |
| 240 | 122.43 | 2.087 | 62.76 | 1.797 |
| Rate constant ($min.^{-1}$) | $1.38 \times 10^{-3}$ | | $1.30 \times 10^{-3}$ | |
| Fig. 1. | Curve 1. | | Curve 2. | |

Table - II.

Dependence of rate constant on chromic acid concentration.

Temp. 75±.1°C; $[H_2SO_4]$ = 5.0M; [Propionic acid] = 2.0M.

| [Chromic acid] | $55.55 \times 10^{-4}$ M | | $41.66 \times 10^{-4}$ M | |
|---|---|---|---|---|
| Time (mins.) | $10^4[Cr^{VI}]$ (M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$ (M) | $4+\log[Cr^{VI}]$ |
| 0 | 55.55 | 1.744 | 41.66 | 1.619 |
| 30 | 52.01 | 1.716 | 36.07 | 1.557 |
| 60 | 49.32 | 1.693 | 34.81 | 1.541 |
| 90 | 46.87 | 1.670 | 33.54 | 1.525 |
| 120 | 45.25 | 1.655 | 30.70 | 1.487 |
| 150 | 43.00 | 1.633 | 30.20 | 1.480 |
| 180 | 40.75 | 1.610 | 28.57 | 1.455 |
| 210 | 39.74 | 1.599 | 26.80 | 1.428 |
| 240 | 38.40 | 1.584 | 23.00 | 1.361 |
| Rate constant (min.$^{-1}$) | $1.50 \times 10^{-3}$ | | $1.52 \times 10^{-3}$ | |
| Fig. 1. | Curve 3. | | Curve 4. | |

Table - III.

Dependence of rate constant on chromic acid concentration.

Temp. 75 ± .1 °C; $[H_2SO_4]$ = 5.0M; [Propionic acid] = 2.0M.

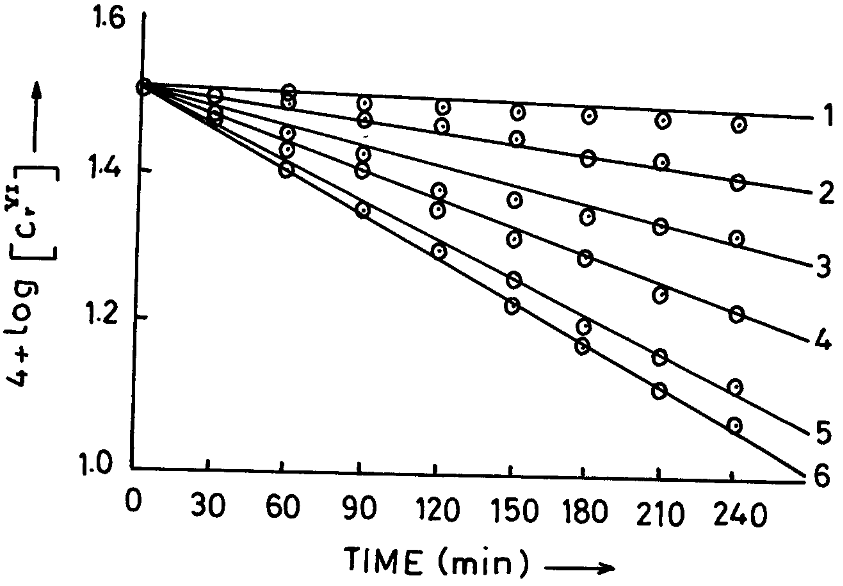
| [Chromic acid] | $33.33 \times 10^{-4}$M | | $27.77 \times 10^{-4}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4 + \log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4 + \log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 27.77 | 1.443 |
| 30 | 27.90 | 1.445 | 21.75 | 1.337 |
| 60 | 27.22 | 1.435 | 19.95 | 1.301 |
| 90 | 25.87 | 1.412 | 19.43 | 1.288 |
| 120 | 25.08 | 1.399 | 18.86 | 1.275 |
| 150 | 23.38 | 1.369 | 17.96 | 1.254 |
| 180 | 22.76 | 1.357 | 17.17 | 1.234 |
| 210 | 22.20 | 1.346 | 16.32 | 1.212 |
| 240 | 20.40 | 1.309 | 15.48 | 1.189 |
| Rate constant ($min.^{-1}$) | $1.47 \times 10^{-3}$ | | $1.56 \times 10^{-3}$ | |
| Fig. 1. | Curve 5. | | Curve 6. | |

## Order in Propionic acid

The order of reaction with respect to propionic acid was determined by varying the propionic acid concentration, keeping chromic acid and sulphuric acid concentrations constant. The rate constants thus obtained at different propionic acid concentrations were plotted against propionic acid concentration. A straight line passing through the origin was obtained which indicated that the order of the reaction with respect to substrate is unity. The plot of rate constant Vs concentration is shown in fig. 3.

FIG. 2

DEPENDENCE OF RATE CONSTANT ON PROPIONIC ACID CONCENTRATION



### Table - IV.

Dependence of rate constant on the concentration of propionic acid.

Temp. $75 \pm .1^{\circ}C$; $[H_2SO_4] = 5.0M$; $[Cr^{VI}] = 33.33 \times 10^{-4} M$.

| [Propionic acid] | 0.2M |  | 0.5M |  |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 30 | 32.36 | 1.516 | 31.98 | 1.505 |
| 60 | 32.06 | 1.510 | 31.18 | 1.494 |
| 90 | 31.98 | 1.505 | 29.78 | 1.474 |
| 120 | 31.40 | 1.497 | 28.84 | 1.460 |
| 150 | 31.04 | 1.492 | 28.24 | 1.456 |
| 180 | 30.62 | 1.486 | 26.92 | 1.430 |
| 210 | 30.20 | 1.480 | 26.18 | 1.418 |
| 240 | 29.78 | 1.474 | 25.11 | 1.400 |
| Rate constant (min.$^{-1}$) | $0.47 \times 10^{-3}$ |  | $1.15 \times 10^{-3}$ |  |
| Fig. 2. | Curve 1. |  | Curve 2. |  |

## Table - V.

Dependence of rate constant on the concentration of propionic acid.

Temp. 75 ± .1°C; $[H_2SO_4] = 5.0M$; $[Cr^{VI}] = 33.33 \times 10^{-4}M$.

| [Propionic acid] | 1.0M | | 1.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 30 | 30.06 | 1.478 | 29.86 | 1.475 |
| 60 | 27.80 | 1.444 | 26.70 | 1.426 |
| 90 | 26.42 | 1.422 | 24.58 | 1.390 |
| 120 | 24.15 | 1.383 | 22.58 | 1.353 |
| 150 | 23.28 | 1.367 | 21.17 | 1.325 |
| 180 | 21.62 | 1.335 | 19.60 | 1.292 |
| 210 | 20.32 | 1.308 | 17.51 | 1.243 |
| 240 | 18.83 | 1.275 | 16.65 | 1.221 |
| Rate constant ($min.^{-1}$) | $2.30 \times 10^{-3}$ | | $3.22 \times 10^{-3}$ | |
| Fig. 2. | Curve 3. | | Curve 4. | |

FIRST ORDER DEPENDENCE OF RATE CONSTANT ON PROPIONIC ACID CONCENTRATION

FIG. 3

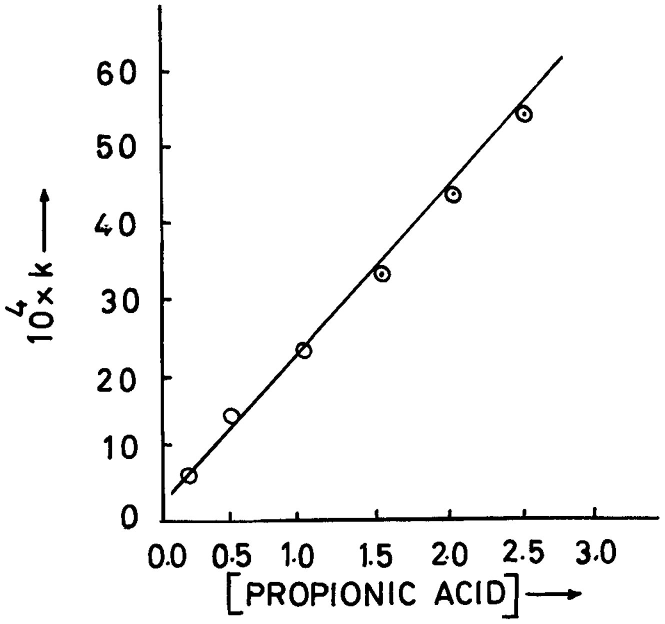


Table - VI.

Dependence of rate constant on the concentration of Propionic acid.

Temp.75±.1°C; $[H_2SO_4]$= 5.0M; $[Cr^{VI}]$= 33.33 x $10^{-4}$M

| [Propionic acid] | 2.0M | | 2.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 30 | 29.82 | 1.474 | 28.53 | 1.465 |
| 60 | 25.41 | 1.405 | 24.96 | 1.397 |
| 90 | 22.30 | 1.331 | 18.78 | 1.273 |
| 120 | 19.67 | 1.293 | 17.22 | 1.236 |
| 150 | 17.77 | 1.250 | 16.65 | 1.221 |
| 180 | 15.88 | 1.201 | 14.54 | 1.162 |
| 210 | 14.34 | 1.156 | 12.96 | 1.112 |
| 240 | 13.14 | 1.118 | 11.68 | 1.067 |
| Rate constant (min.$^{-1}$) | 4.37 x $10^{-3}$ | | 5.37 x $10^{-3}$ | |

Fig. 2. Curve 5. Curve 6.

## Hydrogen ion concentration variation

The influence of hydrogen ion on the rate constant was determined at constant chromic and propionic acid concentration. Sulphuric acid concentration was varied maintaining the ionic strength constant by using sodium hydrogen sulphate. It was observed that the quotients obtained by dividing pseudo first order rate constants by corresponding hydrogen ion concentration vary from run to run. However, when the first order rate constants were divided by square of hydrogen ion concentration, the values so obtained were reasonably constant, showing second order dependence on acidity. The data are presented in the following tables.

FIG. 4

EFFECT OF ACIDITY ON RATE CONSTANT

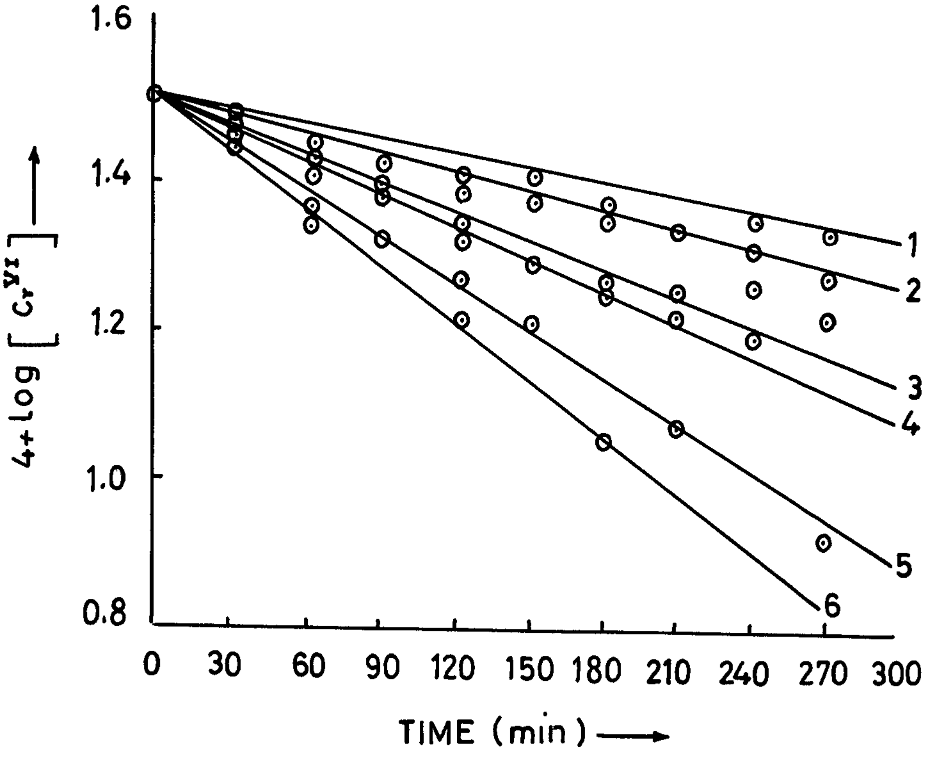


Table - VII.

Acidity dependence of the oxidation rate.

Temp.75±.1°C; $[H_2SO_4]$ + $[NaHSO_4]$ = 6.0M;
$[$Propionic acid$]$ = 2.0M; $[Cr^{VI}]$ = 33.33 x $10^{-4}$M.

| $[H_2SO_4]$ | 3.5M | | 4.0M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 30 | 29.43 | 1.468 | 29.31 | 1.481 |
| 60 | 27.24 | 1.435 | 27.60 | 1.441 |
| 90 | 26.35 | 1.420 | 26.28 | 1.419 |
| 120 | 25.66 | 1.409 | 24.96 | 1.397 |
| 150 | 25.18 | 1.401 | 23.78 | 1.376 |
| 180 | 23.40 | 1.369 | 23.05 | 1.362 |
| 210 | 21.90 | 1.340 | 21.58 | 1.334 |
| 240 | 21.42 | 1.330 | 20.11 | 1.303 |
| 270 | 20.80 | 1.318 | 18.86 | 1.275 |
| Rate constant (min.$^{-1}$) | 1.66 x $10^{-3}$ | | 1.08 x $10^{-3}$ | |
| Fig. 4. | Curve 1. | | Curve 2. | |

Table - VIII.

Acidity dependence of the oxidation rate.

Temp.75±.1°C; $[H_2SO_4] + [NaHSO_4] = 6.0M$;
$[\text{Propionic acid}] = 2.0M$; $[Cr^{VI}] = 33.33 \times 10^{-4}M$.

| $[H_2SO_4]$ | 4.5M | | 6.0M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 30 | 29.14 | 1.464 | 28.25 | 1.451 |
| 60 | 26.70 | 1.426 | 25.18 | 1.401 |
| 90 | 24.82 | 1.394 | 22.90 | 1.360 |
| 120 | 23.56 | 1.372 | 20.44 | 1.310 |
| 150 | 22.24 | 1.347 | 18.70 | 1.271 |
| 180 | 20.85 | 1.319 | 17.23 | 1.236 |
| 210 | 19.10 | 1.281 | 16.22 | 1.210 |
| 240 | 17.84 | 1.251 | 15.63 | 1.194 |
| 270 | 16.60 | 1.220 | 15.23 | 1.182 |
| 300 | - | - | - | - |
| Rate constant (min.$^{-1}$) | $2.56 \times 10^{-3}$ | | $3.65 \times 10^{-3}$ | |
| Fig. 4. | Curve 3. | | Curve 4. | |

Table - IX.

Acidity dependence of the oxidation rate.

Temp. 75 ± .1°C; $[H_2SO_4] + [NaHSO_4] = 6.0M$;
$[\text{Propionic acid}] = 2.0M$; $[Cr^{VI}] = 33.33 \times 10^{-4}M$.

| $[H_2SO_4]$ | 5.5M | |
|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 |
| 30 | 27.18 | 1.434 |
| 60 | 22.90 | 1.360 |
| 90 | 20.50 | 1.310 |
| 120 | 18.14 | 1.258 |
| 150 | 16.42 | 1.215 |
| 180 | 14.70 | 1.167 |
| 210 | 11.45 | 1.060 |
| 240 | 9.17 | 0.962 |
| 270 | 8.28 | 0.918 |
| 300 | - | - |
| Rate constant (min.$^{-1}$) | $4.61 \times 10^{-3}$ | |

Fig. 4. Curve 5.

Table - X.

Acidity dependence of the oxidation rate.

Temp. $75 \pm .1^{\circ}C$; $[H_2SO_4] + [NaHSO_4] = 6.0M$;
[Propionic acid] = 2.0M; $[Cr^{VI}] = 33.33 \times 10^{-4}M$.

| $[H_2SO_4]$ | 6.0M | |
|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 |
| 20 | 28.00 | 1.447 |
| 40 | 24.20 | 1.383 |
| 60 | 20.93 | 1.320 |
| 80 | 18.67 | 1.267 |
| 100 | 17.00 | 1.230 |
| 120 | 16.13 | 1.207 |
| 140 | 14.26 | 1.154 |
| 160 | 12.06 | 1.081 |
| 180 | 11.20 | 1.049 |
| Rate constant ($min.^{-1}$) | $5.37 \times 10^{-3}$ | |

Fig. 4. Curve 6.

## Table - XI.

Effect of acidity on the rate constant.

| $[H^+]$ (M) | $[H^+]^2$ | $k \times 10^3$ (min.$^{-1}$) | $\frac{k}{[H^+]} \times 10^4$ (l.mole$^{-1}$min.$^{-1}$) | $\frac{k}{[H^+]^2} \times 10^4$ (l$^2$.mole$^{-2}$min.$^{-1}$) |
|---|---|---|---|---|
| 3.5 | 12.25 | 1.66 | 4.74 | 1.36 |
| 4.0 | 16.00 | 1.98 | 4.95 | 1.24 |
| 4.5 | 20.25 | 2.56 | 5.60 | 1.26 |
| 5.0 | 25.00 | 3.65 | 7.30 | 1.45 |
| 5.5 | 30.25 | 4.61 | 8.38 | 1.52 |
| 6.0 | 36.0 | 5.37 | 8.59 | 1.49 |

## Temperature dependence

The variation of reaction rate with temperature was utilised to obtain the energy of activation and other thermodynamic parameters. The reaction under consideration was, therefore, studied at five different temperatures at constant concentrations of the reactants. The plot of log K Vs $\frac{1}{T}$ gave a straight line from the slope of which the energy of activation was calculated and found to be 17.0 Kcal. The heat of activation ( $\Delta H^{\ddagger}$) and entropy of activation ( $\Delta S^{\ddagger}$) were calculated by making use of the following equations.

$$k = \frac{KT}{h} e^{-\Delta F^{\ddagger}/RT} \quad \text{(Eyring Equation)}$$

$$\Delta H^{\ddagger} = E - RT$$

$$\Delta S^{\ddagger} = \frac{\Delta H^{\ddagger} - \Delta F^{\ddagger}}{T}$$

Where the symbols have their usual meaning. The values are

$\Delta H^{\ddagger} = 16.3$ Kcal

$\Delta S^{\ddagger} = -30.8$ eu.

FIG. 5

TEMPERATURE DEPENDENCE OF THE RATE CONSTANT

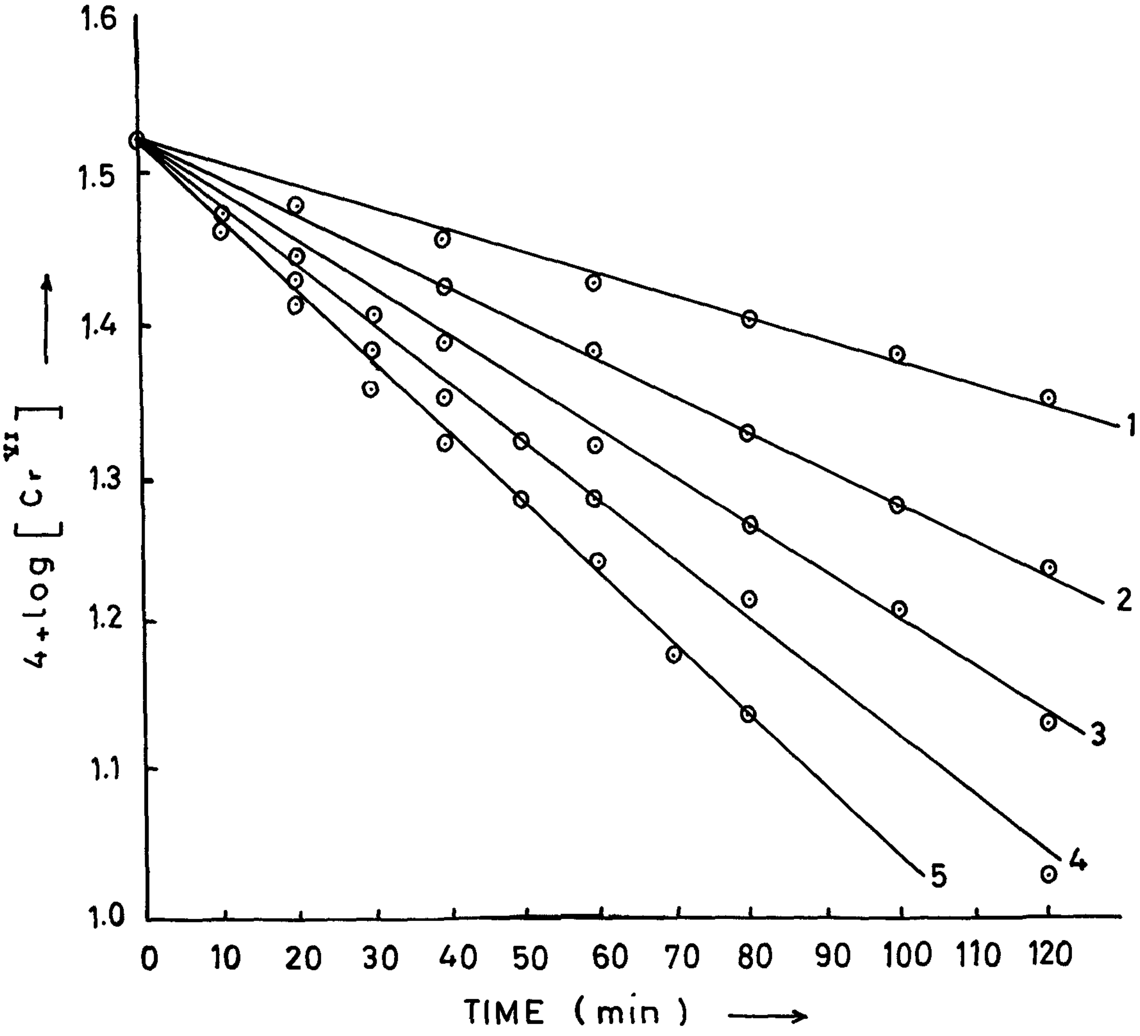


Table - XII

Temperature dependence of the reaction rate.

$[H_2SO_4]$= 5.0M; [Propionic acid]= 2.2M; $[Cr^{VI}]$= 33.33 x $10^{-4}$M.

| Temperature | 343°K | | 348°K | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 20 | 30.20 | 1.480 | 30.06 | 1.478 |
| 40 | 28.37 | 1.453 | 26.80 | 1.428 |
| 60 | 26.66 | 1.426 | 23.70 | 1.375 |
| 80 | 24.94 | 1.397 | 21.62 | 1.335 |
| 100 | 23.72 | 1.375 | 19.05 | 1.280 |
| 120 | 22.50 | 1.352 | 17.70 | 1.248 |
| 150 | 20.04 | 1.302 | 16.60 | 1.220 |
| 180 | 18.75 | 1.273 | 16.03 | 1.188 |
| 210 | 17.30 | 1.238 | 15.20 | 1.148 |
| Rate constant (min.$^{-1}$) | 3.10 x $10^{-3}$ | | 4.62 x $10^{-3}$ | |
| Fig. 5. | Curve 1. | | Curve 2. | |

Table - XIII.

Temperature dependence of the reaction rate.

$[H_2SO_4]$= 5.0M; [Propionic acid]= 2.2M; $[Cr^{VI}]$= 33.33 x $10^{-4}$M.

| Temperature | 353°K | | 358°K | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 10 | 29.78 | 1.474 | 29.37 | 1.468 |
| 20 | 27.92 | 1.446 | 26.92 | 1.430 |
| 30 | 25.82 | 1.412 | 24.10 | 1.382 |
| 40 | 23.87 | 1.378 | 22.18 | 1.346 |
| 50 | 21.92 | 1.341 | 20.80 | 1.318 |
| 60 | 20.55 | 1.313 | 19.10 | 1.281 |
| 80 | 18.32 | 1.263 | 16.82 | 1.226 |
| 100 | 16.52 | 1.218 | 14.38 | 1.158 |
| 120 | 14.96 | 1.175 | 12.82 | 1.108 |
| Rate constant (min.$^{-1}$) | 6.70 x $10^{-3}$ | | 9.23 x $10^{-3}$ | |
| Fig. 5. | Curve 3. | | Curve 4. | |

FIG. 6

ACTIVATION ENERGY

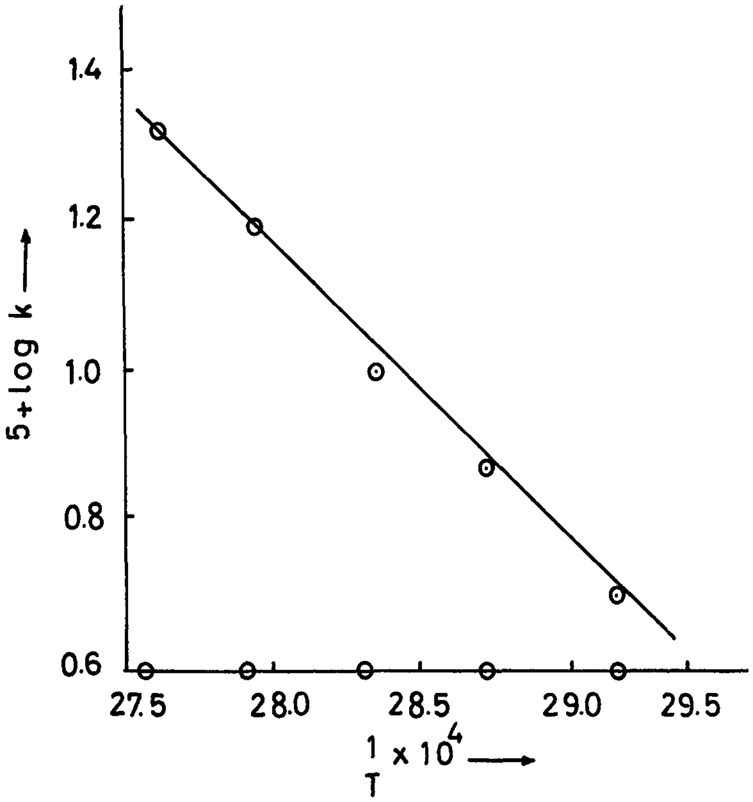


Table - XIV.

Temperature dependence of the reaction rate.

$[H_2SO_4]$= 5.0M; [Propionic acid]= 2.2M; $[Cr^{VI}]$= 33.33 x $10^{-4}$M.

| Temperature | 363°K | |
|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 |
| 10 | 28.84 | 1.460 |
| 20 | 25.40 | 1.405 |
| 30 | 22.70 | 1.356 |
| 40 | 20.74 | 1.317 |
| 50 | 19.10 | 1.281 |
| 60 | 17.37 | 1.240 |
| 70 | 14.90 | 1.173 |
| 80 | 13.18 | 1.120 |
| 90 | 12.13 | 1.084 |
| 100 | 10.86 | 1.036 |
| Rate constant (min.$^{-1}$) | 11.98 x $10^{-3}$ | |

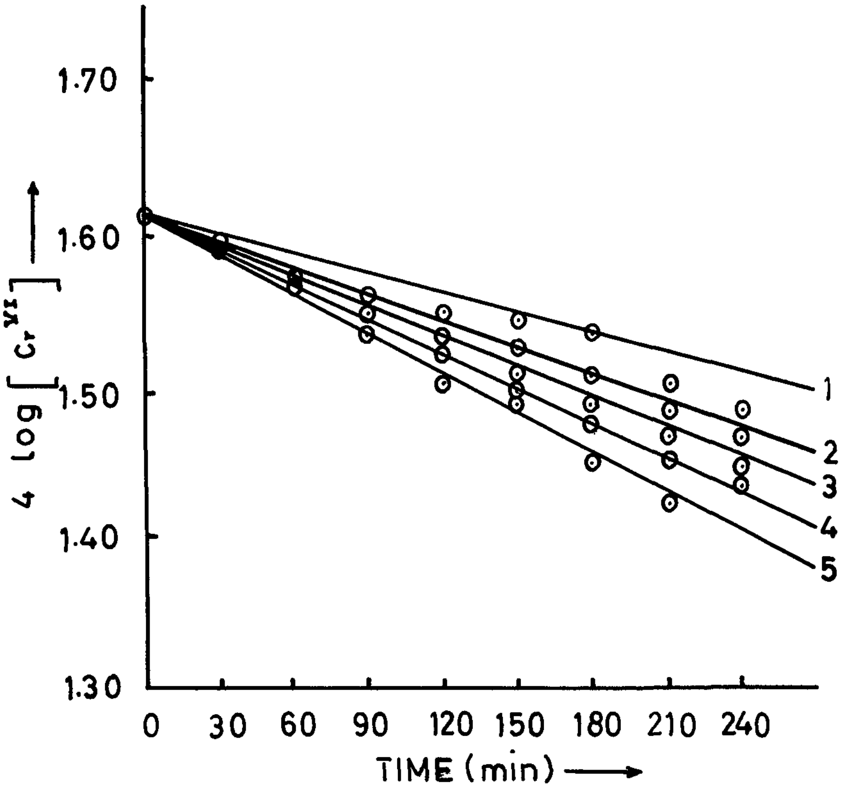
Fig. 5. Curve 5.

## Influence of ionic strength

The effect of ionic strength on the rate constant was examined by adding varying amounts of sodium perchlorate. The other factors such as the concentrations of the reactants and temperature were kept identical. A plot of $\mu^{1/2}$ Vs. log $K$ does not give any significant information because the ionic strengths are not in the range in which Debye-Huckel theory is applicable. The results showing the influence of ionic strength on the rate constant are tabled below.

FIG. 7

DEPENDENCE OF RATE CONSTANT ON IONIC STRENGTH



## Table - XV.

Effect of ionic strength on the rate constant.

Temp. 80$\pm$.1$^{\circ}$C; $[H_2SO_4]$= 4.5M; [Propionic acid]= 2.0M;
$[Cr^{VI}]$= 33.33 x $10^{-4}$M.

| $[NaClO_4]$ | Nil | | 0.5M | |
|---|---|---|---|---|
| ionic strength | 4.5M | | 5.0M | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 41.66 | 1.619 | 41.66 | 1.619 |
| 30 | 38.55 | 1.586 | 38.30 | 1.583 |
| 60 | 37.08 | 1.569 | 37.35 | 1.572 |
| 90 | 35.86 | 1.554 | 37.10 | 1.569 |
| 120 | 34.80 | 1.541 | 35.88 | 1.554 |
| 150 | 33.66 | 1.527 | 34.85 | 1.542 |
| 180 | 32.86 | 1.516 | 34.46 | 1.524 |
| 210 | 32.03 | 1.505 | 32.68 | 1.514 |
| 240 | 31.62 | 1.500 | 31.31 | 1.495 |
| Rate constant (min.$^{-1}$) | 0.96 x $10^{-3}$ | | 1.00 x $10^{-3}$ | |
| Fig. 7. | Curve 1. | | Curve 2. | |

## Table - XVI.

Effect of ionic strength on the rate constant.

Temp. 80$\pm$.1°C; $[H_2SO_4]$= .5M; [Propionic acid]= 2.0M;
$[Cr^{VI}]$= 41.66 x $10^{-4}$M.

| $[NaClO_4]$ | 1.0M | | 1.5M | |
|---|---|---|---|---|
| Ionic strength | 5.5M | | 6.0M | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 41.66 | 1.619 | 41.66 | 1.619 |
| 30 | 29.24 | 1.593 | 39.93 | 1.601 |
| 60 | 38.38 | 1.584 | 37.37 | 1.572 |
| 90 | 37.18 | 1.570 | 36.06 | 1.557 |
| 120 | 36.67 | 1.563 | 34.25 | 1.534 |
| 150 | 35.79 | 1.553 | 33.83 | 1.529 |
| 180 | 34.76 | 1.541 | 32.35 | 1.510 |
| 210 | 32.51 | 1.512 | 31.04 | 1.491 |
| 240 | 30.81 | 1.439 | 29.30 | 1.467 |
| Rate constant (min.$^{-1}$) | 1.10 x $10^{-3}$ | | 1.42 x $10^{-3}$ | |
| Fig. 7. | Curve 3. | | Curve 4. | |

### Table - XVII

Effect of ionic strength on the rate constant.

Temp. 30±.1°C; $[H_2SO_4]$ = [illegible].5M; [Propionic acid] = 2.0M;
$[Cr^{VI}]$ = 41.66 x $10^{-4}$M.

| | | |
|---|---|---|
| $[NaClO_4]$ | 2.0M | |
| Ionic strength | 6.5M | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 41.66 | 1.619 |
| 30 | 39.08 | 1.592 |
| 60 | 37.41 | 1.573 |
| 90 | 35.07 | 1.545 |
| 120 | 31.98 | 1.505 |
| 150 | 31.11 | 1.493 |
| 180 | 28.24 | 1.451 |
| 210 | 26.73 | 1.427 |
| 240 | 25.46 | 1.406 |
| Rate constant (min.$^{-1}$) | 1.53 x $10^{-3}$ | |

Fig. 7. Curve 5.

## Effect of Acetic acid

Rate constants with reference to chromic acid were determined for the reaction in absence and in the presence of various amounts of acetic acid. It was found that the rate constants increased with the increasing amounts of acetic acid. The data are presented below.

FIG. 8

EFFECT OF ACETIC ACID ON RATE CONSTANT

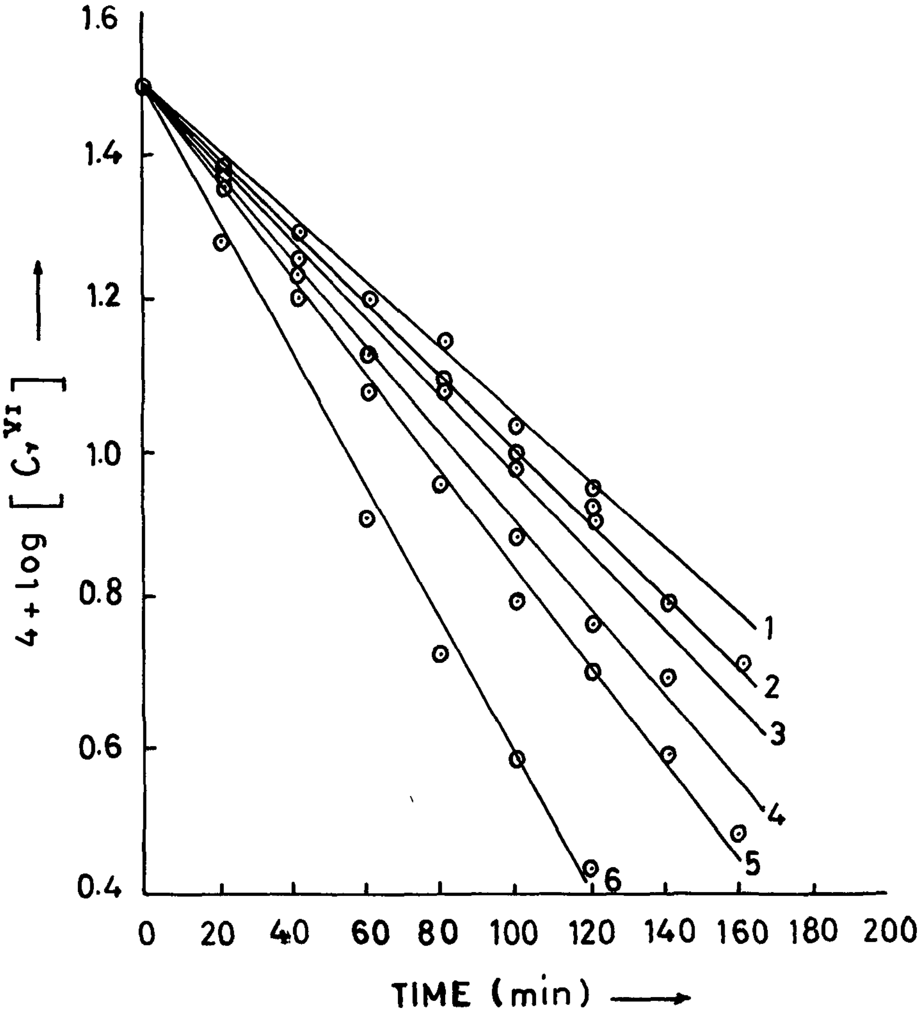


Table - XVIII.

Influence of acetic acid on the rate of oxidation.

Temp.$80\pm.1^{\circ}C$; $[H_2SO_4]$= 5.0M; [Propionic acid]= 2.0M;
$[Cr^{VI}]$= 26.66 x $10^{-4}$M.

| [Acetic acid] | NIL | | 0.2M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 20 | 23.92 | 1.378 | 24.14 | 1.382 |
| 40 | 20.17 | 1.304 | 18.48 | 1.266 |
| 60 | 16.31 | 1.212 | 16.24 | 1.210 |
| 80 | 14.18 | 1.151 | 13.00 | 1.114 |
| 100 | 11.15 | 1.047 | 10.04 | 1.011 |
| 120 | 9.21 | 0.964 | 8.63 | 0.936 |
| 140 | 8.18 | 0.912 | 6.75 | 0.829 |
| 160 | 7.60 | 0.881 | 5.30 | 0.724 |
| 180 | - | - | 3.80 | 0.579 |
| Rate constant ($min.^{-1}$) | 7.98 x $10^{-3}$ | | 11.50 x $10^{-3}$ | |
| Fig. 8. | Curve 1. | | Curve 2. | |

### Table - XIX.

Influence of acetic acid on the rate of oxidation.

Temp.80±.1°C; [$H_2SO_4$] = 5.0M; [Propionic acid] = 2.0M;
[$Cr^{VI}$] = 26.66 x $10^{-4}$M.

| [Acetic acid] | 0.5M | | 1.0M | |
|---|---|---|---|---|
| Time(mins.) | $10^4$[$Cr^{VI}$](M) | 4+log[$Cr^{VI}$] | $10^4$[$Cr^{VI}$](M) | 4+log[$Cr^{VI}$] |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 20 | 23.70 | 1.374 | 23.63 | 1.373 |
| 40 | 19.20 | 1.283 | 17.57 | 1.244 |
| 60 | 14.74 | 1.163 | 13.25 | 1.122 |
| 80 | 12.36 | 1.092 | 10.13 | 1.005 |
| 100 | 9.56 | 0.980 | 7.69 | 0.886 |
| 120 | 8.34 | 0.921 | 5.80 | 0.763 |
| 140 | 7.18 | 0.856 | 5.00 | 0.699 |
| 160 | 5.36 | 0.729 | 3.62 | 0.559 |
| 180 | 3.16 | 0.500 | - | - |
| Rate constant (min.$^{-1}$) | 11.50 x $10^{-3}$ | | 14.04 x $10^{-3}$ | |
| Fig. 8. | Curve 3. | | Curve 4. | |

Table - XX.

Influence of acetic acid on the rate of oxidation.

Temp. $80 \pm .1^{\circ}C$; $[H_2SO_4] = 5.0M$; $[\text{Propionic acid}] = 2.0M$;
$[Cr^{VI}] = 26.66 \times 10^{-4} M$.

| $[\text{Acetic acid}]$ | 1.5M | | 2.0M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 20 | 22.62 | 1.354 | 19.00 | 1.278 |
| 40 | 19.90 | 1.199 | 15.21 | 1.182 |
| 60 | 12.52 | 0.976 | 9.95 | 0.998 |
| 80 | 8.70 | 0.939 | 5.23 | 0.718 |
| 100 | 6.17 | 0.790 | 3.85 | 0.585 |
| 120 | 5.04 | 0.702 | 2.71 | 0.433 |
| 140 | 3.90 | 0.590 | 2.40 | 0.380 |
| 160 | 3.30 | 0.518 | 1.37 | 0.198 |
| 180 | - | - | - | - |
| Rate constant ($min.^{-1}$) | $14.73 \times 10^{-3}$ | | $17.04 \times 10^{-3}$ | |
| Fig. 8. | Curve 5. | | Curve 6. | |

# STUDIES WITH BUTYRIC ACID

## Order in Chromic acid

The rate of disappearance of Cr(VI) was a first order reaction in the presence of butyric acid. However, as the concentration of Cr(VI) was decreased, the magnitude of first order rate constants increased, but not to an extent such that a higher order term in $[Cr^{VI}]$ may be defined. The data representing the variation in rate constants with varying concentrations of $(Cr^{VI})$ are shown in the following tables.

FIG. 9

DEPENDENCE OF RATE CONSTANT ON CHROMIC ACID CONCENTRATION

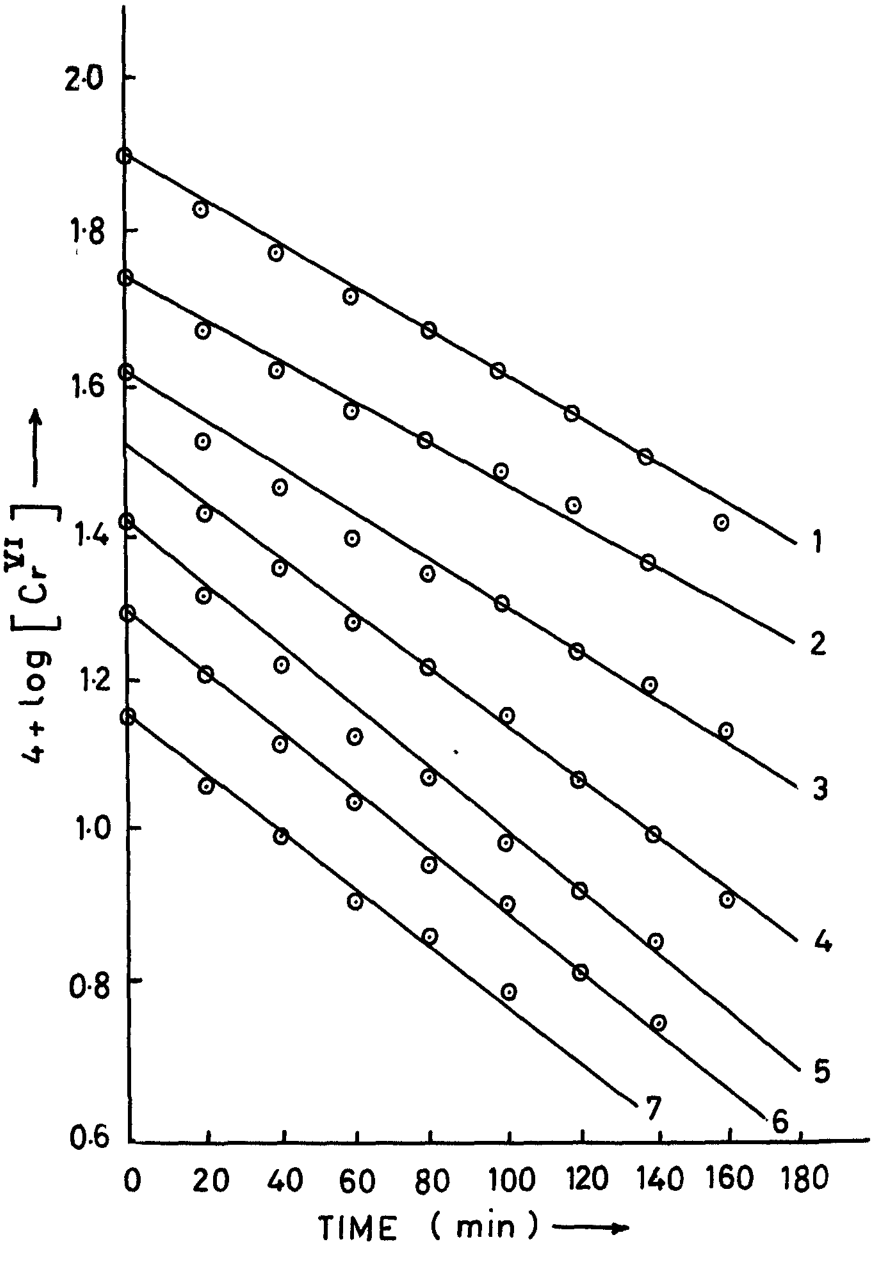


Table - XXI.

Dependence of rate constant on chromic acid concentration.

Temp. 80±.1°C; $[H_2SO_4]$ = 5.0M; [Butyric acid] = 0.5M.

| [Chromic acid] | 83.33 x $10^{-4}$M | | 55.55 x $10^{-4}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 83.33 | 1.920 | 55.55 | 1.744 |
| 20 | 71.04 | 1.850 | 47.86 | 1.680 |
| 40 | 61.77 | 1.790 | 41.69 | 1.620 |
| 60 | 53.02 | 1.724 | 36.02 | 1.556 |
| 80 | 47.18 | 1.673 | 34.26 | 1.534 |
| 100 | 42.36 | 1.627 | 30.98 | 1.491 |
| 120 | 36.40 | 1.561 | 27.33 | 1.436 |
| 140 | 31.71 | 1.501 | 22.17 | 1.346 |
| 160 | 26.26 | 1.419 | 17.38 | 1.240 |
| 180 | 22.08 | 1.343 | - | - |
| Rate constant (min.$^{-1}$) | 6.90 x $10^{-3}$ | | 6.90 x $10^{-3}$ | |
| Fig. 9. | Curve 1. | | Curve 2. | |

### Table - XXII.

Dependence of rate constant on chromic acid concentration.

Temp. $80 \pm .1^\circ C$; $[H_2SO_4]$= 5.0M; [Butyric acid]= 0.5M.

| [Chromic acid] | $41.66 \times 10^{-4}$M | | $33.33 \times 10^{-4}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 41.66 | 1.619 | 33.33 | 1.522 |
| 20 | 34.11 | 1.533 | 27.23 | 1.436 |
| 40 | 28.92 | 1.461 | 22.75 | 1.357 |
| 60 | 25.39 | 1.404 | 19.32 | 1.286 |
| 80 | 22.38 | 1.349 | 16.98 | 1.230 |
| 100 | 20.45 | 1.310 | 14.26 | 1.154 |
| 120 | 17.86 | 1.252 | 12.01 | 1.079 |
| 140 | 15.27 | 1.184 | 10.00 | 1.000 |
| 160 | 13.42 | 1.128 | 8.373 | 0.922 |
| 180 | - | - | - | - |
| Rate constant (min.$^{-1}$) | $7.60 \times 10^{-3}$ | | $7.83 \times 10^{-3}$ | |
| Fig. 9. | Curve 3. | | Curve 4. | |

Table - XXIII.

Dependence of rate constant on chromic acid concentration.

Temp.80±.1°C; $[H_2SO_4]$= 5.0M; [Butyric acid] = 0.5M.

| [Chromic acid] | $27.77 \times 10^{-4}$M | | $23.80 \times 10^{-4}$M | |
|---|---|---|---|---|
| Time(mins) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 27.77 | 1.443 | 23.80 | 1.376 |
| 20 | 20.79 | 1.317 | 16.80 | 1.225 |
| 40 | 16.50 | 1.217 | 13.60 | 1.133 |
| 60 | 13.18 | 1.120 | 10.97 | 1.040 |
| 80 | 11.89 | 1.075 | 9.04 | 0.956 |
| 100 | 9.51 | 0.978 | 8.20 | 0.913 |
| 120 | 8.27 | 0.917 | 6.70 | 0.826 |
| 140 | 7.49 | 0.875 | 5.61 | 0.749 |
| 160 | 6.67 | 0.824 | 4.38 | 0.642 |
| 180 | - | - | - | - |
| Rate constant ($min.^{-1}$) | $8.23 \times 10^{-3}$ | | $8.75 \times 10^{-3}$ | |
| Fig. 9. | Curve 5. | | Curve 6. | |

Table - XXIV.

Dependence of rate constant on chromic acid concentration.

Temp. 80 ± .1°C; $[H_2SO_4]$ = 5.0M; [Butyric acid] = 0.5M.

| [Chromic acid] | 20.83 x $10^{-4}$M | | 18.51 x $10^{-4}$M | |
|---|---|---|---|---|
| Time (mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 20.83 | 1.318 | 18.51 | 1.267 |
| 10 | 18.50 | 1.267 | 14.10 | 1.149 |
| 20 | 16.53 | 1.218 | 12.06 | 1.081 |
| 30 | 14.83 | 1.171 | 10.95 | 1.039 |
| 40 | 13.40 | 1.127 | 10.10 | 1.004 |
| 50 | 12.05 | 1.080 | 9.27 | 0.967 |
| 60 | 11.02 | 1.041 | 8.48 | 0.928 |
| 70 | 10.24 | 1.010 | 7.87 | 0.895 |
| 80 | 9.36 | 0.971 | 7.45 | 0.872 |
| 90 | 8.92 | 0.950 | 7.06 | 0.848 |
| 100 | 8.33 | 0.920 | 6.32 | 0.800 |
| Rate constant ($min.^{-1}$) | 8.23 x $10^{-3}$ | | 8.23 x $10^{-3}$ | |

Fig. 9. Curve 7.

## Order in Butyric acid

The order of the reaction with respect to butyric acid was determined in the same fashion as in the case of propionic acid. Chromic acid and sulphuric acid concentrations were kept constant and butyric acid concentration was varied stepwise. The plot of rate constant Vs concentration gave a straight line indicating first order dependence on butyric acid. The typical plot is shown in figure 11.

FIG.10

DEPENDENCE OF RATE CONSTANT ON BUTYRIC ACID CONCENTRATION

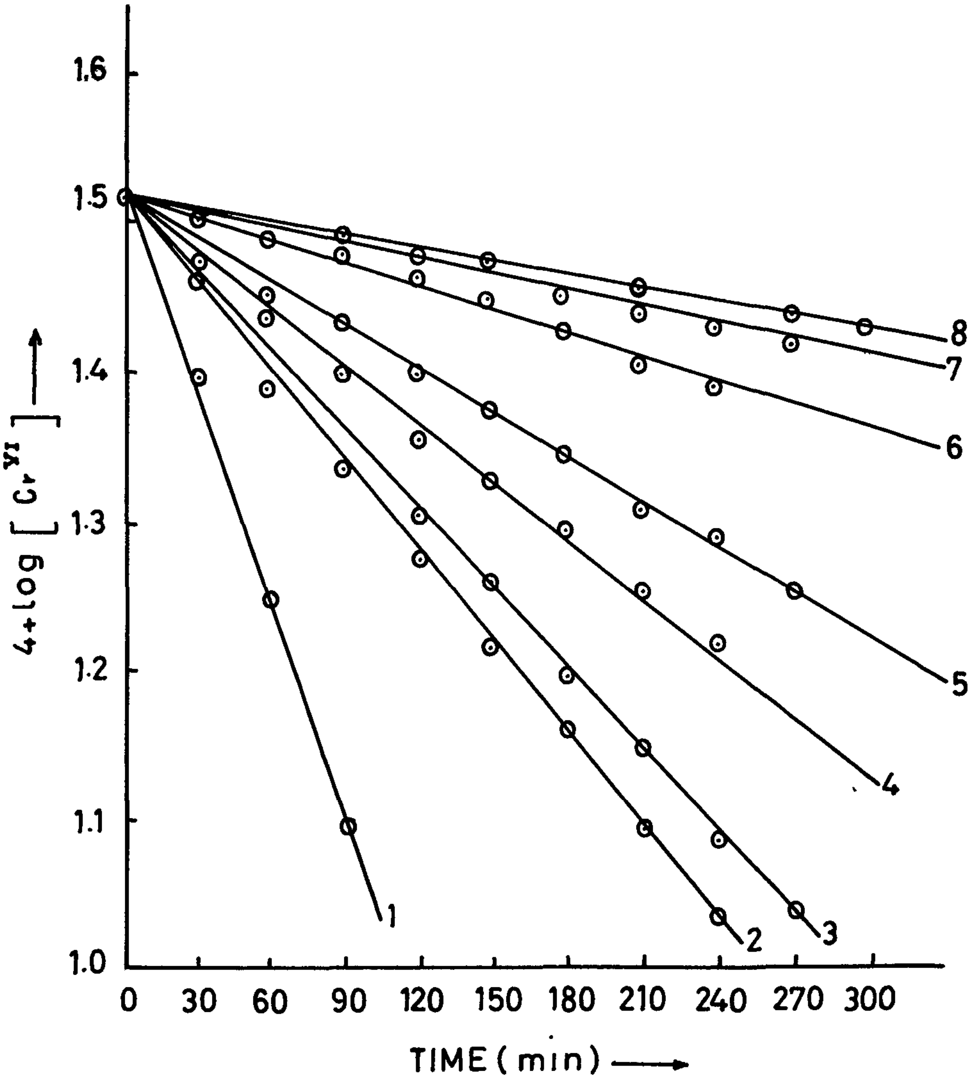


Table - XXV.

Dependence of rate constant on the concentration of butyric acid.

Temp. 80±.1°C; $[H_2SO_4]$ = 5.0M; $[Cr^{VI}]$ = 33.33 x $10^{-4}$M.

| [Butyric acid] | 50.0 x $10^{-2}$M | | 33.0 x $10^{-2}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 30 | 25.31 | 1.403 | 27.40 | 1.437 |
| 60 | 16.80 | 1.225 | 23.86 | 1.377 |
| 90 | 11.77 | 1.071 | 21.11 | 1.324 |
| 120 | 9.14 | 0.960 | 18.28 | 1.262 |
| 150 | 7.78 | 0.890 | 16.10 | 1.206 |
| 180 | 5.37 | 0.730 | 14.33 | 1.156 |
| 210 | - | - | 12.35 | 1.091 |
| 240 | - | - | 10.80 | 1.033 |
| 270 | - | - | 9.74 | 0.988 |
| 300 | - | - | - | - |
| Rate constant (min.$^{-1}$) | 8.44 x $10^{-3}$ | | 4.60 x $10^{-3}$ | |
| Fig. 10. | Curve 1. | | Curve 2. | |

Table - XXVI.

Dependence of rate constant on the concentration of butyric acid.

Temp. 80±.1°C; $[H_2SO_4]$ = 5.0M; $[Cr^{VI}] = 33.33 \times 10^{-4}$ M.

| [Butyric acid] | $25.0 \times 10^{-2}$ M | | $20.0 \times 10^{-2}$ M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 30 | 28.60 | 1.456 | 29.51 | 1.471 |
| 60 | 24.94 | 1.397 | 27.05 | 1.432 |
| 90 | 21.83 | 1.339 | 24.74 | 1.393 |
| 120 | 19.47 | 1.289 | 21.94 | 1.341 |
| 150 | 17.30 | 1.238 | 20.89 | 1.320 |
| 180 | 15.41 | 1.187 | 19.42 | 1.288 |
| 210 | 13.71 | 1.137 | 17.72 | 1.248 |
| 240 | 12.03 | 1.080 | 16.76 | 1.224 |
| 270 | 10.68 | 1.029 | - | - |
| 300 | - | - | - | - |
| Rate constant (min.$^{-1}$) | $4.03 \times 10^{-3}$ | | $2.88 \times 10^{-3}$ | |
| Fig. 10. | Curve 3. | | Curve 4. | |

### Table - XXVII.

Dependence of rate constant on the concentration of butyric acid.

Temp. $80 \pm .1^\circ C$; $[H_2SO_4] = 5.0M$; $[Cr^{VI}] = 33.33 \times 10^{-4}M$.

| [Butyric acid] | $13.3 \times 10^{-2}M$ | | $10.0 \times 10^{-2}M$ | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}](M)$ | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}](M)$ | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 30 | 30.60 | 1.485 | 32.31 | 1.509 |
| 60 | 28.00 | 1.447 | 30.90 | 1.490 |
| 90 | 26.94 | 1.430 | 30.30 | 1.481 |
| 120 | 25.05 | 1.398 | 29.34 | 1.467 |
| 150 | 23.55 | 1.372 | 28.26 | 1.451 |
| 180 | 21.85 | 1.339 | 26.71 | 1.426 |
| 210 | 20.16 | 1.304 | 25.56 | 1.407 |
| 240 | 19.24 | 1.284 | 24.42 | 1.387 |
| 270 | 17.85 | 1.251 | - | - |
| 300 | - | - | - | - |
| Rate constant (min.$^{-1}$) | $2.30 \times 10^{-3}$ | | $1.38 \times 10^{-3}$ | |
| Fig. 10. | Curve 5. | | Curve 6. | |

FIRST ORDER DEPENDENCE OF RATE CONSTANT ON BUTYRIC ACID CONCENTRATION

FIG. 11

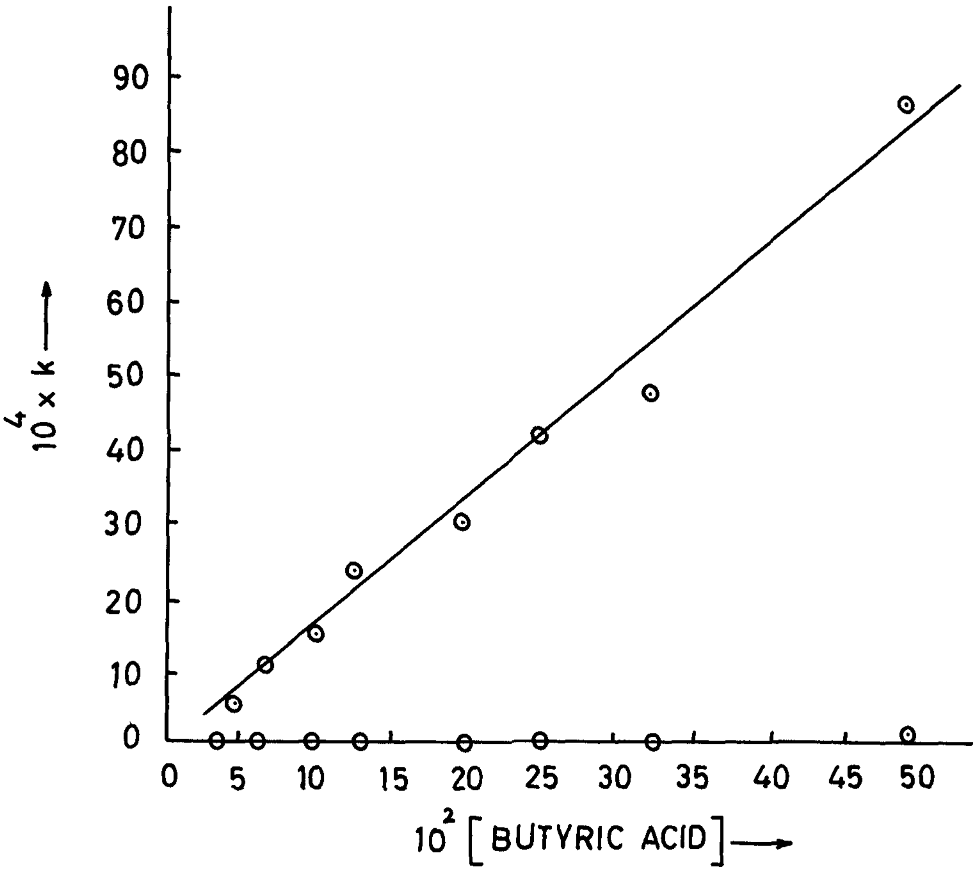


Table - XXVIII.

Dependence of rate constant on the concentration of butyric acid.

Temp. 80±.1°C; $[H_2SO_4]$ = 5.0M; $[Cr^{VI}]$ = 33.33 x $10^{-4}$M.

| [Butyric acid] | $6.6 \times 10^{-2}$M | | $4.0 \times 10^{-2}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 30 | 31.10 | 1.492 | 31.65 | 1.500 |
| 60 | 29.82 | 1.474 | 30.64 | 1.486 |
| 90 | 29.44 | 1.469 | 29.88 | 1.475 |
| 120 | 28.30 | 1.451 | 29.51 | 1.471 |
| 150 | 27.92 | 1.445 | 29.01 | 1.462 |
| 180 | 26.82 | 1.428 | 28.51 | 1.455 |
| 210 | 26.32 | 1.420 | 28.13 | 1.449 |
| 240 | 25.55 | 1.407 | 27.82 | 1.444 |
| 270 | 24.85 | 1.395 | 27.51 | 1.439 |
| 300 | - | - | - | - |
| Rate constant ($min.^{-1}$) | $0.96 \times 10^{-3}$ | | $0.46 \times 10^{-3}$ | |

Fig. 10. Curve 7. Curve 8.

## Hydrogen ion concentration variation

For studying the effect of hydrogen ion on the rate, experiments were performed with different concentrations of sulphuric acid. Ionic strength and sulphate content of the reaction mixture was maintained constant by adding requisite amounts of sodium hydrogen sulphate. The concentration of hydrogen ion was calculated on the assumption that first dissociation of sulphuric acid

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

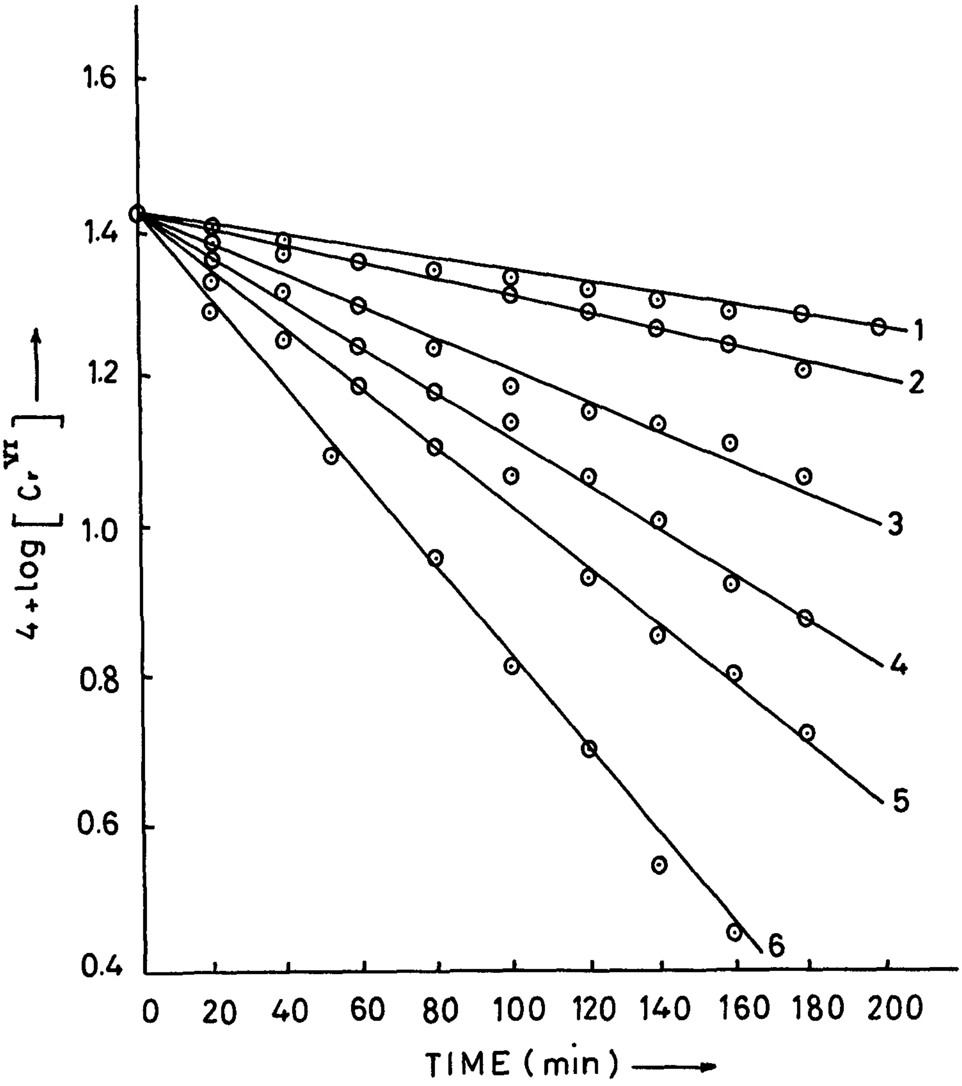
is complete and the second dissociation is negligible.

$$HSO_4^- \rightleftharpoons H^+ + SO_4^=$$

Observations at various hydrogen ion concentrations are tabled below.

FIG.12

ACIDITY DEPENDENCE OF THE RATE CONSTANT



## Table - XXIX.

Acidity dependence of the oxidation rate.

Temp.70±.1°C; $[H_2SO_4]$ + $[NaHSO_4]$ = 6.0M;
$[\text{Butyric acid}]$ = 0.5M; $[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| $[H_2SO_4]$ | 3.0M | | 3.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 20 | 25.32 | 1.403 | 24.98 | 1.397 |
| 40 | 24.18 | 1.383 | 23.76 | 1.376 |
| 60 | 22.67 | 1.355 | 22.87 | 1.359 |
| 80 | 21.70 | 1.336 | 21.81 | 1.338 |
| 100 | 21.43 | 1.331 | 20.76 | 1.317 |
| 120 | 20.90 | 1.320 | 19.13 | 1.281 |
| 140 | 20.34 | 1.308 | 18.23 | 1.260 |
| 160 | 19.88 | 1.298 | 17.60 | 1.245 |
| 180 | 18.90 | 1.276 | 16.18 | 1.209 |
| 200 | 18.22 | 1.260 | 15.28 | 1.184 |
| Rate constant (min.$^{-1}$) | 2.92 x $10^{-3}$ | | 3.70 x $10^{-3}$ | |
| Fig. 12. | Curve 1. | | Curve 2. | |

Table - XXX.

Acidity dependence of the oxidation rate.

Temp.70$\pm$.1$^{\circ}$C; $[H_2SO_4] + [NaHSO_4] = 6.0M$; $[\text{Butyric acid}] = 0.5M$;
$[Cr^{VI}] = 26.66 \times 10^{-4}M$.

| $[H_2SO_4]$ | 4.0M | | 4.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 20 | 22.51 | 1.352 | 21.42 | 1.330 |
| 40 | 20.24 | 1.306 | 19.24 | 1.284 |
| 60 | 18.30 | 1.262 | 17.01 | 1.230 |
| 80 | 17.22 | 1.236 | 14.62 | 1.165 |
| 100 | 15.11 | 1.179 | 13.64 | 1.135 |
| 120 | 14.35 | 1.157 | 11.63 | 1.065 |
| 140 | 13.50 | 1.130 | 10.00 | 1.000 |
| 160 | 13.06 | 1.116 | 8.15 | 0.911 |
| 180 | 11.82 | 1.072 | 7.28 | 0.862 |
| 200 | - | - | - | - |
| Rate constant (min.$^{-1}$) | $4.90 \times 10^{-3}$ | | $6.83 \times 10^{-3}$ | |
| Fig. 12. | Curve 3. | | Curve 4. | |

Table - XXXI.

Acidity dependence of the oxidation rate.

Temp. 70±.1°C; $[H_2SO_4] + [NaHSO_4] = 6.0M$;
$[\text{Butyric acid}] = 0.5M$; $[Cr^{VI}] = 26.66 \times 10^{-4}M$.

| $[H_2SO_4]$ | 5.0M | | 5.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}](M)$ | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}](M)$ | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 20 | 19.94 | 1.299 | 18.80 | 1.274 |
| 40 | 17.00 | 1.230 | 17.37 | 1.240 |
| 60 | 14.56 | 1.163 | 14.81 | 1.170 |
| 80 | 12.35 | 1.091 | 9.12 | 0.960 |
| 100 | 11.50 | 1.060 | 6.37 | 0.804 |
| 120 | 7.92 | 0.898 | 5.11 | 0.708 |
| 140 | 6.88 | 0.837 | 3.30 | 0.518 |
| 160 | 6.02 | 0.779 | 2.74 | 0.439 |
| 180 | 5.20 | 0.716 | 1.92 | 0.284 |
| 200 | - | - | - | - |
| Rate constant ($min.^{-1}$) | $8.64 \times 10^{-3}$ | | $11.06 \times 10^{-3}$ | |
| Fig. 12. | Curve 5. | | Curve 6. | |

Table - XXXII.

Effect of acidity on the rate constant

| $[H^+]$ (M) | $[H^+]^2$ | $k \times 10^3$ (min.$^{-1}$) | $\frac{k}{[H^+]} \times 10^3$ (l.mole$^{-1}$ min.$^{-1}$) | $\frac{k}{[H^+]^2} \times 10^4$ (l$^2$.mole$^{-2}$min.$^{-1}$) |
|---|---|---|---|---|
| 3.0 | 9.00 | 2.92 | 0.97 | 3.26 |
| 3.5 | 12.25 | 3.70 | 1.05 | 3.02 |
| 4.0 | 16.00 | 4.90 | 1.22 | 3.06 |
| 4.5 | 20.25 | 6.83 | 1.51 | 3.37 |
| 5.0 | 25.00 | 8.64 | 1.72 | 3.44 |
| 5.5 | 30.25 | 11.06 | 2.01 | 3.65 |

## Temperature dependence

Under identical conditions of reactants concentrations and at constant ionic strength, the reaction has been studied at five different temperatures. The reaction could not be studied at lower temperature because the rate is too slow to be kinetically studied. However, the activation energy and other thermodyname functions of the process were calculated from three equations given earlier. The energy of activation was found to be 18.4 Kcal and the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 17.7 Kcal and -26.1 eu respectively.

FIG.13

TEMPERATURE DEPENDENCE OF THE OXIDATION RATE

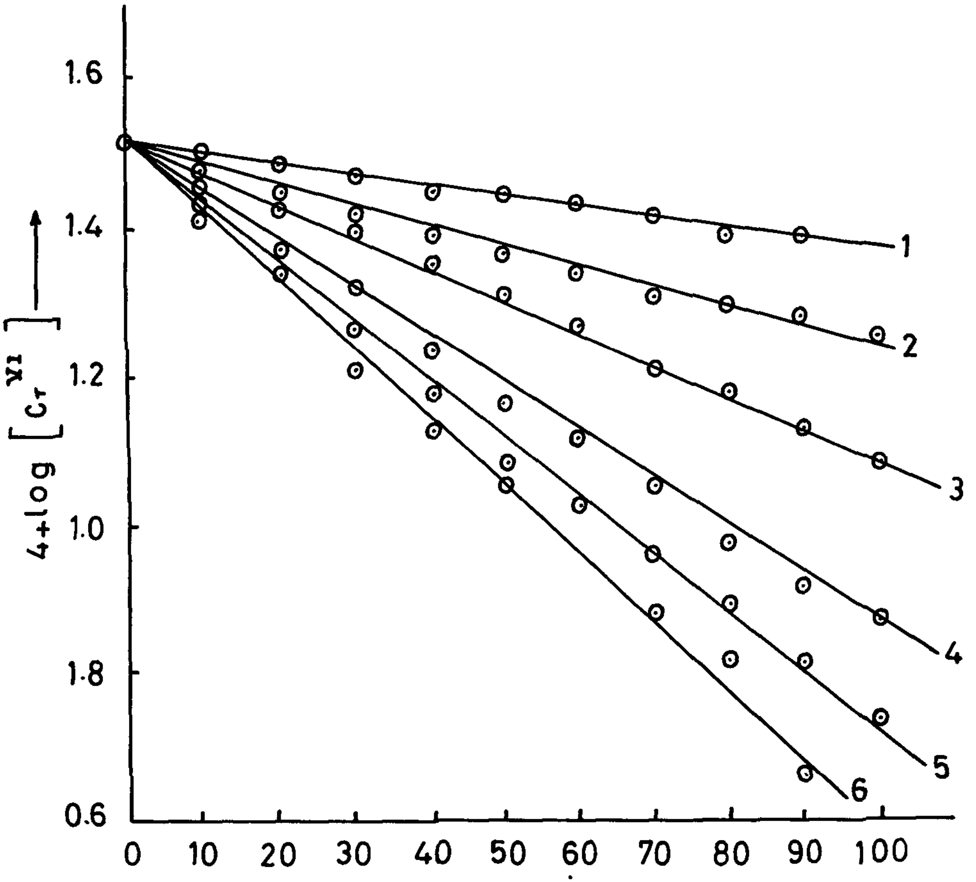


Table - XXXIII.

Temperature dependence of the reaction rate.

$[H_2SO_4] = 6.0M$; [Butyric acid] = 0.5M;

$[Cr^{VI}] = 33.33 \times 10^{-4}M$.

| Temperature | 343°K | | 348°K | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 10 | 32.81 | 1.516 | 30.11 | 1.478 |
| 20 | 31.40 | 1.497 | 28.01 | 1.447 |
| 30 | 30.31 | 1.481 | 25.98 | 1.414 |
| 40 | 29.41 | 1.468 | 25.19 | 1.401 |
| 50 | 28.44 | 1.454 | 23.03 | 1.362 |
| 60 | 27.54 | 1.441 | 21.92 | 1.340 |
| 70 | 25.00 | 1.417 | 20.60 | 1.314 |
| 80 | 24.28 | 1.387 | 19.91 | 1.301 |
| 90 | 21.23 | 1.327 | 19.28 | 1.285 |
| 100 | - | - | 18.50 | 1.267 |
| Rate constant (min.$^{-1}$) | $3.60 \times 10^{-3}$ | | $6.08 \times 10^{-3}$ | |
| Fig. 13. | Curve 1. | | Curve 2. | |

Table - XXXIV.

Temperature dependence of the reaction rate.

$[H_2SO_4] = 5.0M$; [Butyric acid] = 0.5M;
$[Cr^{VI}] = 33.33 \times 10^{-4}M.$

| Temperature | 353°K | | 358°K | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 10 | 30.06 | 1.478 | 28.01 | 1.447 |
| 20 | 27.24 | 1.435 | 23.50 | 1.371 |
| 30 | 24.80 | 1.394 | 20.64 | 1.314 |
| 40 | 22.62 | 1.354 | 17.26 | 1.237 |
| 50 | 20.51 | 1.312 | 14.20 | 1.152 |
| 60 | 18.67 | 1.271 | 12.94 | 1.112 |
| 70 | 17.40 | 1.240 | 11.22 | 1.050 |
| 80 | 16.28 | 1.211 | 9.16 | 0.962 |
| 90 | 15.20 | 1.181 | 8.23 | 0.915 |
| 100 | 13.97 | 1.145 | 7.50 | 0.875 |
| Rate constant ($min.^{-1}$) | $9.00 \times 10^{-3}$ | | $13.88 \times 10^{-3}$ | |
| Fig. 13. | Curve 3. | | Curve 4. | |

FIG. 14
ACTIVATION ENERGY

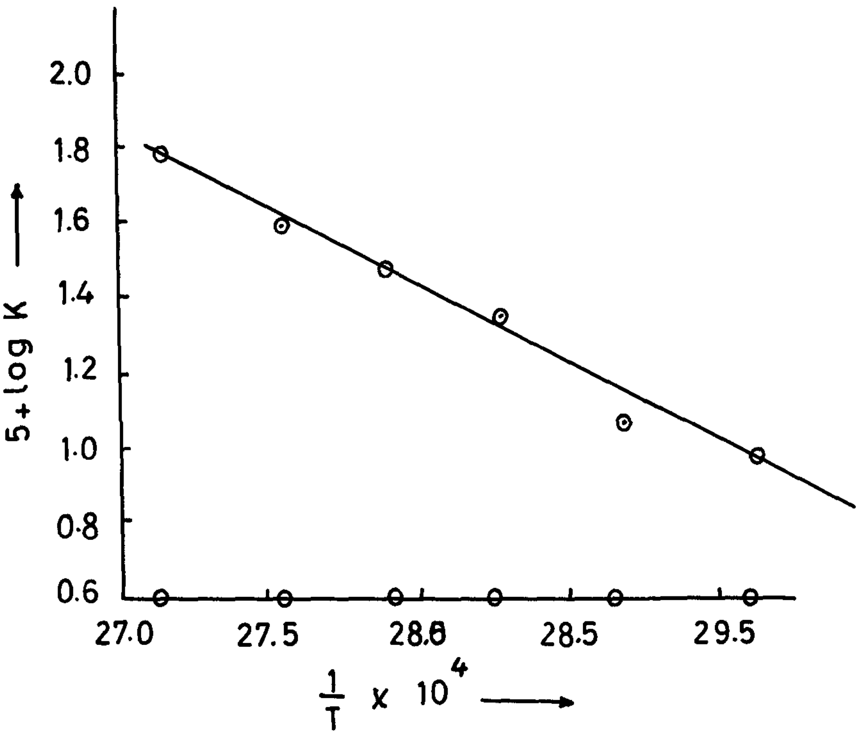


Table - XXXV.

Temperature dependence of the reaction rate.

$[H_2SO_4]$ = 5.0M; [Butyric acid] = 0.5M;
$[Cr^{VI}]$ = 33.33 x $10^{-4}$M.

| Temperature | 363°K | | 368°K | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 10 | 26.75 | 1.427 | 26.32 | 1.420 |
| 20 | 22.13 | 1.345 | 23.71 | 1.374 |
| 30 | 17.70 | 1.248 | 16.15 | 1.208 |
| 40 | 14.97 | 1.175 | 13.60 | 1.133 |
| 50 | 12.10 | 1.083 | 11.53 | 1.061 |
| 60 | 10.43 | 1.018 | 10.72 | 1.030 |
| 70 | 8.98 | 0.953 | 8.07 | 0.907 |
| 80 | 7.80 | 0.892 | 6.78 | 0.831 |
| 90 | 6.51 | 0.813 | 5.42 | 0.734 |
| 100 | 5.72 | 0.758 | 4.06 | 0.608 |
| Rate constant (min.$^{-1}$) | 17.66 x $10^{-3}$ | | 24.00 x $10^{-3}$ | |
| Fig. 13. | Curve 5. | | Curve 6. | |

## Effect of ionic strength

By varying the concentration of sodium perchlorate, the ionic strength of the reaction mixture was regulated. The other reaction conditions were maintained identical. A slight increase in the rate constant with increasing ionic strength was observed and is shown below.

FIG. 15

DEPENDENCE OF RATE CONSTANT ON IONIC STRENGTH

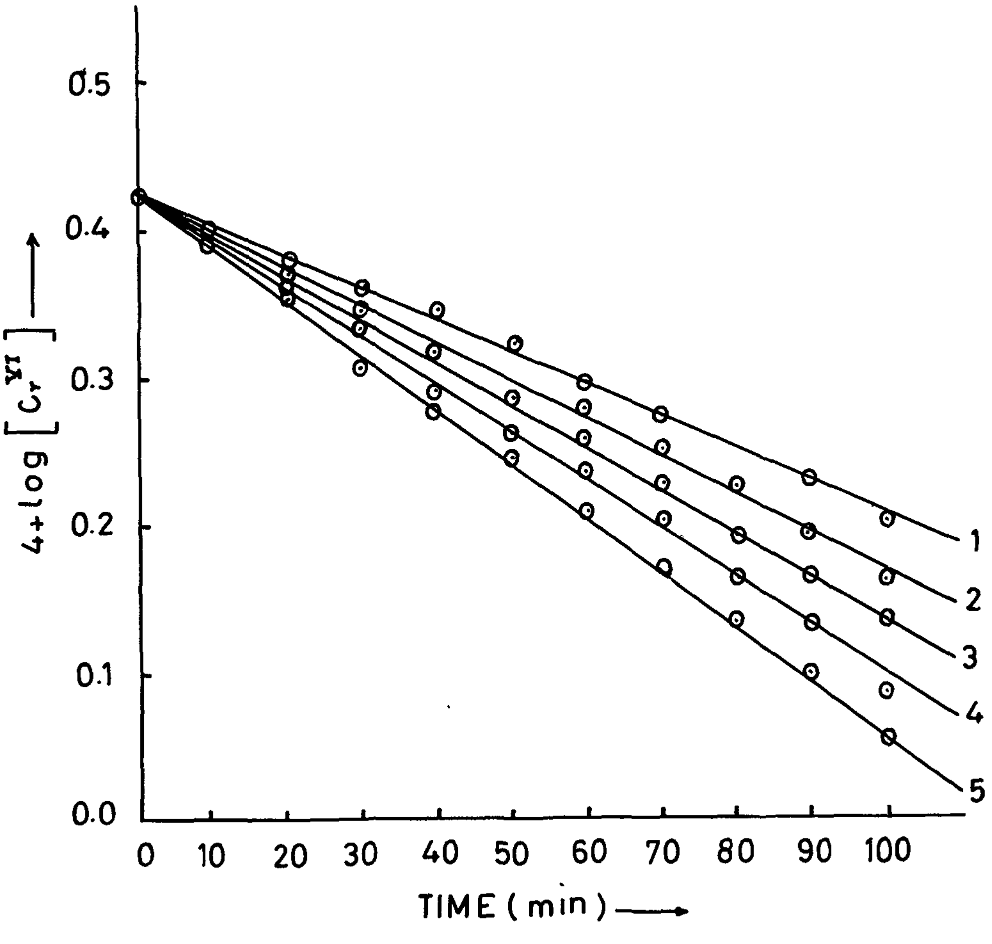


Table - XXXVI.

Effect of ionic strength on the rate of oxidation.

Temp.75±.1°C; $[H_2SO_4]$ = 4.5M; [Butyric acid]= 0.5M;
$[Cr^{VI}] = 26.66 \times 10^{-4}$M.

| $[NaClO_4]$ | 0.0M | | 0.5M | |
|---|---|---|---|---|
| Ionic strength | 4.5M | | 5.0M | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 25.48 | 1.406 | 25.23 | 1.402 |
| 20 | 24.36 | 1.386 | 23.72 | 1.375 |
| 30 | 23.52 | 1.371 | 22.80 | 1.358 |
| 40 | 22.64 | 1.354 | 21.28 | 1.328 |
| 50 | 21.36 | 1.329 | 19.77 | 1.296 |
| 60 | 20.06 | 1.302 | 18.88 | 1.276 |
| 70 | 18.76 | 1.273 | 18.23 | 1.263 |
| 80 | 17.78 | 1.250 | 17.70 | 1.248 |
| 90 | 17.38 | 1.240 | 16.06 | 1.206 |
| 100 | 16.60 | 1.220 | 15.41 | 1.188 |
| Rate constant ($min.^{-1}$) | $4.8 \times 10^{-3}$ | | $5.75 \times 10^{-3}$ | |
| Fig. 15. | Curve 1. | | Curve 2. | |

## Table - XXXVII.

Effect of ionic strength on the rate of oxidation.

Temp. 75±.1°C; $[H_2SO_4] = 4.5M$; [Butyric acid] = 0.5M;
$[Cr^{VI}] = 26.66 \times 10^{-4}$ M.

| $[NaClO_4]$ | 1.0M | | 1.5M | |
|---|---|---|---|---|
| Ionic strength | 5.5M | | 6.0M | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 25.41 | 1.405 | 25.00 | 1.398 |
| 20 | 23.44 | 1.370 | 23.44 | 1.370 |
| 30 | 21.67 | 1.336 | 21.72 | 1.337 |
| 40 | 20.60 | 1.314 | 19.67 | 1.294 |
| 50 | 19.50 | 1.290 | 18.62 | 1.270 |
| 60 | 18.32 | 1.263 | 17.62 | 1.246 |
| 70 | 17.06 | 1.232 | 16.60 | 1.220 |
| 80 | 15.63 | 1.194 | 14.96 | 1.175 |
| 90 | 14.92 | 1.174 | 14.32 | 1.156 |
| 100 | 13.67 | 1.136 | 12.88 | 1.110 |
| Rate constant $(min.^{-1})$ | $6.32 \times 10^{-3}$ | | $7.10 \times 10^{-3}$ | |
| Fig. 16. | Curve 3. | | Curve 4. | |

## Table - XXXVIII.

Effect of ionic strength on the rate of oxidation.

Temp. 75 ± .1°C; $[H_2SO_4]$ = 4.5M; [Butyric acid] = 0.5M; $[Cr^{VI}]$ = $26.66 \times 10^{-4}$M.

| $[NaClO_4]$ | 2.0M | |
|---|---|---|
| Ionic strength | 6.5M | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.426 |
| 10 | 25.00 | 1.398 |
| 20 | 23.22 | 1.366 |
| 30 | 20.60 | 1.314 |
| 40 | 18.83 | 1.275 |
| 50 | 17.50 | 1.243 |
| 60 | 16.60 | 1.221 |
| 70 | 14.90 | 1.173 |
| 80 | 13.33 | 1.125 |
| 90 | 12.85 | 1.109 |
| 100 | 10.13 | 1.005 |
| Rate constant (min.$^{-1}$) | $8.22 \times 10^{-3}$ | |

Fig. 15. Curve 5.

FIG. 16

EFFECT OF ACETIC ACID ON THE OXIDATION RATE

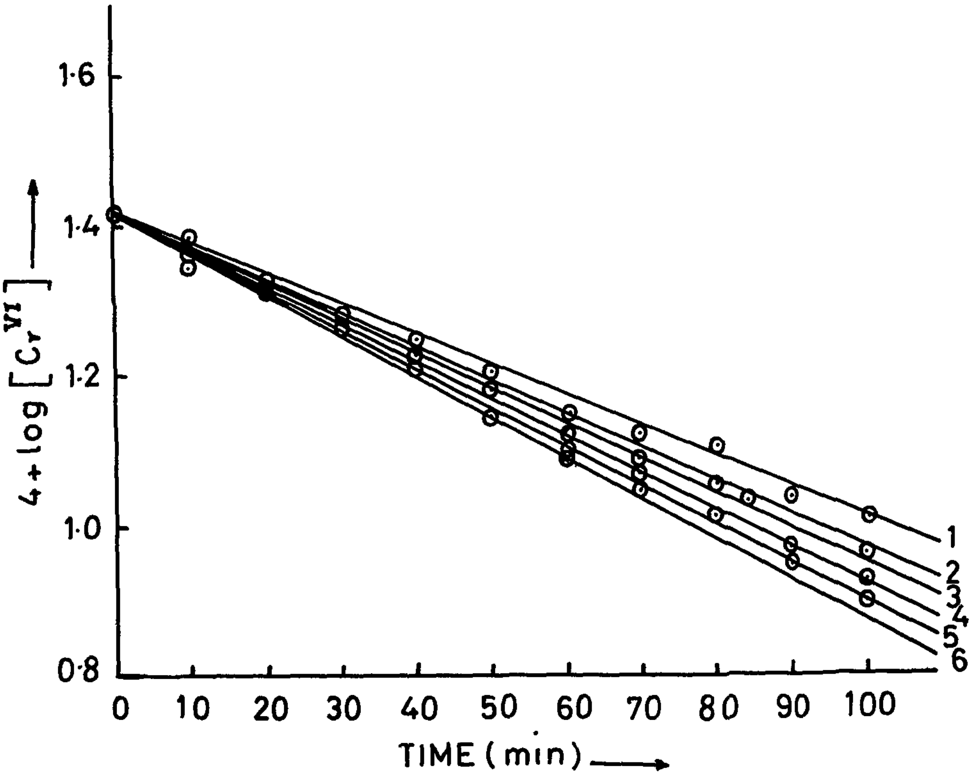


Table - XXXIX.

Influence of acetic acid on the rate of oxidation.

Temp. 75±.1°C; $[H_2SO_4]$ = 5.0M; [Butyric acid] = 0.5M;
$[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| [Acetic acid] | NIL | | 0.2M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 24.14 | 1.382 | 21.90 | 1.340 |
| 20 | 21.77 | 1.338 | 20.58 | 1.313 |
| 30 | 19.44 | 1.288 | 18.46 | 1.266 |
| 40 | 17.37 | 1.240 | 16.75 | 1.224 |
| 50 | 15.76 | 1.197 | 15.30 | 1.184 |
| 60 | 14.15 | 1.150 | 14.00 | 1.146 |
| 70 | 13.44 | 1.128 | 13.26 | 1.122 |
| 80 | 13.02 | 1.114 | 12.86 | 1.109 |
| 90 | 12.56 | 1.098 | 12.00 | 1.080 |
| 100 | 11.86 | 1.074 | 11.26 | 1.051 |
| Rate constant (min.$^{-1}$) | 9.05 x $10^{-3}$ | | 9.70 x $10^{-3}$ | |
| Fig. 16. | Curve 1. | | Curve 2. | |

Table - XL.

Influence of acetic acid on the rate of oxidation.

Temp.70±.1°C; $[H_2SO_4]$ = 5.0M; [Butyric acid] = 0.5M;
$[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| [Acetic acid] | 0.6M | | 0.7M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$ | 4+log $[Cr^{VI}]$ |
| 0 | 26.66 | 1.426 | 26.66 | 1.426 |
| 10 | 24.65 | 1.355 | 23.48 | 1.370 |
| 20 | 20.57 | 1.311 | 20.20 | 1.305 |
| 30 | 18.08 | 1.257 | 19.03 | 1.279 |
| 40 | 16.81 | 1.225 | 16.64 | 1.221 |
| 50 | 15.44 | 1.188 | 15.20 | 1.181 |
| 60 | 14.80 | 1.170 | 13.42 | 1.127 |
| 70 | 13.44 | 1.127 | 12.18 | 1.085 |
| 80 | 11.87 | 1.074 | 11.66 | 1.066 |
| 90 | 10.92 | 1.038 | 10.78 | 1.032 |
| 100 | 10.34 | 1.015 | 10.04 | 1.001 |
| Rate constant ($min.^{-1}$) | 10.20 x $10^{-3}$ | | 10.52 x $10^{-3}$ | |
| Fig. 16. | Curve 3. | | Curve 4. | |

Table - XLI.

Influence of acetic acid on the oxidation rate.

Temp. $70\pm.1^{\circ}C$; $[H_2SO_4] = 5.0M$; [Butyric acid] = 0.5M;
$[Cr^{VI}] = 26.66 \times 10^{-4}M$.

| [Acetic acid] | 1.0M | | 1.2M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$ | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 23.34 | 1.368 | 21.98 | 1.342 |
| 20 | 20.71 | 1.316 | 20.56 | 1.313 |
| 30 | 18.51 | 1.267 | 18.25 | 1.261 |
| 40 | 16.42 | 1.215 | 15.98 | 1.203 |
| 50 | 15.02 | 1.176 | 13.81 | 1.140 |
| 60 | 13.36 | 1.125 | 12.55 | 1.098 |
| 70 | 12.18 | 1.085 | 11.59 | 1.064 |
| 80 | 11.48 | 1.060 | 10.52 | 1.022 |
| 90 | 9.87 | 0.994 | 9.32 | 0.969 |
| 100 | 9.12 | 0.960 | 8.41 | 0.925 |
| Rate constant ($min.^{-1}$) | $11.18 \times 10^{-3}$ | | $11.84 \times 10^{-3}$ | |
| Fig. 16. | Curve 5. | | Curve 6. | |

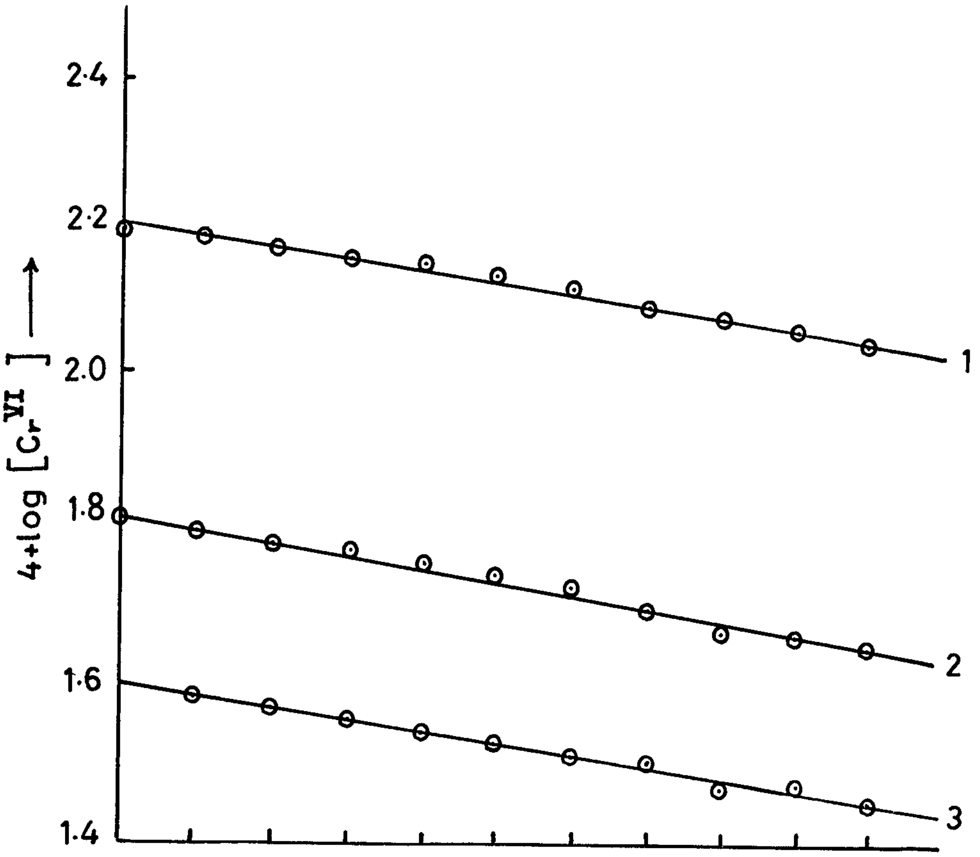
# STUDIES WITH VALERIC ACID

## Order in Chromic acid

The progress of the reaction was followed by an identical method described for propionic and butyric acids. The plot of log chromic acid concentration Vs time gave good straight lines and the slopes were used for the determination of first order rate constants. Tables given below record the first order dependence of the reaction on chromic acid concentration.

FIG. 17( A)

DEPENDENCE OF RATE CONSTANT ON CHROMIC ACID CONCENTRATION



## Table - XLII.

Dependence of rate constant on chromic acid concentration.

Temp. 75 ± .1 °C; $[H_2SO_4] = 5.0M$; [Valeric acid] = 0.1M.

| [Chromic acid] | 166.67 x $10^{-4}$M | | 66.66 x $10^{-4}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 166.67 | 2.221 | 66.66 | 1.823 |
| 10 | 166.04 | 2.220 | 63.90 | 1.805 |
| 20 | 157.62 | 2.197 | 62.82 | 1.798 |
| 30 | 152.58 | 2.183 | 61.94 | 1.791 |
| 40 | 149.72 | 2.175 | 59.42 | 1.773 |
| 50 | 142.80 | 2.154 | 56.10 | 1.749 |
| 60 | 137.75 | 2.139 | 52.32 | 1.718 |
| 70 | 129.87 | 2.113 | 49.48 | 1.694 |
| 80 | 123.88 | 2.093 | 48.06 | 1.681 |
| 90 | 118.20 | 2.071 | 46.17 | 1.664 |
| 100 | 112.85 | 2.052 | 44.60 | 1.649 |
| Rate constant ($min.^{-1}$) | 4.28 x $10^{-3}$ | | 4.34 x $10^{-3}$ | |
| Fig. 17(a). | Curve 1. | | Curve 2. | |

FIG. 17 (B)

DEPENDENCE OF RATE CONSTANT ON CHROMIC ACID CONCENTRATION

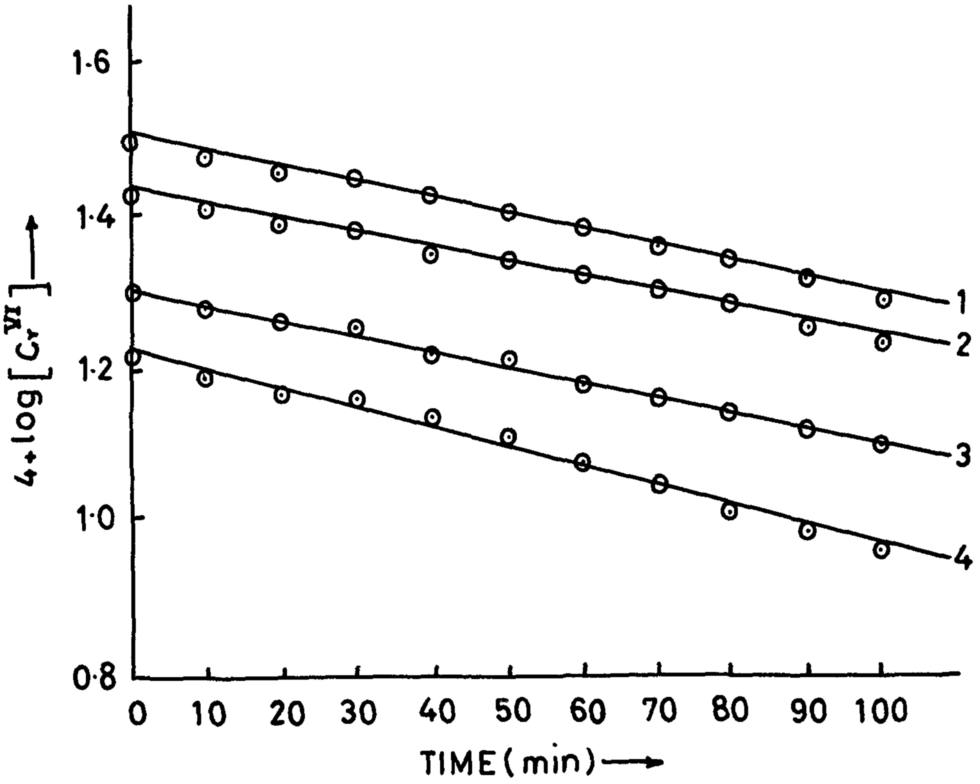


Table - XLIII.

Dependence of rate constant on chromic acid concentration.

Temp.75±.1°C; $[H_2SO_4]$ = 5.0M; [Valeric acid] = 0.1M.

| [Chromic acid] | $41.66 \times 10^{-4}$M | | $33.33 \times 10^{-4}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 41.66 | 1.619 | 33.33 | 1.522 |
| 10 | 40.24 | 1.604 | 31.74 | 1.501 |
| 20 | 38.37 | 1.583 | 30.30 | 1.481 |
| 30 | 37.42 | 1.573 | 29.47 | 1.469 |
| 40 | 35.34 | 1.548 | 28.17 | 1.449 |
| 50 | 33.65 | 1.526 | 26.95 | 1.430 |
| 60 | 32.07 | 1.506 | 25.25 | 1.402 |
| 70 | 31.06 | 1.492 | 23.46 | 1.370 |
| 80 | 29.74 | 1.473 | 22.15 | 1.345 |
| 90 | 28.92 | 1.461 | 21.08 | 1.324 |
| 100 | 27.22 | 1.435 | 19.93 | 1.298 |
| Rate constant (min.$^{-1}$) | $4.23 \times 10^{-3}$ | | $5.12 \times 10^{-3}$ | |

Fig. 17(a). Curve 3. Fig. 17(b) Curve 1.

## Table - XLIV.

Dependence of rate constant on chromic acid concentration.

Temp. 75±.1°C; [$H_2SO_4$] = 5.0N; [Valeric acid] = 0.1M.

| [Chromic acid] | $27.77 \times 10^{-4}$M | | $20.83 \times 10^{-4}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4$[$Cr^{VI}$](M) | 4+log[$Cr^{VI}$] | $10^4$[$Cr^{VI}$](M) | 4+log[$Cr^{VI}$] |
| 0 | 27.77 | 1.443 | 20.83 | 1.318 |
| 10 | 26.66 | 1.425 | 19.92 | 1.299 |
| 20 | 25.78 | 1.411 | 19.05 | 1.280 |
| 30 | 25.35 | 1.403 | 18.57 | 1.269 |
| 40 | 23.76 | 1.376 | 17.15 | 1.234 |
| 50 | 22.94 | 1.360 | 16.45 | 1.216 |
| 60 | 22.19 | 1.346 | 15.59 | 1.192 |
| 70 | 20.87 | 1.319 | 14.82 | 1.171 |
| 80 | 20.05 | 1.302 | 14.09 | 1.149 |
| 90 | 18.67 | 1.271 | 13.37 | 1.126 |
| 100 | 17.92 | 1.253 | 12.61 | 1.008 |
| Rate constant (min.$^{-1}$) | $4.47 \times 10^{-3}$ | | $5.25 \times 10^{-3}$ | |
| Fig. 17(b). | Curve 2. | | Curve 3. | |

Table - XLV.

Dependence of rate constant on chromic acid concentration

Temp.75±.1°C; $[H_2SO_4]$= 5.0M; [Valeric acid]= 0.1M.

| [Chromic acid] | $16.66 \times 10^{-4}$M | |
|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 16.66 | 1.221 |
| 10 | 15.96 | 1.203 |
| 20 | 15.35 | 1.186 |
| 30 | 14.76 | 1.170 |
| 40 | 14.00 | 1.146 |
| 50 | 13.27 | 1.122 |
| 60 | 12.44 | 1.094 |
| 70 | 11.53 | 1.062 |
| 80 | 10.53 | 0.022 |
| 90 | 9.87 | 0.994 |
| 100 | 9.14 | 0.961 |
| Rate constant (min.$^{-1}$) | $5.22 \times 10^{-3}$ | |

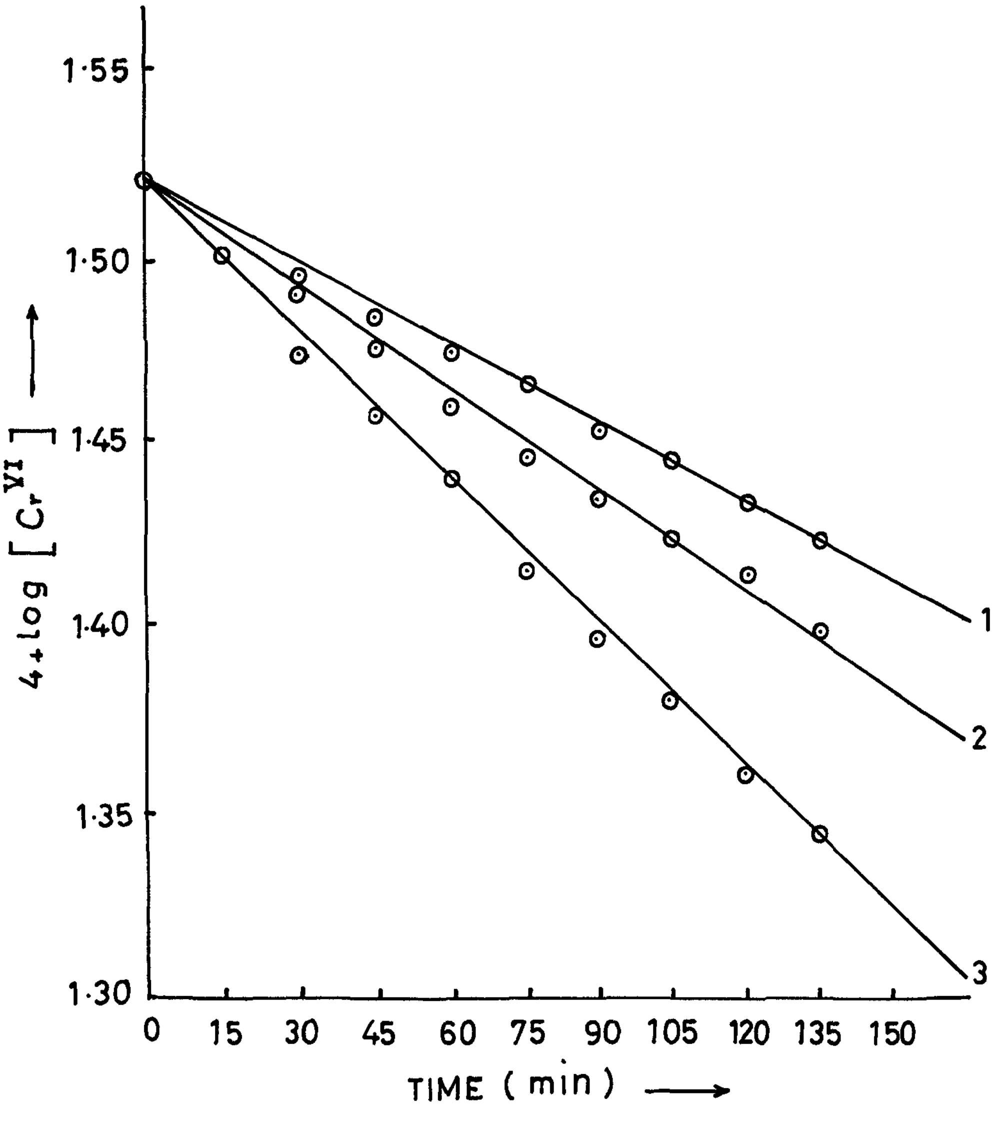
Fig. 17(b). Curve 4.

## Order in substrate

Rate constants at different substrate concentrations were obtained by varying valeric acid concentration keeping other factors constant. The first order dependence on substrate was inferred from the plot of rate constant Vs. substrate concentration where a straight line passing through the origin was obtained. The plot is shown in figure 19.

FIG. 18(A)

DEPENDENCE OF RATE CONSTANT ON VALERIC ACID CONCENTRATION



### Table - XLVI.

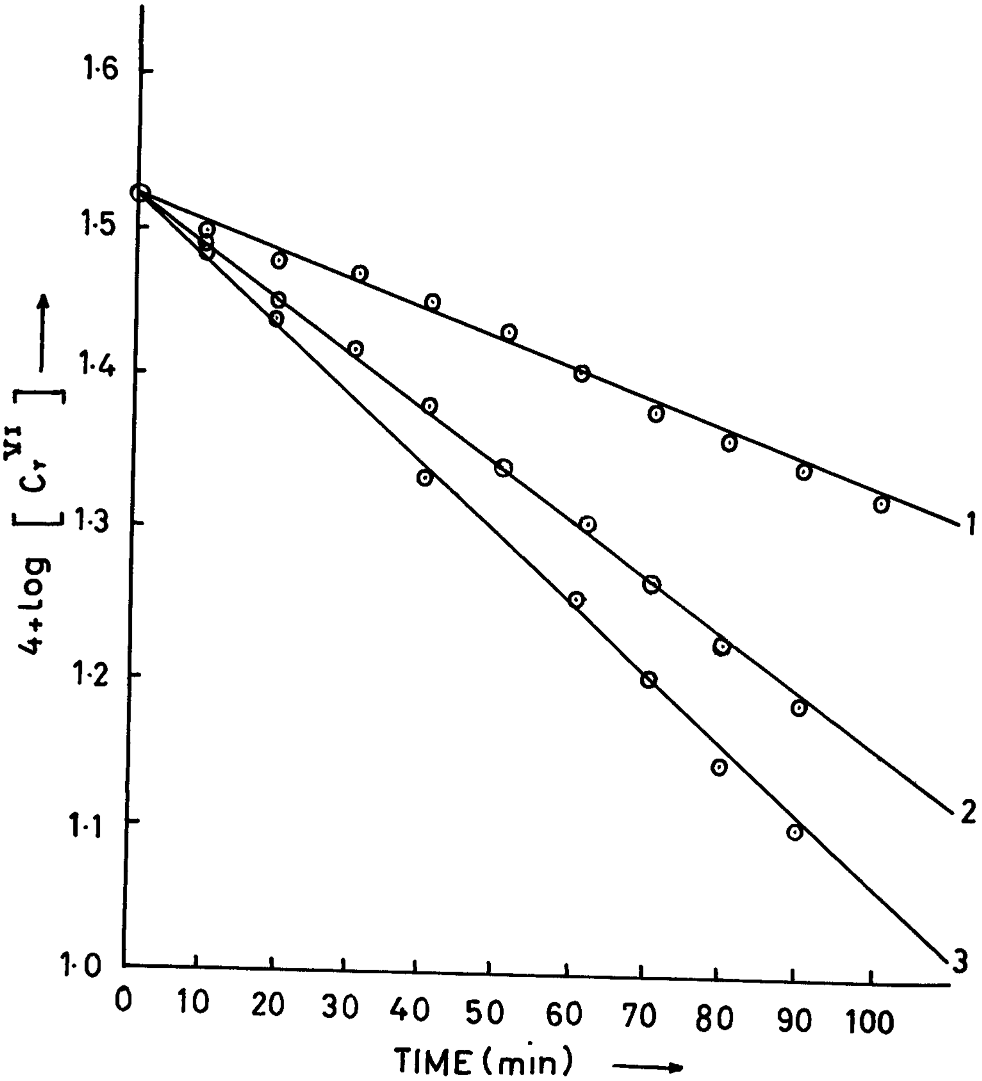
Dependence of rate constant on the concentration of valeric acid.

Temp.75±.1°C; $[\mathrm{H_2SO_4}]$ = 5.0M; $[\mathrm{Cr^{VI}}]$ = 33.33 x $10^{-4}$M.

| [Valeric acid] | $4.0 \times 10^{-2}$M | | $5.0 \times 10^{-2}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[\mathrm{Cr^{VI}}]$(M) | $4+\log[\mathrm{Cr^{VI}}]$ | $10^4[\mathrm{Cr^{VI}}]$(M) | $4+\log[\mathrm{Cr^{VI}}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 15 | 31.90 | 1.503 | 31.98 | 1.504 |
| 30 | 31.43 | 1.497 | 31.03 | 1.491 |
| 45 | 30.54 | 1.485 | 29.95 | 1.476 |
| 60 | 29.87 | 1.475 | 28.92 | 1.461 |
| 75 | 28.86 | 1.460 | 27.97 | 1.446 |
| 90 | 28.45 | 1.454 | 27.15 | 1.433 |
| 105 | 27.77 | 1.443 | 26.54 | 1.423 |
| 120 | 27.23 | 1.435 | 25.97 | 1.413 |
| 135 | 26.55 | 1.424 | 25.17 | 1.401 |
| 150 | 26.04 | 1.415 | 24.48 | 1.388 |
| Rate constant (min.$^{-1}$) | $2.03 \times 10^{-3}$ | | $2.66 \times 10^{-3}$ | |
| Fig. 18(a). | Curve 1. | | Curve 2. | |

FIG. 18 (B)

DEPENDENCE OF RATE CONSTANT ON VALERIC ACID CONCENTRATION



## Table - XLVII.

Dependence of rate constant on the concentration of valeric acid.

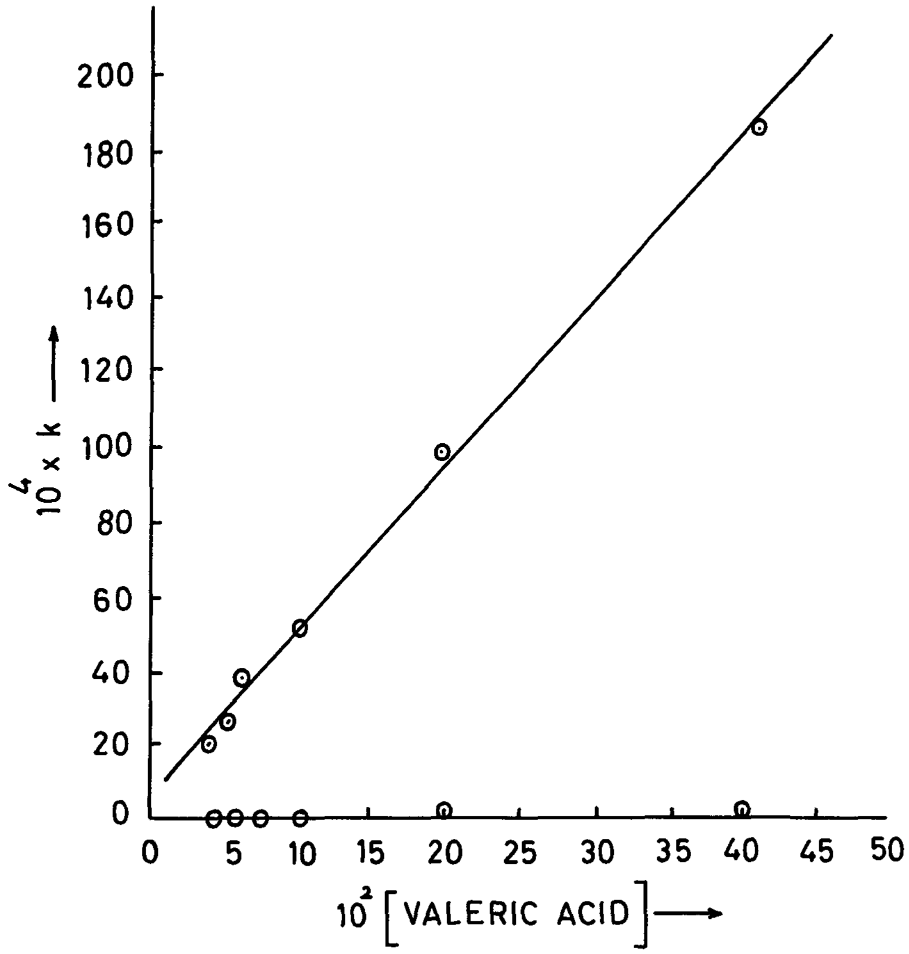
Temp.75±.1°C; $[H_2SO_4]$ = 5.0M; $[Cr^{VI}]$ = 33.33 x $10^{-4}$M.

| [Valeric acid] | 6.6 x $10^{-2}$M | | 10.0 x $10^{-2}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 15 | 31.16 | 1.493 | 31.74 | 1.501 |
| 30 | 29.74 | 1.473 | 29.29 | 1.466 |
| 45 | 28.80 | 1.459 | 28.47 | 1.454 |
| 60 | 27.59 | 1.441 | 27.17 | 1.434 |
| 75 | 25.96 | 1.414 | 25.95 | 1.414 |
| 90 | 24.94 | 1.397 | 24.25 | 1.384 |
| 105 | 23.99 | 1.380 | 22.48 | 1.351 |
| 120 | 22.98 | 1.361 | 21.08 | 1.323 |
| 135 | 22.02 | 1.342 | 19.93 | 1.299 |
| 150 | 21.28 | 1.326 | 19.02 | 1.279 |
| Rate constant (min.$^{-1}$) | 3.80 x $10^{-3}$ | | 5.30 x $10^{-3}$ | |

Fig. 18(a) Curve 3. Fig. 18(b) Curve 1.

FIRST ORDER DEPENDENCE OF RATE CONSTANT ON VALERIC ACID CONCENTRATION

FIG. 19



### Table - XLVIII.

Dependence of rate constant on the concentration of valeric acid.

Temp. 75±.1°C; $[H_2SO_4]$ = 5.0M; $[Cr^{VI}]$ = 33.33 x $10^{-4}$M.

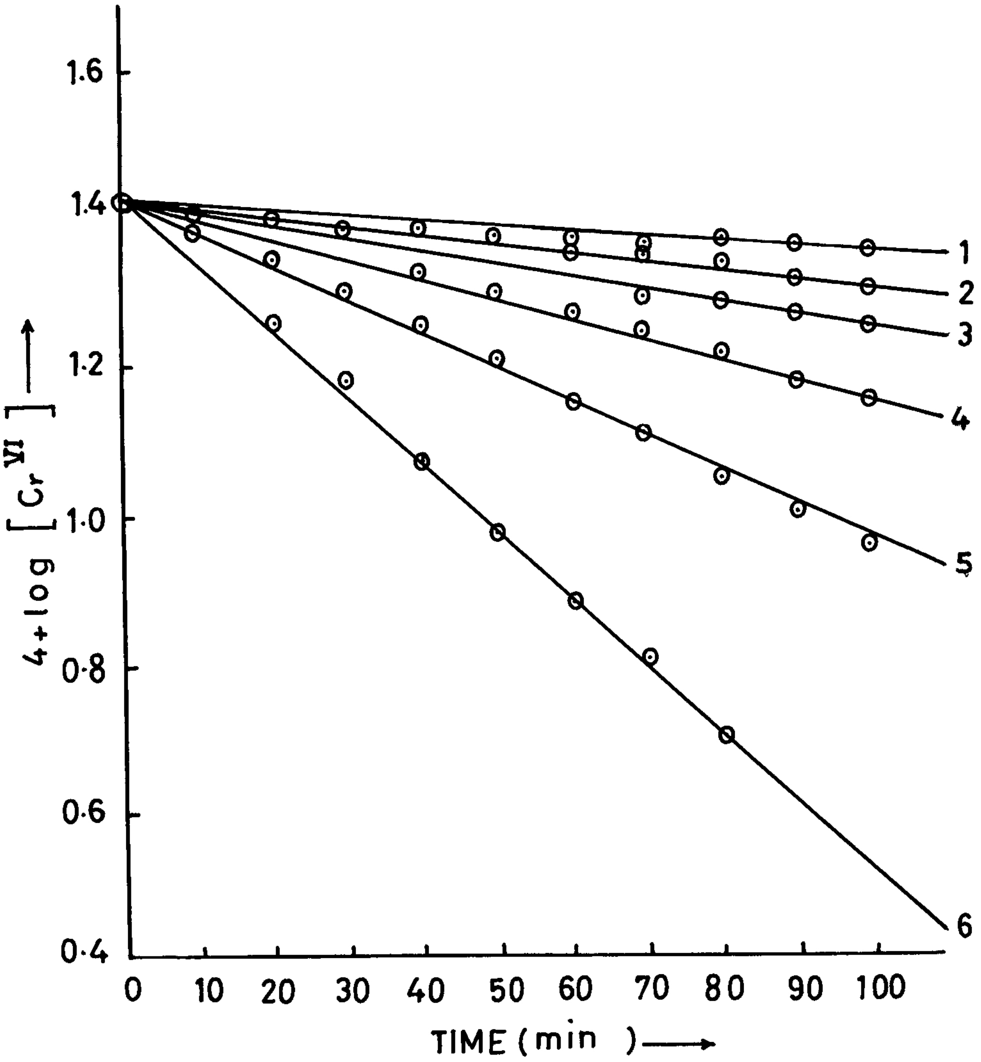
| [Valeric acid] | 20.0 x $10^{-2}$M | | 40.0 x $10^{-2}$M | |
|---|---|---|---|---|
| Time (mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 10 | 30.72 | 1.487 | 30.25 | 1.480 |
| 20 | 28.68 | 1.457 | 27.19 | 1.434 |
| 30 | 26.84 | 1.428 | 25.23 | 1.402 |
| 40 | 24.58 | 1.391 | 23.15 | 1.364 |
| 50 | 22.07 | 1.343 | 20.55 | 1.312 |
| 60 | 20.35 | 1.308 | 17.64 | 1.246 |
| 70 | 18.25 | 1.261 | 15.43 | 1.188 |
| 80 | 16.21 | 1.210 | 13.21 | 1.121 |
| 90 | 14.50 | 1.161 | 11.70 | 1.068 |
| 100 | 12.34 | 1.091 | 10.56 | 1.023 |
| Rate constant (min.$^{-1}$) | 9.87 x $10^{-3}$ | | 18.60 x $10^{-3}$ | |
| Fig. 18(b). | Curve 2. | | Curve 3. | |

## Variation of rate constant with acidity

The effect of hydrogen ion concentration on the oxidation rate was studied exactly in the same manner as in the oxidation of propionic and butyric acid. It is seen from table LII that at lower acidities the oxidation rate varies almost exactly as the square of hydrogen ion concentration but in solutions of high ionic strength and high acidity, the reaction velocity changes at a rate somewhat greater than that required for second order dependence. However, the plot of logarithm of rate constant against modified acidity function $H_- + \log \frac{a_{H_2O}}{a_{H_A}}$ yielded a straight line but the slope was quite high.

FIG. 20

ACIDITY DEPENDENCE OF THE OXIDATION RATE



### Table - XLIX.

Acidity dependence of the oxidation rate.

Temp.75±.1°C; $[H_2SO_4] + [NaHSO_4] = 6.0M$;
$[\text{Valeric acid}] = 0.2M$; $[Cr^{VI}] = 26.66 \times 10^{-4}M$.

| $[H_2SO_4]$ | 3.0M | | 3.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 26.03 | 1.415 | 25.66 | 1.409 |
| 20 | 25.56 | 1.407 | 25.40 | 1.404 |
| 30 | 24.87 | 1.395 | 24.55 | 1.390 |
| 40 | 24.55 | 1.391 | 24.18 | 1.383 |
| 50 | 24.45 | 1.388 | 23.86 | 1.377 |
| 60 | 24.02 | 1.380 | 23.12 | 1.364 |
| 70 | 23.18 | 1.365 | 22.60 | 1.354 |
| 80 | 22.92 | 1.361 | 21.90 | 1.340 |
| 90 | 22.65 | 1.355 | 21.17 | 1.325 |
| 100 | 22.33 | 1.349 | 20.16 | 1.304 |
| Rate constant (min.$^{-1}$) | $2.04 \times 10^{-3}$ | | $2.80 \times 10^{-3}$ | |
| Fig. 20. | Curve 1. | | Curve 2. | |

Table - L.

Acidity dependence of the oxidation rate.

Temp. 75 ± .1°C; $[H_2SO_4] + [NaHSO_4] = 6.0M$;
$[\text{Valeric acid}] = 0.2M$; $[Cr^{VI}] = 26.66 \times 10^{-4}M$.

| $[H_2SO_4]$ | 4.0M | | 4.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 25.71 | 1.411 | 25.71 | 1.410 |
| 20 | 24.45 | 1.388 | 24.44 | 1.388 |
| 30 | 23.93 | 1.378 | 23.22 | 1.365 |
| 40 | 23.14 | 1.364 | 21.47 | 1.331 |
| 50 | 21.72 | 1.336 | 20.30 | 1.307 |
| 60 | 20.76 | 1.317 | 19.05 | 1.279 |
| 70 | 20.37 | 1.309 | 17.87 | 1.252 |
| 80 | 19.77 | 1.296 | 16.58 | 1.219 |
| 90 | 18.72 | 1.272 | 15.25 | 1.183 |
| 100 | 17.62 | 1.246 | 14.18 | 1.510 |
| Rate constant (min.$^{-1}$) | $3.88 \times 10^{-3}$ | | $6.25 \times 10^{-3}$ | |
| Fig. 20. | Curve 3. | | Curve 4. | |

Table - LI.

Acidity dependence of the oxidation rate.

Temp.75$\pm$.1$^{\circ}$C; $[H_2SO_4]$ + $[NaHSO_4]$= 6.0M;
$[$Valoric acid$]$= 0.2M; $[Cr^{VI}]$= 26.66 x 10$^{-4}$M.

| $[H_2SO_4]$ | 5.0M | | 5.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 25.57 | 1.407 | 24.26 | 1.385 |
| 20 | 23.44 | 1.370 | 21.20 | 1.326 |
| 30 | 20.76 | 1.317 | 16.30 | 1.212 |
| 40 | 18.73 | 1.272 | 12.10 | 1.083 |
| 50 | 16.83 | 1.226 | 9.92 | 0.996 |
| 60 | 14.53 | 1.162 | 8.07 | 0.906 |
| 70 | 13.00 | 1.114 | 6.76 | 0.830 |
| 80 | 11.42 | 1.057 | 5.01 | 0.700 |
| 90 | 10.25 | 1.011 | 3.68 | 0.566 |
| 100 | 9.28 | 0.968 | 2.18 | 0.359 |
| Rate constant (min.$^{-1}$) | 9.02 x 10$^{-3}$ | | 11.32 x 10$^{-3}$ | |
| Fig. 20. | Curve 5. | | Curve 6. | |

Table - LII.

Effect of acidity on the rate constant

| $[H^+]$ (M) | $[H^+]^2$ | $k \times 10^3$ ($min.^{-1}$) | $\frac{k}{[H^+]} \times 10^3$ ($1. mole^{-1} min.^{-1}$) | $\frac{k}{[H^+]^2} \times 10^4$ ($1^2.mole^{-2} min^{-1}$) |
|---|---|---|---|---|
| 3.0 | 9.00 | 2.04 | 0.68 | 2.26 |
| 3.5 | 12.25 | 2.80 | 0.80 | 2.28 |
| 4.0 | 16.00 | 3.88 | 0.95 | 2.42 |
| 4.5 | 20.25 | 6.25 | 1.38 | 3.08 |
| 5.0 | 25.00 | 9.02 | 1.80 | 3.60 |
| 5.5 | 30.25 | 11.32 | 2.58 | 3.74 |

## Temperature dependence

Reaction was studied under identical conditions. Activation energy was calculated graphically - and other thermodynamic parameters were calculated from the formulae mentioned earlier. The values of $E_a$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were found to be 20.7 Kcal, 20.0 Kcal and -19.1 eu respectively. The observations at various temperatures are presented below:

FIG. 21

TEMPERATURE DEPENDENCE OF THE OXIDATION RATE

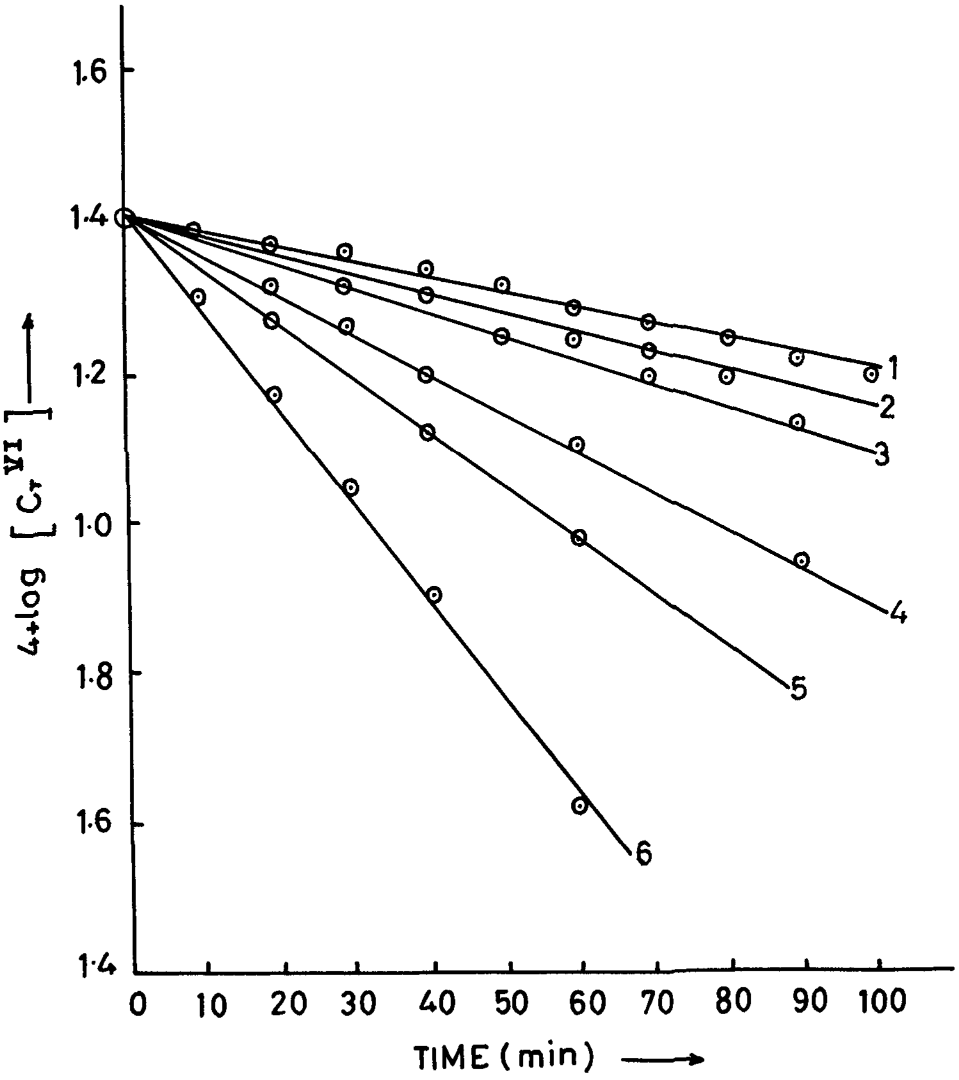


Table - LIII.

Temperature dependence of the reaction rate.

$[H_2SO_4] = 5.0M$; $[\text{Valeric acid}] = 0.2M$;
$[Cr^{VI}] = 26.66 \times 10^{-4}M$.

| Temperature | 343°K | | 348°K | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 26.06 | 1.416 | 25.56 | 1.407 |
| 20 | 24.68 | 1.392 | 24.56 | 1.390 |
| 30 | 23.91 | 1.378 | 23.58 | 1.372 |
| 40 | 23.35 | 1.368 | 22.43 | 1.350 |
| 50 | 21.92 | 1.340 | 21.22 | 1.326 |
| 60 | 20.48 | 1.311 | 19.68 | 1.294 |
| 70 | 19.32 | 1.286 | 18.14 | 1.258 |
| 80 | 17.78 | 1.249 | 16.44 | 1.216 |
| 90 | 16.95 | 1.229 | 13.30 | 1.124 |
| 100 | 15.84 | 1.200 | 11.38 | 1.056 |
| Rate constant (min.$^{-1}$) | $5.14 \times 10^{-3}$ | | $6.14 \times 10^{-3}$ | |
| Fig. 21. | Curve 1. | | Curve 2. | |

Table - LIV.

Temperature dependence of the reaction rate.

$[H_2SO_4] = 5.0M$; $[\text{Valeric acid}] = 0.2M$; $[Cr^{VI}] = 26.66 \times 10^{-4}M$.

| Temperature | $353^\circ K$ | | $358^\circ K$ | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 25.35 | 1.404 | 25.18 | 1.401 |
| 20 | 24.04 | 1.381 | 21.22 | 1.326 |
| 30 | 23.09 | 1.363 | 18.86 | 1.275 |
| 40 | 20.98 | 1.321 | 15.67 | 1.195 |
| 50 | 19.89 | 1.298 | 12.48 | 1.096 |
| 60 | 17.95 | 1.258 | 9.84 | 0.993 |
| 70 | 15.85 | 1.200 | 7.31 | 0.864 |
| 80 | 13.83 | 1.141 | 5.60 | 0.748 |
| 90 | 11.97 | 1.078 | 4.61 | 0.664 |
| 100 | 9.92 | 0.996 | 3.74 | 0.572 |
| Rate constant (min.$^{-1}$) | $11.51 \times 10^{-3}$ | | $20.34 \times 10^{-3}$ | |
| Fig. 21. | Curve 3. | | Curve 4. | |

FIG. 22

ACTIVATION ENERGY

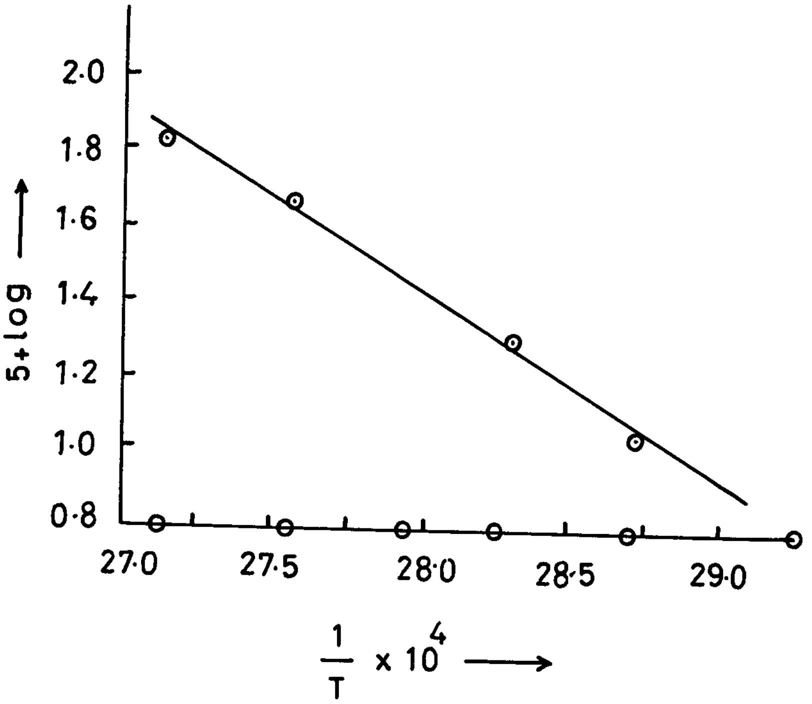


Table - LV.

Temperature dependence of the reaction rate.

$[H_2SO_4]$ = 5.0M; [Valeric acid] = 0.2M; $[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| Temperature | 363°K | | 368°K | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 5 | 25.32 | 1.403 | 24.68 | 1.392 |
| 10 | 24.11 | 1.382 | 22.05 | 1.343 |
| 15 | 22.46 | 1.351 | 18.83 | 1.275 |
| 20 | 20.51 | 1.312 | 15.29 | 1.184 |
| 25 | 19.08 | 1.280 | 11.96 | 1.078 |
| 30 | 17.02 | 1.231 | 7.19 | 0.856 |
| 35 | 15.28 | 1.184 | 6.27 | 0.797 |
| 40 | 13.16 | 1.119 | 5.09 | 0.707 |
| 45 | 11.52 | 1.061 | 4.02 | 0.604 |
| 50 | 9.77 | 0.990 | 3.38 | 0.529 |
| Rate constant ($min.^{-1}$) | 27.63 x $10^{-3}$ | | 40.68 x $10^{-3}$ | |
| Fig. 21. | Curve 5. | | Curve 6. | |

## Effect of ionic strength

Ionic strength of the medium was varied by adding various amounts of sodium perchlorate. A slight increase in the rate constant with increasing ionic strength was found. The data are given in the following tables.

FIG. 23

DEPENDENCE OF RATE CONSTANT ON IONIC STRENGTH

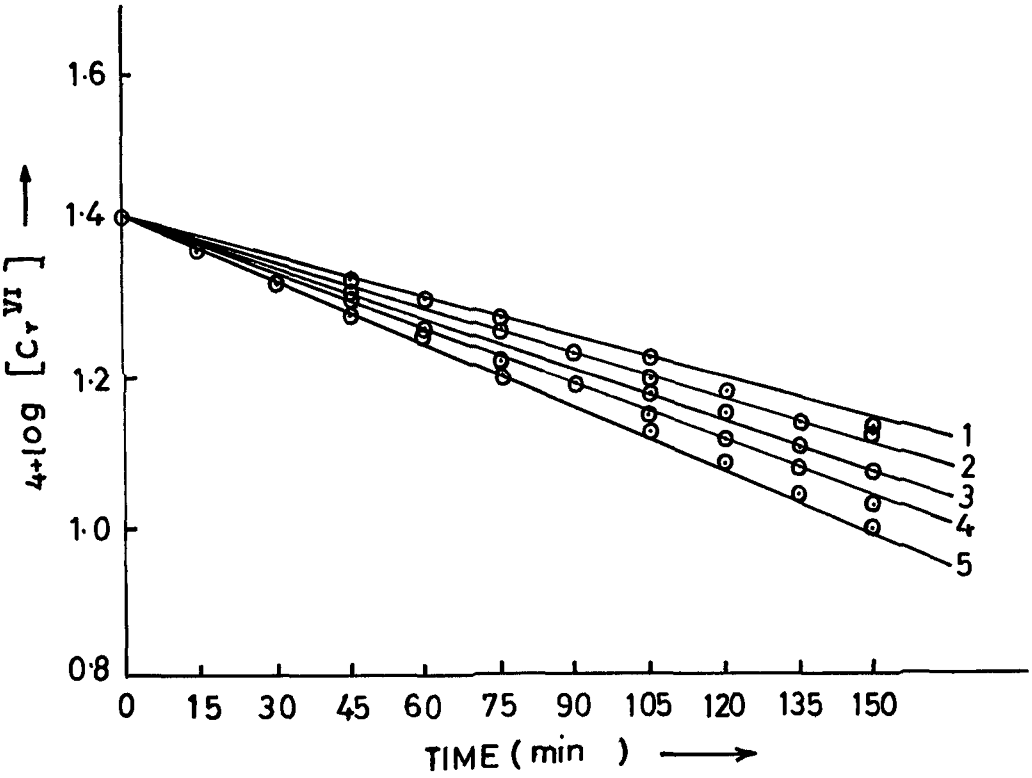


Table - LVI.

Effect of ionic strength on the rate constant.

Temp. 75$\pm$.1°C; $[H_2SO_4]$ = 4.5M; [Valeric acid] = 0.1M;
$[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| $[NaClO_4]$ | Nil | | 0.5M | |
|---|---|---|---|---|
| Ionic strength | 4.5M | | 5.0M | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 15 | 24.61 | 1.391 | 24.50 | 1.389 |
| 30 | 23.14 | 1.364 | 22.71 | 1.356 |
| 45 | 22.40 | 1.350 | 21.52 | 1.333 |
| 60 | 21.15 | 1.325 | 20.82 | 1.307 |
| 75 | 19.74 | 1.295 | 19.20 | 1.287 |
| 90 | 17.80 | 1.250 | 17.80 | 1.250 |
| 105 | 16.50 | 1.217 | 16.06 | 1.205 |
| 120 | 15.46 | 1.189 | 14.87 | 1.172 |
| 135 | 14.44 | 1.159 | 13.46 | 1.129 |
| 150 | 13.20 | 1.120 | 12.11 | 1.083 |
| Rate constant (min.$^{-1}$) | 4.82 x $10^{-3}$ | | 5.37 x $10^{-3}$ | |
| Fig. 23. | Curve 1. | | Curve 2. | |

Table - LVII.

Effect of ionic strength on the rate constant.

Temp.75±.1°C; $[H_2SO_4]$ = 4.5M; [Valeric acid] = 0.1M;
$[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| $[NaClO_4]$ | 1.00M | | 1.5M | |
|---|---|---|---|---|
| Ionic strength | 5.50M | | 6.0M | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 15 | 24.36 | 1.386 | 23.31 | 1.385 |
| 30 | 22.91 | 1.360 | 22.52 | 1.352 |
| 45 | 21.15 | 1.325 | 20.43 | 1.310 |
| 60 | 19.54 | 1.291 | 18.74 | 1.272 |
| 75 | 18.10 | 1.257 | 17.36 | 1.239 |
| 90 | 17.08 | 1.232 | 15.83 | 1.199 |
| 105 | 15.57 | 1.192 | 14.55 | 1.163 |
| 120 | 14.24 | 1.153 | 13.58 | 1.133 |
| 135 | 13.00 | 1.114 | 12.30 | 1.090 |
| 150 | 11.56 | 1.063 | 10.82 | 1.034 |
| Rate constant (min.$^{-1}$) | 5.48 x $10^{-3}$ | | 5.80 x $10^{-3}$ | |
| Fig. 23. | Curve 3. | | Curve 4. | |

Table - LVIII.

Effect of ionic strength on the rate constant.

Temp.75$\pm$.1°C; $[H_2SO_4]$= 4.5M; [Valeric acid]= 0.1M;
$[Cr^{VI}]$= 26.66 x $10^{-4}$M.

| $[NaClO_4]$ | 2.00M | |
|---|---|---|
| Ionic strength | 6.50M | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 |
| 15 | 24.43 | 1.388 |
| 30 | 22.35 | 1.349 |
| 45 | 20.22 | 1.305 |
| 60 | 18.35 | 1.263 |
| 75 | 16.73 | 1.223 |
| 90 | 15.40 | 1.187 |
| 105 | 14.04 | 1.147 |
| 120 | 12.72 | 1.104 |
| 135 | 11.40 | 1.057 |
| 150 | 10.20 | 1.008 |
| Rate constant (min.$^{-1}$) | 6.26 x $10^{-3}$ | |

Fig. 23. Curve 5.

FIG. 24

EFFECT OF ACETIC ACID ON THE OXIDATION RATE

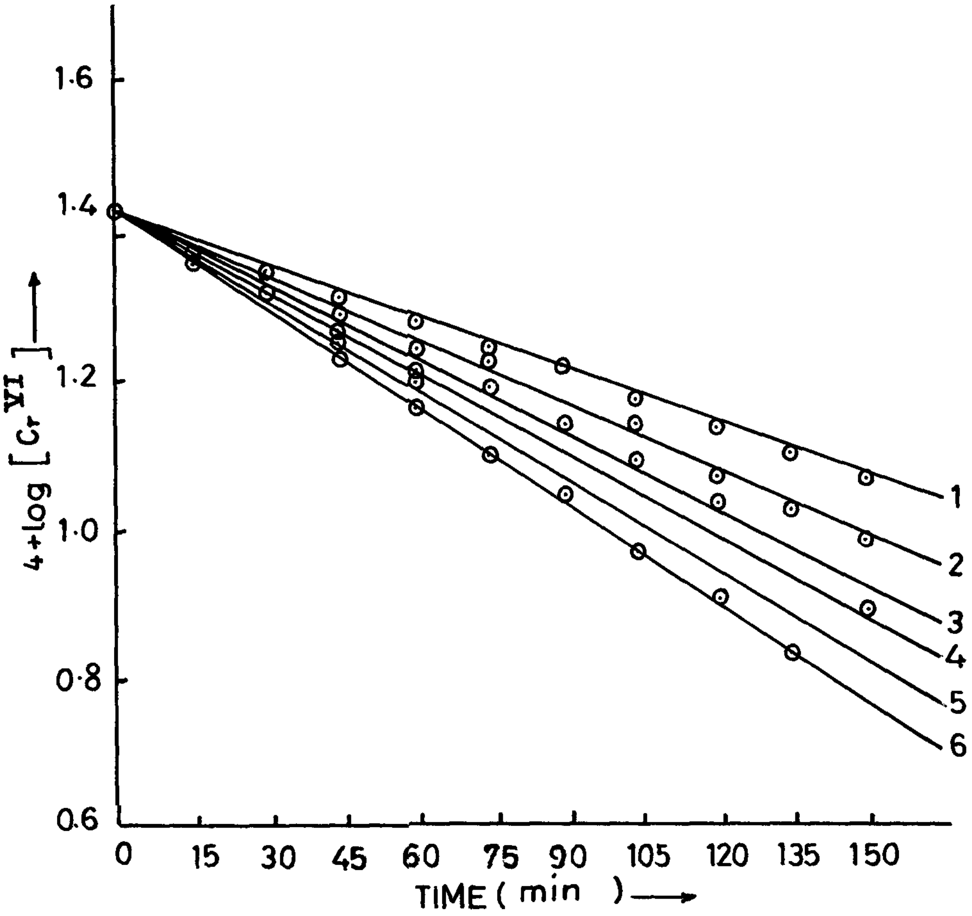


Table - LIX.

Influence of acetic acid on the oxidation rate.

Temp.75±.1°C; $[H_2SO_4]$ = 5.0M; [Valeric acid] = 0.2M;
$[Cr^{VI}]$ = $26.66 \times 10^{-4}$M.

| [Acetic acid] | 0.1M | | 0.2M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 15 | 24.39 | 1.387 | 24.90 | 1.396 |
| 30 | 23.48 | 1.370 | 23.08 | 1.363 |
| 45 | 21.60 | 1.334 | 21.04 | 1.323 |
| 60 | 19.56 | 1.291 | 19.22 | 1.283 |
| 75 | 18.02 | 1.255 | 17.50 | 1.243 |
| 90 | 16.70 | 1.223 | 15.92 | 1.202 |
| 105 | 15.24 | 1.183 | 14.10 | 1.149 |
| 120 | 13.53 | 1.131 | 12.00 | 1.078 |
| 135 | 12.45 | 1.095 | 10.52 | 1.022 |
| 150 | 11.20 | 1.049 | 9.26 | 0.967 |
| Rate constant (min.$^{-1}$) | $6.26 \times 10^{-3}$ | | $7.82 \times 10^{-3}$ | |
| Fig. 24. | Curve 1. | | Curve 2. | |

Table - IX.

Influence of acetic acid on the oxidation rate.

Temp.75±.1°C; $[H_2SO_4]$= 5.0M; [Valeric acid]= 0.2M;
$[Cr^{VI}]$= 26.66 x $10^{-4}$M.

| [Acetic acid] | 0.6M | | 0.7M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 15 | 24.11 | 1.382 | 23.98 | 1.379 |
| 30 | 22.40 | 1.350 | 21.68 | 1.336 |
| 45 | 20.08 | 1.302 | 19.00 | 1.278 |
| 60 | 17.70 | 1.248 | 16.64 | 1.221 |
| 75 | 16.11 | 1.207 | 14.45 | 1.160 |
| 90 | 13.67 | 1.135 | 12.43 | 1.094 |
| 105 | 12.08 | 1.082 | 11.17 | 1.048 |
| 120 | 10.66 | 1.028 | 9.52 | 0.978 |
| 135 | 8.96 | 0.952 | 8.43 | 0.926 |
| 150 | 7.81 | 0.893 | 7.44 | 0.872 |
| Rate constant ($min.^{-1}$) | 8.44 x $10^{-3}$ | | 8.82 x $10^{-3}$ | |
| Fig. 24. | Curve 3. | | Curve 4. | |

Table - LXI.

Influence of acetic acid on the oxidation rate.

Temp. 75$\pm$.1$^{o}$C; $[H_2SO_4]$ = 5.0M; $[$Valeric acid$]$ = 0.2M;
$[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| $[$Acetic acid$]$ | 1.0M | | 1.2M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 15 | 23.38 | 1.368 | 23.05 | 1.363 |
| 30 | 20.91 | 1.320 | 20.64 | 1.314 |
| 45 | 18.24 | 1.262 | 17.90 | 1.253 |
| 60 | 16.20 | 1.209 | 14.51 | 1.161 |
| 75 | 13.90 | 1.143 | 12.43 | 1.094 |
| 90 | 12.10 | 1.082 | 11.28 | 1.052 |
| 105 | 10.51 | 1.021 | 8.91 | 0.950 |
| 120 | 9.05 | 0.956 | 8.03 | 0.905 |
| 135 | 8.26 | 0.917 | 6.40 | 0.806 |
| 150 | 6.80 | 0.832 | 4.81 | 0.682 |
| Rate constant (min.$^{-1}$) | 8.95 x $10^{-3}$ | | 9.97 x $10^{-3}$ | |
| Fig. 24. | Curve 5. | | Curve 6. | |

# CHAPTER III

# KINETICS OF OXIDATION OF BRANCHED CHAIN FATTY ACIDS

## INTRODUCTION

The knowledge of the influence of structure on reactivity is not only important from synthetic point of view but also represents an important tool in the study of reaction mechanism. The dependence of the oxidation rate on carboxylic acid structure has not been investigated systematically. It was, therefore, thought worthwhile to study the effect of branching on the rate of oxidation of fatty acids. For this purpose, studies on the oxidation of isobutyric, isovaleric and pivalic acids by chromic acid were carried out under different experimental conditions.

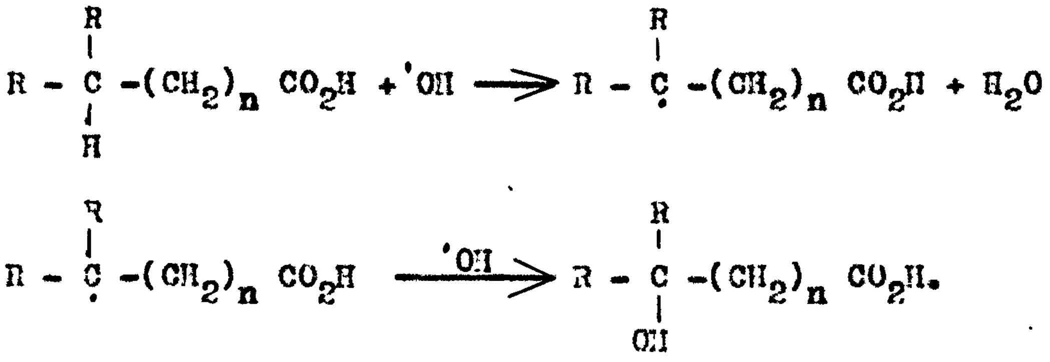
The oxidation of carboxylic acids containing tertiary carbon atom was studied by Symons and Kenyon[128]. They obtained hydroxy carboxylic acids from the corresponding branched chain carboxylic acids by using potassium permanganate in concentrated alkaline solution,

$$RR'CH(CH_2)_n\,CO_2H \longrightarrow RR'C(OH)(CH_2)_n\,CO_2H.$$

The reaction was slow in dilute alkaline solution even at elevated temperatures and resulted in the degradation of acid. In concentrated alkaline solution, the reaction was faster and proceeded at room temperature leading to hydroxy acids which were not further attacked. They interpreted it by postulating that for reactions with permanganate, the active oxidant was the free hydroxyl radical or the $\overset{-}{O}^{\cdot}$ radical ion.

A survey of oxidations of organic compounds by alkaline solutions of potassium manganate as well as by strongly alkaline solutions of potassium hypomanganate has been reported by Pode and Waters[129]. They observed that a slight reaction occurred with isobutyric and isovaleric acids in 10N potassium hydroxide. Inspired by the above studies Beckwith and Goodrich[130] carried out the detailed investigation of oxidation of various branched chain carboxylic acids by (a) $K_2MnO_4$ in dilute alkali; (b) $KMnO_4$ in concentrated alkali; (c) $K_2S_2O_8$ in dilute alkali; (d) $K_2S_2O_8$ in dilute acid. They suggested that the reaction proceeded via free hydroxyl radicals according to the following scheme:

$$MnO_4^- + \overset{-}{O}H \rightleftharpoons MnO_4^= + {}^{\cdot}OH$$



$$R-\underset{H}{\overset{R}{C}}-(CH_2)_n\,CO_2H + {}^{\cdot}OH \longrightarrow R-\overset{R}{\dot{C}}-(CH_2)_n\,CO_2H + H_2O$$

$$R-\overset{R}{\dot{C}}-(CH_2)_n\,CO_2H \xrightarrow{{}^{\cdot}OH} R-\underset{OH}{\overset{R}{C}}-(CH_2)_n\,CO_2H.$$

Persulphate was believed to provide hydroxyl radicals on thermal decomposition in the following way:

$$S_2O_8^{2-} \rightleftharpoons 2SO_4^{\cdot -}$$

$$\overline{SO}_4^{\cdot} + H_2O \longrightarrow SO_4^{-} + H^{+} + {}^{\cdot}OH$$

Evidence for hydroxylation as the major effect in the persulphate oxidation of organic compounds has also been reported by Bacon and Bott[131]. They found that aqueous solution of sodium persulphate containing little amount of silver nitrate as catalyst, converted the branched chain fatty acids into alcohols with loss of carbon dioxide. Pivalic acid gave tert-butanol and isobutyric acid, a mixture of isopropanol and methyl acetate in the ratio of 20:1. The following mechanism was proposed:

$$R\,CO_2H + \overline{SO}_4^{\cdot} \longrightarrow R\,COO^{\cdot}$$

$$R\,COO^{\cdot} \longrightarrow R^{\cdot} + CO_2$$

$$R^{\cdot} + SO_3OO\overline{SO}_3^{\cdot} \longrightarrow RO\overline{SO}_3 + SO_4^{\cdot}$$

$$RO\,\overline{SO}_3 + H_2O \longrightarrow ROH + HSO_4^{-}$$

In the case of isobutyric acid, the $\alpha$-hydrogen atom was attacked followed by decarboxylation to propane. A qualitative study of oxidation of isobutyric acid and its ester has been reported by Fichter and Heer[132].

Oxidative degradation by chromium trioxide in acetic acid was developed as an effective method for the location of a branch in higher saturated carbon chain acids[133]. Detection of end products by gas chromatography indicated that the expected cleavage products were obtained from the branched chain acids. The oxidation of a series of branched alkyl carboxylic acids by Cr(VI) oxide was studied by Rocek[93] who determined the retardation factor due to inductive effect of the carboxyl group.

Besides permanganate, persulphate and chromic acid other oxidants have also been used. A slight attack on isobutyric acid by vanadium in concentrated sulphuric acid has been reported[122]. The oxidation of carboxylic acids by Co(III) was studied by Clifford and Waters[123]. They showed that the rate of oxidation of isobutyric and pivalic acids were of the first order with respect to the concentrations of the organic acid and inversely proportional to the concentration of the perchloric acid. Acetone was detected to be the oxidation product of isobutyric acid while t-butanol was found in the oxidation of pivalic acid.

# STUDIES WITH ISOBUTYRIC ACID

## Order in Chromic acid

The oxidation rate was measured as a function of chromic acid concentration. In all the experiments the concentration of chromic acid was kept so low in comparison to those of substrate and sulphuric acid concentrations that the latter remained essentially constant during any one run. A slight increase in the rate constant was observed when chromic acid concentration was decreased. The data are given in the tables.

FIG. 1

DEPENDENCE OF RATE CONSTANT ON CHROMIC ACID CONCENTRATION

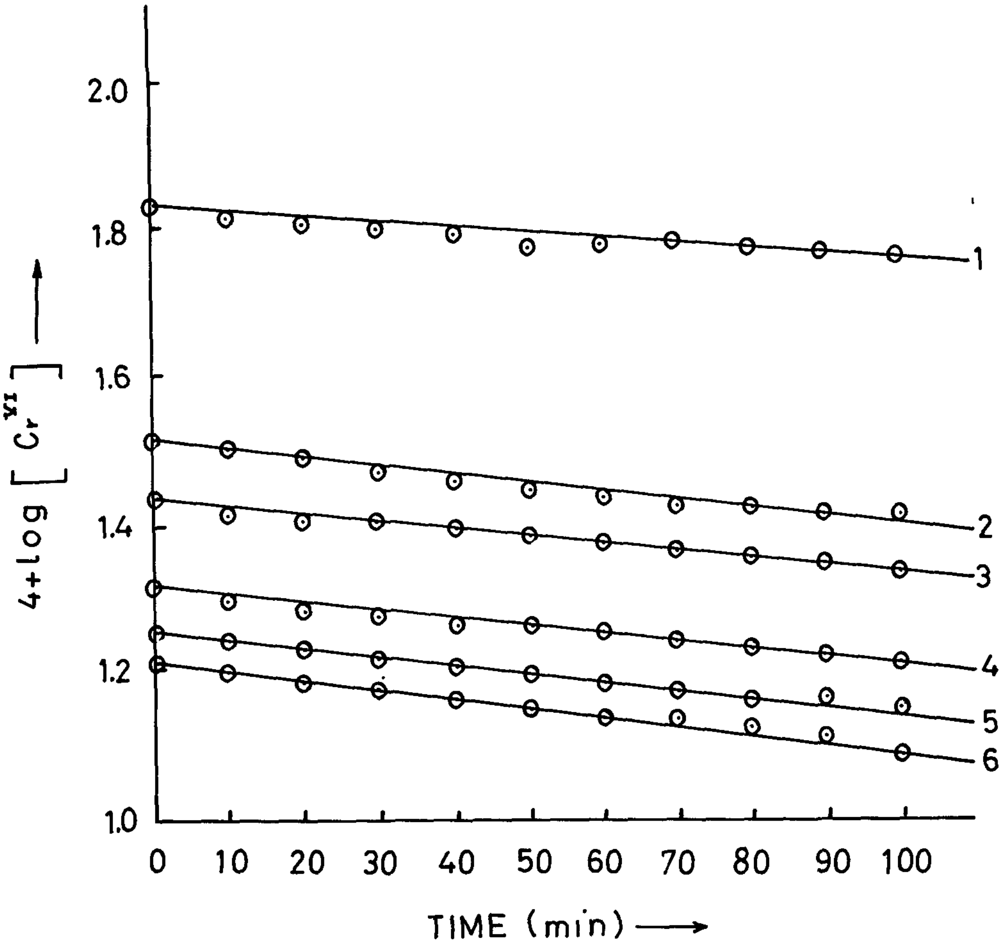


Table - I.

Dependence of rate constant on chromic acid concentration.

Temp.= 75 ± .1°C; $[H_2SO_4]$ = 5.0M; [Isobutyric acid] = 0.1M

| [Chromic acid] | $66.66 \times 10^{-4}$M | | $33.33 \times 10^{-4}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 66.66 | 1.823 | 33.33 | 1.522 |
| 10 | 64.30 | 1.808 | 31.70 | 1.501 |
| 20 | 62.86 | 1.798 | 30.78 | 1.488 |
| 30 | 61.94 | 1.791 | 29.65 | 1.472 |
| 40 | 60.88 | 1.784 | 29.02 | 1.462 |
| 50 | 60.24 | 1.779 | 28.60 | 1.456 |
| 60 | 59.45 | 1.774 | 28.31 | 1.452 |
| 70 | 58.93 | 1.770 | 28.03 | 1.447 |
| 80 | 58.24 | 1.765 | 27.46 | 1.438 |
| 90 | 57.75 | 1.761 | 26.90 | 1.429 |
| 100 | 56.96 | 1.755 | 26.20 | 1.418 |
| Rate constant (min.$^{-1}$) | $1.98 \times 10^{-3}$ | | $2.00 \times 10^{-3}$ | |
| Fig. 1. | Curve 1 | | Curve 2 | |

Table - II.

Dependence of rate constant on chromic acid concentration.

Temp.= 75 ± .1°C; [$H_2SO_4$]= 5.0M; [Isobutyric acid]= 0.1M

| [chromic acid] | $27.77 \times 10^{-4}$M | | $20.83 \times 10^{-4}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 27.77 | 1.443 | 20.83 | 1.318 |
| 10 | 26.85 | 1.429 | 20.12 | 1.303 |
| 20 | 26.10 | 1.416 | 19.53 | 1.290 |
| 30 | 25.64 | 1.409 | 19.08 | 1.280 |
| 40 | 25.18 | 1.401 | 18.70 | 1.272 |
| 50 | 24.77 | 1.393 | 18.28 | 1.262 |
| 60 | 24.18 | 1.383 | 17.83 | 1.251 |
| 70 | 23.72 | 1.375 | 17.45 | 1.242 |
| 80 | 23.26 | 1.366 | 17.16 | 1.234 |
| 90 | 22.64 | 1.354 | 16.53 | 1.218 |
| 100 | 22.00 | 1.342 | 16.00 | 1.204 |
| Rate constant (min.$^{-1}$) | $2.17 \times 10^{-3}$ | | $2.43 \times 10^{-3}$ | |
| Fig. 1. | Curve 3. | | Curve 4. | |

**Table - III.**

Dependence of rate constant on chromic acid concentration.

Temp.= 75° ± .1°C; $[H_2SO_4]$= 4.0M; [Isobutyric acid]= 0.1M

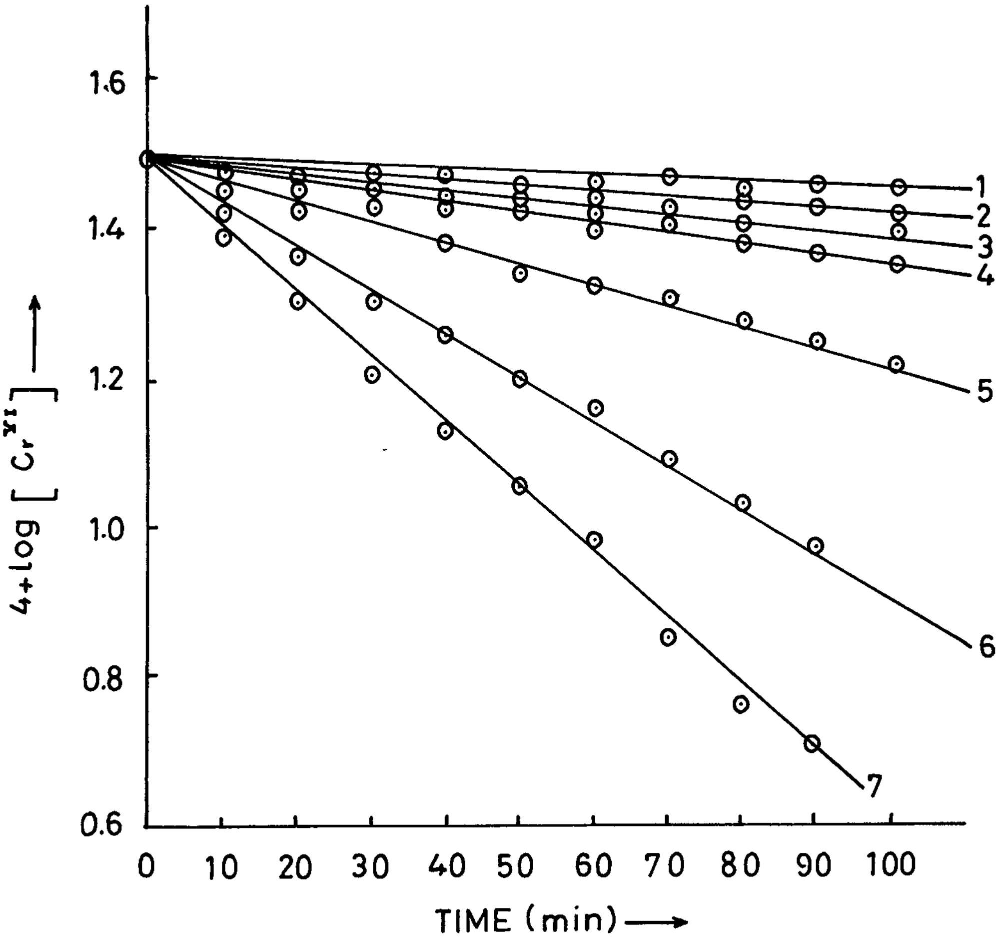
| [Chromic acid] | $18.51 \times 10^{-4}$ M | | $16.66 \times 10^{-4}$ M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 18.51 | 1.267 | 16.66 | 1.221 |
| 10 | 17.77 | 1.249 | 15.94 | 1.202 |
| 20 | 17.37 | 1.239 | 15.51 | 1.190 |
| 30 | 16.66 | 1.221 | 15.18 | 1.181 |
| 40 | 16.30 | 1.212 | 14.70 | 1.167 |
| 50 | 16.04 | 1.205 | 14.33 | 1.156 |
| 60 | 15.70 | 1.196 | 13.97 | 1.145 |
| 70 | 15.33 | 1.185 | 13.58 | 1.133 |
| 80 | 15.00 | 1.176 | 13.24 | 1.122 |
| 90 | 14.45 | 1.160 | 12.94 | 1.112 |
| 100 | 14.32 | 1.155 | 12.52 | 1.097 |
| Rate constant ($min.^{-1}$) | $2.37 \times 10^{-3}$ | | $2.63 \times 10^{-3}$ | |
| Fig. 1. | Curve 5. | | Curve 6. | |

## Order in Isobutyric acid

To determine the order with reference to isobutyric acid, experiments were performed with different concentrations of the substrate keeping the other factors constant. The order was inferred from the plot of rate constant Vs. isobutyric acid concentration. The straight line passing through the origin indicated the first order dependence on the substrate.

FIG. 2

EFFECT OF RATE CONSTANT ON ISOBUTYRIC ACID CONCENTRATION



### Table - IV.

Dependence of rate constant on the concentration of isobutyric acid.

Temp.= 70 ± .1°C; $[H_2SO_4]$= 5.0M; $[Cr^{VI}]$= 33.33 x $10^{-4}$M.

| [Isobutyric acid] | 4.0 x $10^{-2}$M | | 5.0 x $10^{-2}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 10 | 31.84 | 1.503 | 31.27 | 1.495 |
| 20 | 31.45 | 1.497 | 30.63 | 1.486 |
| 30 | 31.20 | 1.494 | 30.24 | 1.480 |
| 40 | 31.00 | 1.491 | 29.86 | 1.475 |
| 50 | 30.81 | 1.488 | 29.73 | 1.473 |
| 60 | 30.54 | 1.485 | 29.54 | 1.470 |
| 70 | 30.30 | 1.481 | 29.00 | 1.462 |
| 80 | 29.97 | 1.476 | 28.90 | 1.460 |
| 90 | 29.71 | 1.472 | 28.64 | 1.457 |
| 100 | 29.45 | 1.469 | 28.25 | 1.451 |
| Rate constant (min.$^{-1}$) | 0.85 x $10^{-3}$ | | 1.06 x $10^{-3}$ | |
| Fig. 2. | Curve 1. | | Curve 2. | |

Table - V.

Dependence of rate constant on the concentration of isobutyric acid.

Temp.= 70 ± .1°C; $[H_2SO_4]$= 5.0M; $[Cr^{VI}]$= $33.33 \times 10^{-4}$M.

| [Isobutyric acid] | $10.0 \times 10^{-2}$M | | $25.0 \times 10^{-2}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 10 | 30.67 | 1.486 | 31.60 | 1.499 |
| 20 | 30.28 | 1.481 | 30.41 | 1.483 |
| 30 | 29.62 | 1.471 | 28.82 | 1.459 |
| 40 | 29.02 | 1.462 | 27.63 | 1.441 |
| 50 | 28.23 | 1.450 | 27.00 | 1.431 |
| 60 | 27.56 | 1.440 | 26.40 | 1.423 |
| 70 | 27.23 | 1.435 | 25.84 | 1.412 |
| 80 | 26.76 | 1.427 | 24.90 | 1.396 |
| 90 | 26.30 | 1.420 | 24.31 | 1.385 |
| 100 | 25.90 | 1.413 | 23.98 | 1.381 |
| Rate constant (min.$^{-1}$) | $2.07 \times 10^{-3}$ | | $3.94 \times 10^{-3}$ | |
| Fig. 2. | Curve 3. | | Curve 4. | |

## Table - VI.

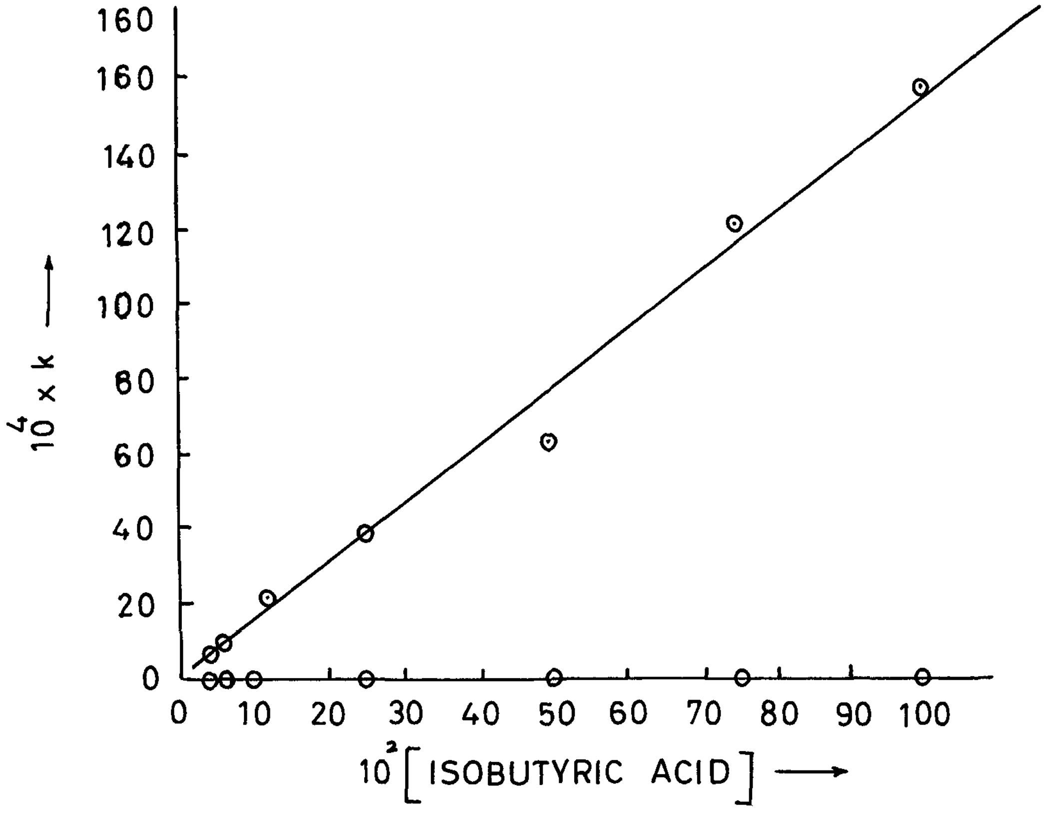
Dependence of rate constant on the concentration of isobutyric acid.

Temp.= 70 ± .1°C; $[H_2SO_4]$= 5.0M; $[Cr^{VI}]$ = $33.33 \times 10^{-4}$M.

| [Isobutyric acid] | $50.0 \times 10^{-2}$M | | $75.0 \times 10^{-2}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 10 | 30.28 | 1.481 | 28.08 | 1.448 |
| 20 | 28.08 | 1.448 | 24.28 | 1.385 |
| 30 | 26.13 | 1.417 | 21.10 | 1.324 |
| 40 | 24.57 | 1.390 | 18.88 | 1.276 |
| 50 | 23.14 | 1.364 | 16.90 | 1.228 |
| 60 | 21.98 | 1.342 | 15.59 | 1.193 |
| 70 | 20.87 | 1.319 | 12.69 | 1.103 |
| 80 | 19.84 | 1.297 | 11.28 | 1.053 |
| 90 | 18.28 | 1.262 | 9.93 | 0.997 |
| 100 | 17.05 | 1.231 | - | - |
| Rate constant (min.$^{-1}$) | $6.50 \times 10^{-3}$ | | $12.15 \times 10^{-3}$ | |
| Fig. 2. | Curve 5. | | Curve 6. | |

FIRST ORDER DEPENDENCE OF RATE CONSTANT ON ISOBUTYRIC ACID CONCENTRATION

FIG. 3



## Table - VII.

Dependence of rate constant on the concentration of isobutyric acid.

Temp.= 70 ± .1°C $[H_2SO_4]$= 5.0M; $[Cr^{VI}]$= 33.33 x $10^{-4}$M.

| [Isobutyric acid] | 100.0 x $10^{-2}$M | |
|---|---|---|
| Time (mins.) | $10^4[Cr^{VI}]$(M) | 4 + log $[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 |
| 10 | 25.60 | 1.408 |
| 20 | 21.24 | 1.327 |
| 30 | 15.61 | 1.193 |
| 40 | 13.83 | 1.40 |
| 50 | 11.06 | 1.070 |
| 60 | 9.83 | 0.992 |
| 70 | 7.20 | 0.857 |
| 80 | 5.98 | 0.777 |
| 90 | 5.20 | 0.716 |
| 100 | 4.84 | 0.684 |
| Rate constant (min.$^{-1}$) | 15.84 x $10^{-3}$ | |

Fig. 2. Curve 7.

## Variation of rate constant with hydrogen ion concentration

At high acidities it is difficult to study the influence of hydrogen ions on the reaction velocity by varying the pH of the medium. Nevertheless, hydrogen ions as such have been varied by varying the sulphuric acid content of the reaction mixture. The ionic strength was adjusted by sodium hydrogen sulphate. The rate constants at various concentrations of sulphuric acid are registered below. The rate constants obtained by dividing pseudo first order rate constants by corresponding hydrogen ion concentration and by the square of hydrogen ion concentration are shown in table XI. It is seen that the order of the reaction is two with respect to hydrogen ions.

FIG. 4

ACIDITY DEPENDENCE OF THE REACTION RATE

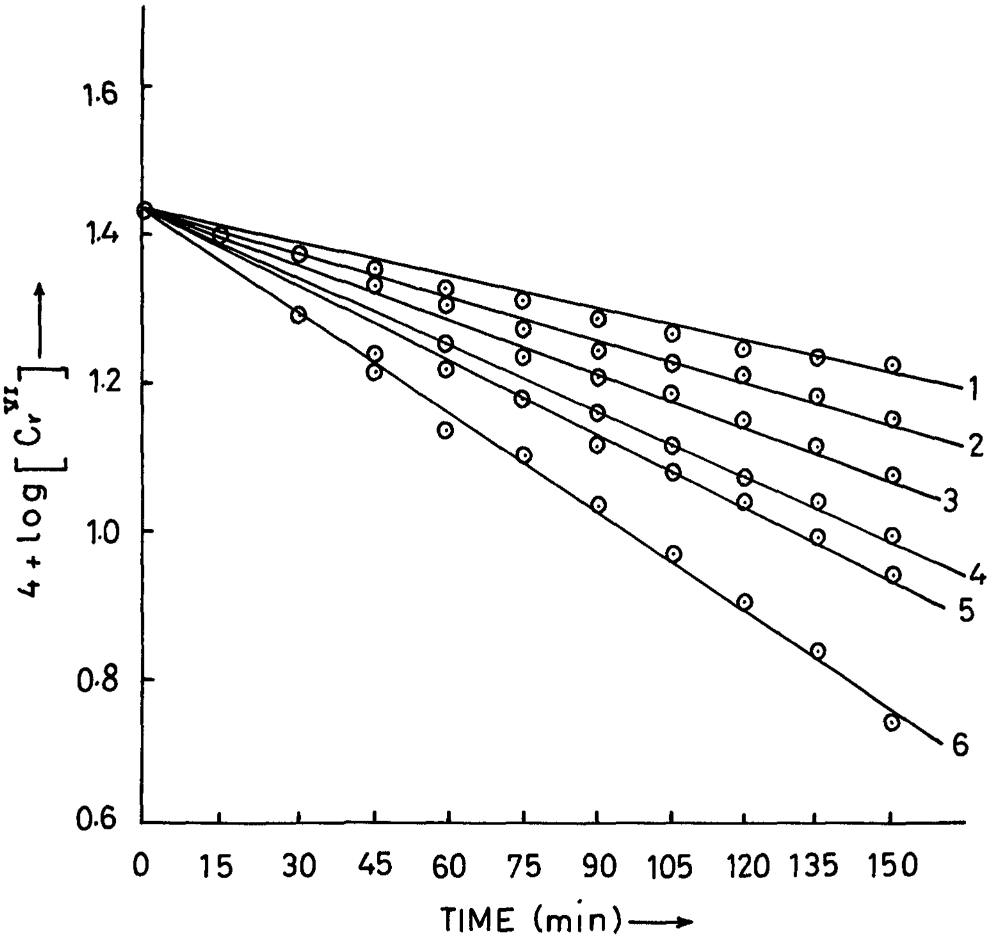


Table - VIII.

Acidity dependence of the oxidation rate.

Temp.= 75 ± .1°C $[H_2SO_4] + [NaHSO_4] = 6.0M$;

$[\text{Isobutyric acid}] = 0.2M$ $[Cr^{VI}] = 26.66 \times 10^{-4}M$.

| $[H_2SO_4]$ | 3.0M | | 3.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$ | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.426 |
| 15 | 24.74 | 1.393 | 23.93 | 1.360 |
| 30 | 23.22 | 1.365 | 22.25 | 1.347 |
| 45 | 22.20 | 1.346 | 21.20 | 1.326 |
| 60 | 21.00 | 1.322 | 20.24 | 1.306 |
| 75 | 20.12 | 1.300 | 19.12 | 1.281 |
| 90 | 19.13 | 1.281 | 18.17 | 1.260 |
| 105 | 18.45 | 1.266 | 17.16 | 1.234 |
| 120 | 17.50 | 1.243 | 16.50 | 1.217 |
| 135 | 17.10 | 1.233 | 15.70 | 1.196 |
| 150 | 16.68 | 1.222 | 14.93 | 1.174 |
| Rate constant (min.$^{-1}$) | $3.18 \times 10^{-3}$ | | $3.72 \times 10^{-3}$ | |
| Fig. 4. | Curve 1. | | Curve 2. | |

Table - IX.

Temp.= 75 ± .1°C $[H_2SO_4]$ + $[NaHSO_4]$ = 6.0M;
$[\text{Isobutyric acid}]$ = 0.2M; $[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| $[H_2SO_4]$ | 4.0M | | 4.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 15 | 22.38 | 1.349 | 21.58 | 1.342 |
| 30 | 20.50 | 1.311 | 19.45 | 1.289 |
| 45 | 18.86 | 1.275 | 18.04 | 1.256 |
| 60 | 17.70 | 1.247 | 16.28 | 1.211 |
| 75 | 16.58 | 1.219 | 15.20 | 1.182 |
| 90 | 15.80 | 1.198 | 14.23 | 1.153 |
| 105 | 15.12 | 1.179 | 13.05 | 1.115 |
| 120 | 13.88 | 1.142 | 11.80 | 1.071 |
| 135 | 12.90 | 1.110 | 11.06 | 1.043 |
| 150 | 12.10 | 1.082 | 10.15 | 1.006 |
| Rate constant (min.$^{-1}$) | 4.70 x $10^{-3}$ | | 5.60 x $10^{-3}$ | |
| Fig. 4. | Curve 3. | | Curve 4. | |

Table - X.

Acidity dependence of the oxidation rate.

Temp.= 75 ± .1°C $[H_2SO_4] + [NaHSO_4] = 6.0M$;

$[\text{Isobutyric acid}] = 0.2M$; $[Cr^{VI}] = 26.66 \times 10^{-4} M$.

| $[H_2SO_4]$ | 5.0M | | 5.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.426 |
| 15 | 21.46 | 1.331 | 20.63 | 1.314 |
| 30 | 19.20 | 1.283 | 17.70 | 1.248 |
| 45 | 17.00 | 1.230 | 15.63 | 1.194 |
| 60 | 15.80 | 1.198 | 13.68 | 1.136 |
| 75 | 14.30 | 1.155 | 12.64 | 1.101 |
| 90 | 13.33 | 1.125 | 11.32 | 1.053 |
| 105 | 11.97 | 1.078 | 9.54 | 0.979 |
| 120 | 11.00 | 1.046 | 8.16 | 0.911 |
| 135 | 9.83 | 0.992 | 7.12 | 0.852 |
| 150 | 8.98 | 0.953 | 5.57 | 0.746 |
| Rate constant (min.$^{-1}$) | $6.47 \times 10^{-3}$ | | $9.65 \times 10^{-3}$ | |
| Fig. 4. | Curve 5. | | Curve 6. | |

Table - XI.

Effect of acidity on the rate constant.

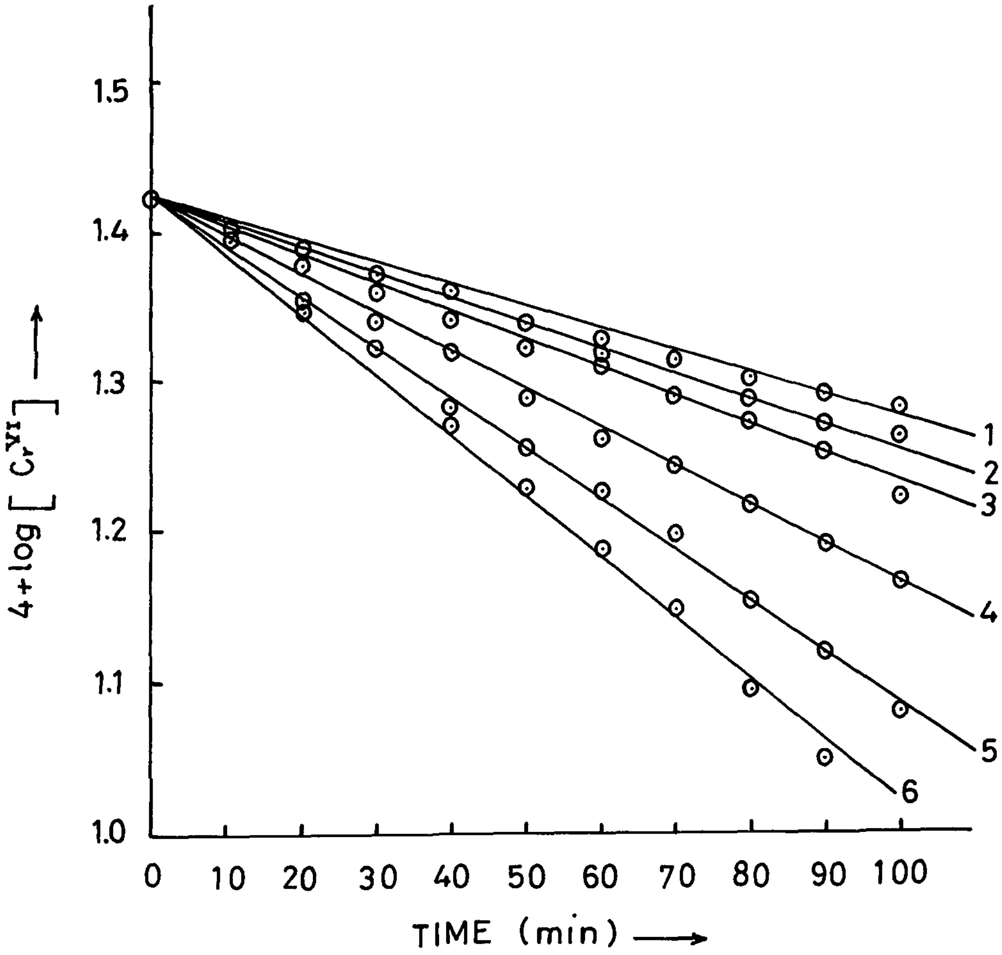
| $[H^+]$ (M) | $[H^+]^2$ | $k \times 10^3$ ($min.^{-1}$) | $\frac{k}{[H^+]} \times 10^3$ ($l.mole^{-1} min^{-1}$) | $\frac{k}{[H^+]^2} \times 10^4$ ($l^2.mole^{-2} min^{-1}$) |
|---|---|---|---|---|
| 3.0 | 9.00 | 3.18 | 1.06 | 3.53 |
| 3.5 | 12.25 | 3.72 | 1.07 | 3.03 |
| 4.0 | 16.00 | 4.70 | 1.17 | 2.93 |
| 4.5 | 20.25 | 5.80 | 1.28 | 2.86 |
| 5.0 | 25.00 | 6.47 | 1.29 | 2.58 |
| 5.5 | 30.25 | 9.65 | 1.75 | 3.19 |

## Temperature dependence

The oxidation of isobutyric acid was studied at six different temperatures under identical conditions of reactants concentrations and ionic strength. The plot of log k Vs. $\frac{1}{T}$ yielded a straight line and the energy of activation was calculated from the slope. The value was found to 14.7 Kcal. The other thermodynamic parameters i.e. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated from the equations given in Chapter II and the values are 14.0 Kcal and -37.5 eu. respectivly.

FIG. 5

TEMPERATURE DEPENDENCE OF THE REACTION RATE



### Table - XII.

Temperature dependence of the oxidation rate.

$[H_2SO_4] = 5.0M$; [Isobutyric acid] $= 0.2M$; $[Cr^{VI}] = 26.66 \times 10^{-4}M$.

| Temperature | 338°K | | 343°K | |
|---|---|---|---|---|
| Time (mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 25.74 | 1.410 | 25.72 | 1.410 |
| 20 | 24.92 | 1.396 | 24.80 | 1.394 |
| 30 | 24.10 | 1.382 | 23.90 | 1.378 |
| 40 | 23.18 | 1.365 | 23.28 | 1.367 |
| 50 | 22.26 | 1.347 | 22.50 | 1.352 |
| 60 | 21.64 | 1.335 | 21.77 | 1.338 |
| 70 | 21.03 | 1.322 | 21.20 | 1.326 |
| 80 | 20.46 | 1.311 | 20.53 | 1.312 |
| 90 | 20.06 | 1.302 | 19.90 | 1.299 |
| 100 | 19.60 | 1.292 | 19.23 | 1.284 |
| Rate constant ($min.^{-1}$) | $2.32 \times 10^{-3}$ | | $3.10 \times 10^{-3}$ | |
| Fig. 5. | Curve 1. | | Curve 2. | |

Table - XIII.

Temperature dependence of the oxidation rate.

$[H_2SO_4]$ = 5.0M; [Isobutyric acid] = 0.2M; $[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| Temperature | 348°K | | 353°K | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 25.50 | 1.406 | 24.94 | 1.397 |
| 20 | 24.42 | 1.387 | 23.23 | 1.366 |
| 30 | 23.62 | 1.373 | 22.15 | 1.345 |
| 40 | 22.72 | 1.356 | 20.97 | 1.321 |
| 50 | 21.65 | 1.335 | 19.85 | 1.297 |
| 60 | 20.74 | 1.316 | 18.72 | 1.272 |
| 70 | 19.90 | 1.298 | 17.86 | 1.252 |
| 80 | 19.03 | 1.279 | 16.84 | 1.226 |
| 90 | 18.23 | 1.261 | 15.77 | 1.197 |
| 100 | 17.12 | 1.233 | 14.90 | 1.173 |
| Rate constant (min.$^{-1}$) | 4.00 x $10^{-3}$ | | 5.60 x $10^{-3}$ | |

Fig. 5. Curve 3. Curve 4.

FIG. 6

ACTIVATION ENERGY

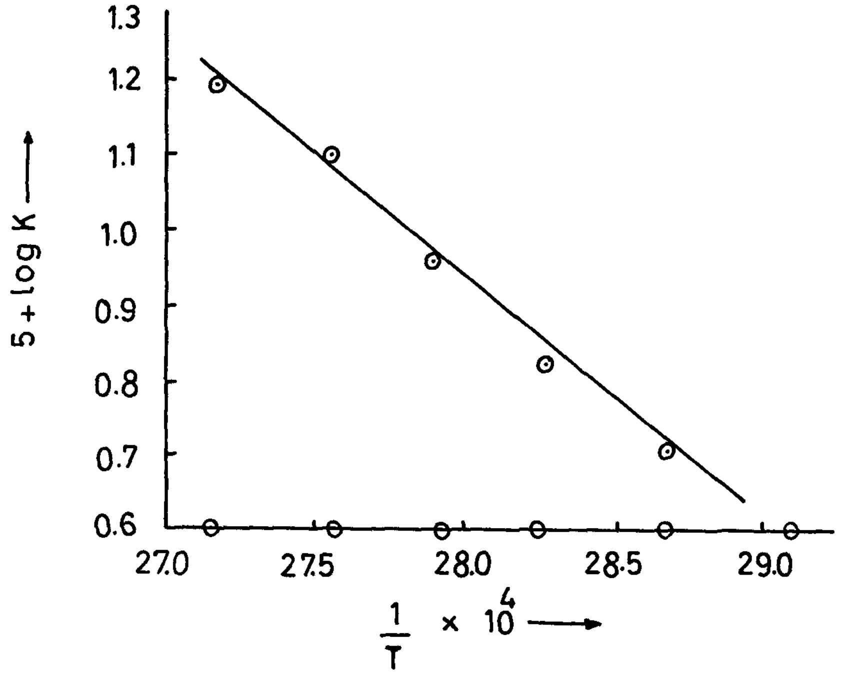


Table - XIV

Temperature dependence of the oxidation rate.

$[H_2SO_4]$= 5.0M, [Isobutyric acid]= 0.2M.
$[Cr^{VI}]$= 26.66 x $10^{-4}$M.

| Temperature | 358°K |  | 363°K |  |
|---|---|---|---|---|
| Time (mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 24.77 | 1.394 | 24.74 | 1.393 |
| 20 | 22.77 | 1.357 | 22.50 | 1.352 |
| 30 | 21.10 | 1.324 | 20.94 | 1.321 |
| 40 | 19.60 | 1.292 | 19.23 | 1.284 |
| 50 | 18.35 | 1.263 | 17.51 | 1.243 |
| 60 | 17.25 | 1.236 | 15.80 | 1.198 |
| 70 | 16.10 | 1.206 | 14.40 | 1.158 |
| 80 | 14.35 | 1.157 | 12.63 | 1.101 |
| 90 | 13.36 | 1.125 | 10.70 | 1.029 |
| 100 | 12.25 | 1.088 | 9.66 | 0.984 |
| Rate constant (min.$^{-1}$) | 7.56 x $10^{-3}$ |  | 9.37 x $10^{-3}$ |  |

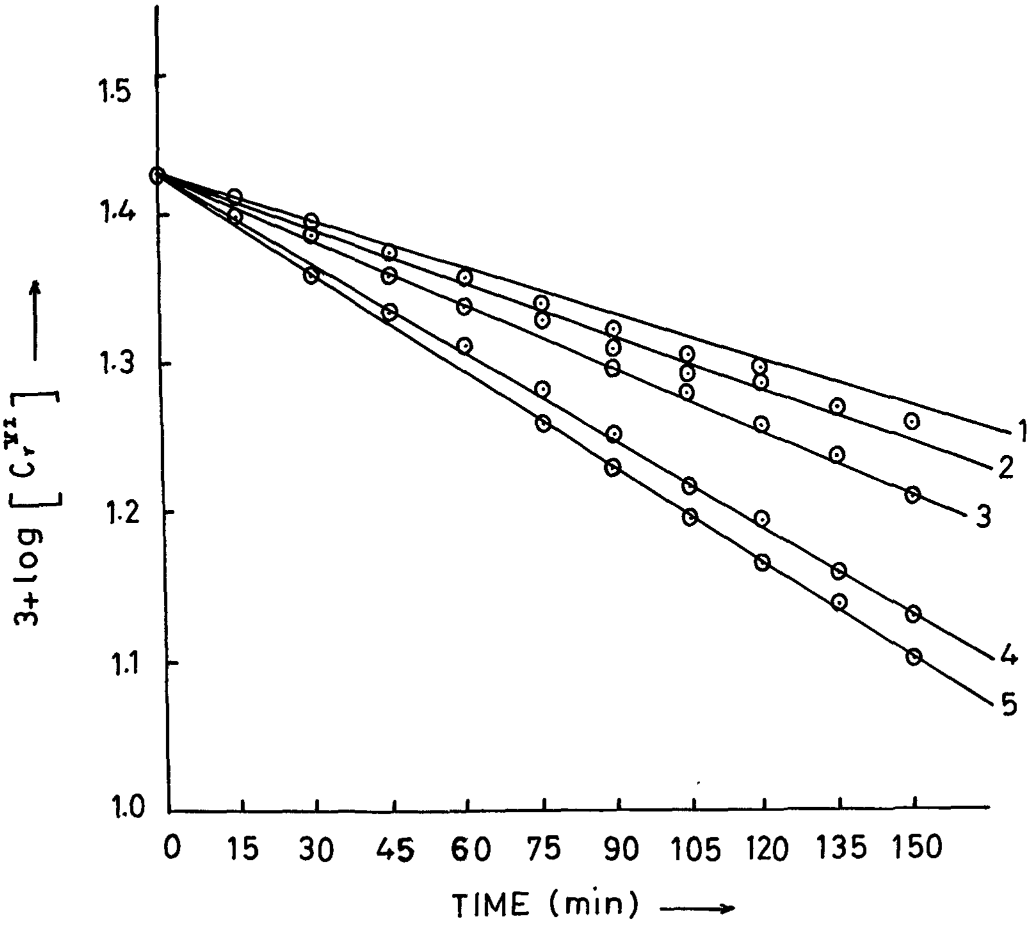
Fig. 5. Curve 5. Curve 6.

## Variation with ionic strength

The method of calculation applied to evaluate the ionic strength has been described earlier. Studies with isobutyric acid show a positive salt effect. However, the plot of $\mu^{1/2}$ Vs-log K do not give any information about the reaction mechanism. The tables below record the observations at various ionic strengths.

FIG. 7

DEPENDENCE OF REACTION RATE ON IONIC STRENGTH



### Table - XV.

Effect of ionic strength on the rate constant.

Temp. 75 ± .1°C $[H_2SO_4]$= 4.5M; [Isobutyric acid]= 0.2M;
$[Cr^{VI}]$= 26.66 x $10^{-4}$M.

| $[NaClO_4]$ | Nil | | 0.5M | |
|---|---|---|---|---|
| Ionic strength | 4.5M | | 5.0M | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 15 | 25.30 | 1.403 | 25.68 | 1.410 |
| 30 | 24.18 | 1.383 | 23.83 | 1.377 |
| 45 | 22.88 | 1.359 | 22.87 | 1.359 |
| 60 | 22.18 | 1.346 | 22.00 | 1.342 |
| 75 | 21.48 | 1.332 | 21.15 | 1.325 |
| 90 | 20.77 | 1.317 | 20.20 | 1.305 |
| 105 | 20.07 | 1.301 | 19.28 | 1.285 |
| 120 | 19.43 | 1.288 | 18.42 | 1.265 |
| 135 | 18.90 | 1.276 | 17.56 | 1.245 |
| 150 | 18.40 | 1.264 | 16.70 | 1.222 |
| Rate constant (min.$^{-1}$) | 2.56 x $10^{-3}$ | | 3.00 x $10^{-3}$ | |
| Fig. 7. | Curve 1. | | Curve 2. | |

Table - XVI.

Effect of ionic strength on the rate constant

Temp. 75 ± .1°C $[H_2SO_4]$ = 4.5M; [Isobutyric acid] = 0.2M;
$[Cr^{VI}]$ = 26.66 x $10^{-4}$M

| $[NaClO_4]$ | 1.0M | | 1.5M | |
|---|---|---|---|---|
| [Ionic strength] | 5.5M | | 6.0M | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.426 | 26.66 | 1.425 |
| 15 | 25.53 | 1.407 | 24.86 | 1.395 |
| 30 | 23.36 | 1.368 | 23.35 | 1.368 |
| 45 | 22.34 | 1.349 | 22.05 | 1.343 |
| 60 | 21.20 | 1.326 | 20.90 | 1.320 |
| 75 | 20.10 | 1.303 | 19.44 | 1.288 |
| 90 | 19.07 | 1.280 | 18.30 | 1.262 |
| 105 | 18.32 | 1.262 | 16.90 | 1.227 |
| 120 | 17.47 | 1.242 | 15.84 | 1.199 |
| 135 | 16.62 | 1.220 | 14.68 | 1.166 |
| 150 | 15.50 | 1.190 | 13.53 | 1.131 |
| Rate constant ($min.^{-1}$) | 3.38 x $10^{-3}$ | | 4.60 x $10^{-3}$ | |
| Fig. 7. | Curve 3. | | Curve 4. | |

Table - XVII.

Effect of ionic strength on the rate constant.

Temp. 75 ± .1°C $[H_2SO_4] = 4.5M$; $[\text{Isobutyric acid}] = 0.2M$; $[Cr^{VI}] = 26.66 \times 10^{-4} M$.

| $[NaClO_4]$ | 2.0M | |
|---|---|---|
| Ionic strength | 6.5M | |
| Time(mins.) | $10^4 [Cr^{VI}]$ (M) | $4 + \log [Cr^{VI}]$ |
| 0 | 26.66 | 1.425 |
| 15 | 24.90 | 1.396 |
| 30 | 23.32 | 1.367 |
| 45 | 21.90 | 1.340 |
| 60 | 19.37 | 1.287 |
| 75 | 17.38 | 1.252 |
| 90 | 16.00 | 1.204 |
| 105 | 15.62 | 1.193 |
| 120 | 14.12 | 1.160 |
| 135 | 13.04 | 1.115 |
| 150 | 12.34 | 1.091 |
| Rate constant (min.$^{-1}$) | $5.20 \times 10^{-3}$ | |

Fig. 7. Curve 5.

FIG. 8

EFFECT OF ACETIC ACID ON THE OXIDATION RATE

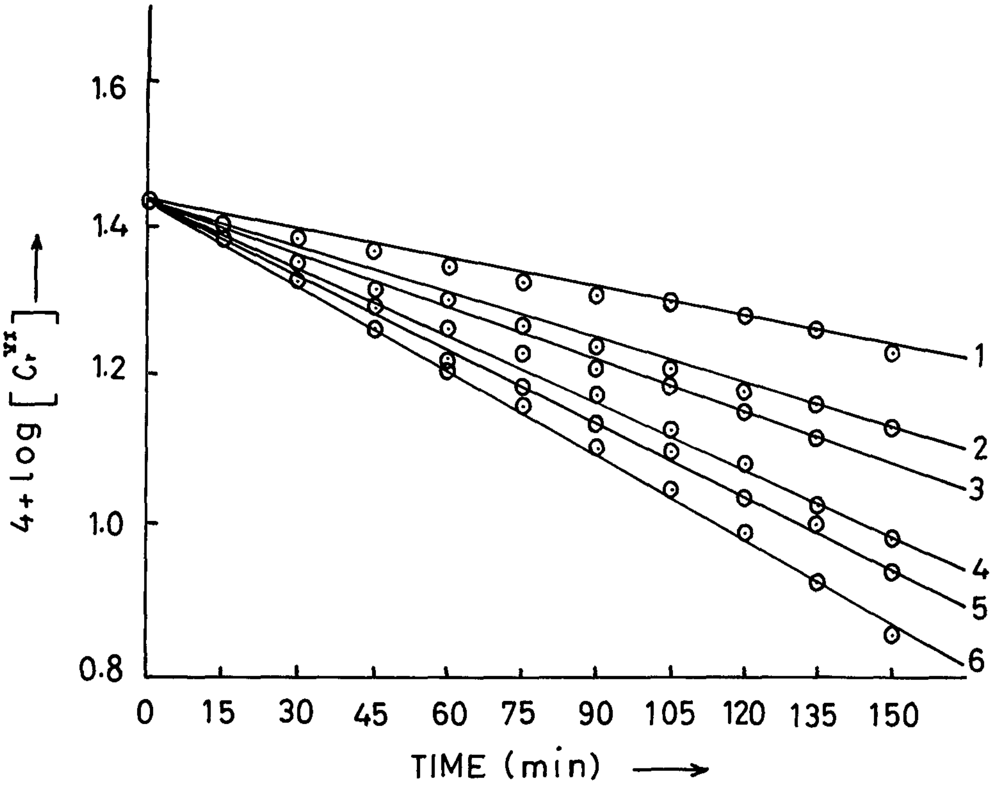


Table - XVIII.

Influence of acetic acid on the rate of oxidation.

Temp. 75 ± .1°C $[H_2SO_4]$ = 5.0M; [Isobutyric acid] = 0.2M;
$[Cr^{VI}] = 26.66 \times 10^{-4}$M.

| [Acetic acid] | NIL | | 0.1M | |
|---|---|---|---|---|
| Time (mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.426 |
| 15 | 25.50 | 1.406 | 24.34 | 1.386 |
| 30 | 24.43 | 1.387 | 22.65 | 1.355 |
| 45 | 23.62 | 1.373 | 21.23 | 1.327 |
| 60 | 22.72 | 1.356 | 19.95 | 1.300 |
| 75 | 21.65 | 1.335 | 18.95 | 1.277 |
| 90 | 20.74 | 1.316 | 17.63 | 1.246 |
| 105 | 19.98 | 1.301 | 16.26 | 1.211 |
| 120 | 19.03 | 1.279 | 15.10 | 1.179 |
| 135 | 18.24 | 1.261 | 14.52 | 1.162 |
| 150 | 17.12 | 1.233 | 13.57 | 1.132 |
| Rate constant (min.$^{-1}$) | $4.00 \times 10^{-3}$ | | $4.95 \times 10^{-3}$ | |
| Fig. 8. | Curve 1. | | Curve 2. | |

Table - XIX.

Influence of acetic acid on the rate of oxidation.

Temp. 75 ± .1°C $[H_2SO_4]$= 5.0M; [Isobutyric acid]= 0.2M;
$[Cr^{VI}]$= 26.66 x $10^{-4}$M.

| [Acetic acid] | 0.2M | | 0.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 15 | 24.03 | 1.380 | 23.44 | 1.370 |
| 30 | 22.14 | 1.345 | 21.80 | 1.338 |
| 45 | 20.50 | 1.312 | 20.34 | 1.308 |
| 60 | 19.03 | 1.280 | 18.34 | 1.263 |
| 75 | 18.20 | 1.260 | 17.07 | 1.232 |
| 90 | 16.68 | 1.227 | 15.33 | 1.185 |
| 105 | 15.78 | 1.198 | 13.75 | 1.138 |
| 120 | 14.62 | 1.165 | 12.38 | 1.093 |
| 135 | 13.40 | 1.127 | 10.86 | 1.036 |
| 150 | 12.35 | 1.092 | 9.90 | 0.995 |
| Rate constant (min.$^{-1}$) | 5.68 x $10^{-3}$ | | 6.90 x $10^{-3}$ | |
| Fig. 8. | Curve 3. | | Curve 4. | |

Table - XX.

Influence of acetic acid on the rate of oxidation.

Temp. 75 ± .1°C $[H_2SO_4]$ = 5.0M; [Isobutyric acid] = 0.2M; $[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| [Acetic acid] | 0.7M | | 1.0M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 22.78 | 1.357 | 21.64 | 1.335 |
| 20 | 20.38 | 1.309 | 19.23 | 1.284 |
| 30 | 18.14 | 1.258 | 17.36 | 1.239 |
| 40 | 16.82 | 1.225 | 15.97 | 1.203 |
| 50 | 15.33 | 1.185 | 14.26 | 1.154 |
| 60 | 13.73 | 1.137 | 12.66 | 1.102 |
| 70 | 12.50 | 1.097 | 11.00 | 1.041 |
| 80 | 11.44 | 1.058 | 9.83 | 0.992 |
| 90 | 10.16 | 1.007 | 8.44 | 0.926 |
| 100 | 9.88 | 0.994 | 6.90 | 0.838 |
| Rate constant (min.$^{-1}$) | 7.50 x $10^{-3}$ | | 8.94 x $10^{-3}$ | |

Fig. 8. Curve 5. Curve 6.

# STUDIES WITH ISOVALERIC ACID

## Order in Chromic acid

In order to determine the order of reaction with reference to oxidant, experiments were performed varying the concentration of chromic acid at constant isobutyric and sulphuric acid concentrations. The plot of log $[Cr^{VI}]$ Vs. time yielded good straight lines in all the cases. The rate constants were determined from the slopes of these lines and were found to be almost constant indicating first order dependence on oxidant concentration. The rate data are shown below:

FIG. 9

DEPENDENCE OF RATE CONSTANT ON CHROMIC ACID CONCENTRATION

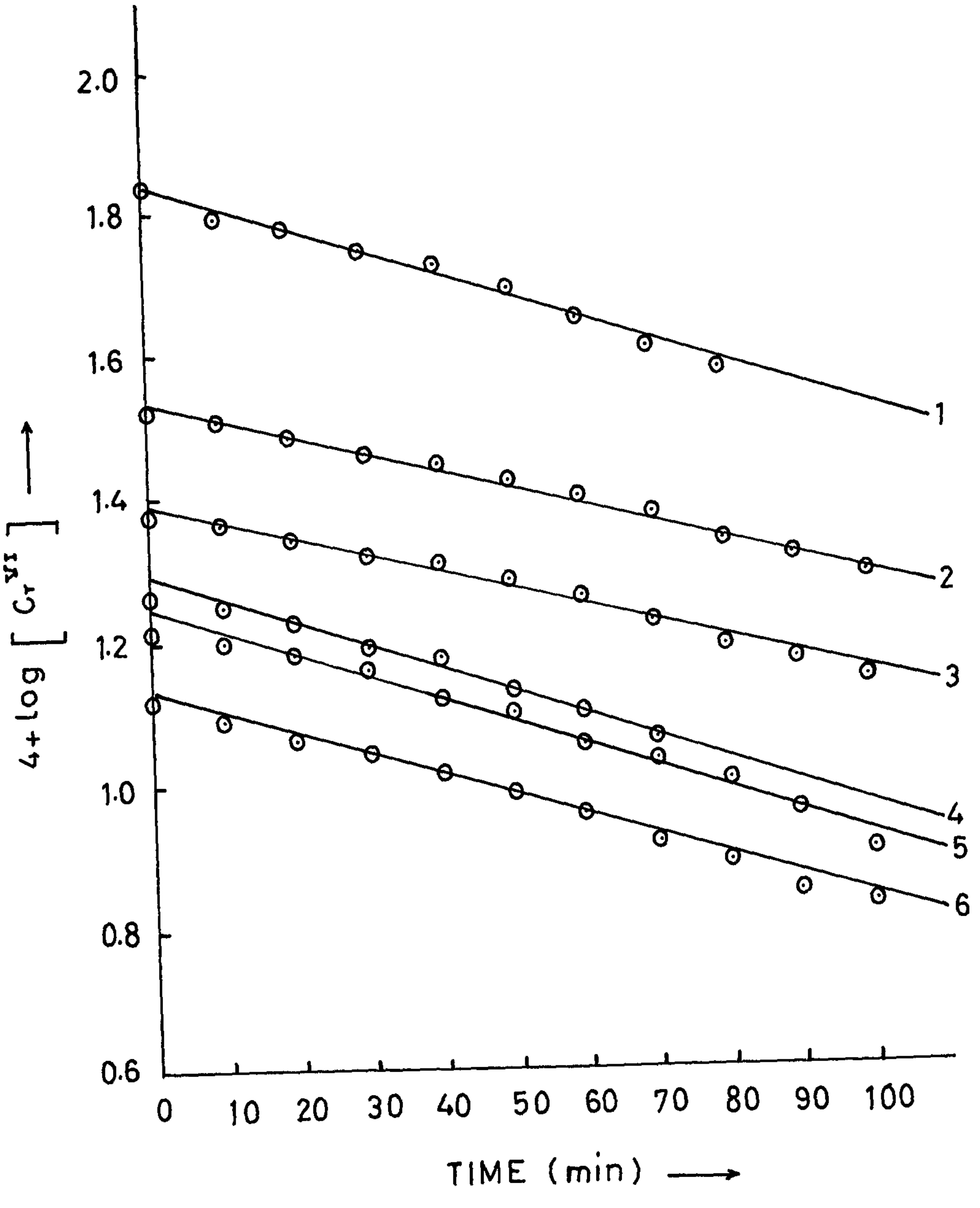


Table - XXI.

Dependence of rate constant on chromic acid concentration.

Temp. 75 ± .1°C; $[H_2SO_4] = 5.0M$; [Isovaleric acid] = 0.1M.

| [Chromic acid] | $66.66 \times 10^{-4}M$ | | $33.33 \times 10^{-4}M$ | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 66.66 | 1.823 | 33.33 | 1.522 |
| 10 | 63.12 | 1.800 | 31.74 | 1.501 |
| 20 | 60.31 | 1.780 | 30.22 | 1.480 |
| 30 | 57.26 | 1.757 | 29.10 | 1.463 |
| 40 | 53.95 | 1.732 | 27.56 | 1.440 |
| 50 | 50.00 | 1.698 | 26.28 | 1.419 |
| 60 | 44.90 | 1.652 | 25.10 | 1.399 |
| 70 | 41.23 | 1.615 | 23.83 | 1.377 |
| 80 | 37.14 | 1.569 | 22.15 | 1.345 |
| 90 | 32.62 | 1.513 | 20.46 | 1.311 |
| 100 | 28.95 | 1.461 | 18.98 | 1.278 |
| Rate constant ($min.^{-1}$) | $6.80 \times 10^{-3}$ | | $6.40 \times 10^{-3}$ | |
| Fig. 9. | Curve 1. | | Curve 2. | |

## Table - XXII.

Dependence of rate constant on chromic acid concentration.

Temp. 75 ± .1°C; $[H_2SO_4]$= 5.0M; [Iso-valeric acid]= 0.1M.

| [Chromic acid] | $23.80 \times 10^{-4}$M | | $18.51 \times 10^{-4}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 23.80 | 1.376 | 18.51 | 1.267 |
| 10 | 23.26 | 1.366 | 17.97 | 1.254 |
| 20 | 22.03 | 1.343 | 16.87 | 1.227 |
| 30 | 21.22 | 1.326 | 16.10 | 1.206 |
| 40 | 20.46 | 1.310 | 14.77 | 1.169 |
| 50 | 19.43 | 1.288 | 13.60 | 1.133 |
| 60 | 18.56 | 1.268 | 12.56 | 1.099 |
| 70 | 17.14 | 1.234 | 11.33 | 1.054 |
| 80 | 15.60 | 1.193 | 10.20 | 1.008 |
| 90 | 14.89 | 1.173 | 9.10 | 0.959 |
| 100 | 13.77 | 1.139 | 7.96 | 0 .901 |
| Rate constant ($min.^{-1}$) | $6.40 \times 10^{-3}$ | | $7.22 \times 10^{-3}$ | |

Fig. 9. Curve 3. Curve 4.

## Table - XXIII

Dependence of rate constant on chromic acid concentration.

Temp. 75 ± .1°C; [$H_2SO_4$] = 5.0M; [Iso-valeric acid] = 0.1M.

| [Chromic acid] | 16.66 x $10^{-4}$M | | 13.33 x $10^{-4}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4$[$Cr^{VI}$](M) | 4+log[$Cr^{VI}$] | $10^4$[$Cr^{VI}$](M) | 4+log[$Cr^{VI}$] |
| 0 | 16.66 | 1.221 | 13.33 | 1.124 |
| 10 | 16.18 | 1.209 | 12.40 | 1.093 |
| 20 | 15.40 | 1.188 | 11.86 | 1.074 |
| 30 | 14.74 | 1.168 | 11.22 | 1.050 |
| 40 | 13.84 | 1.141 | 10.50 | 1.021 |
| 50 | 12.90 | 1.111 | 9.83 | 0.993 |
| 60 | 11.63 | 1.066 | 9.16 | 0.962 |
| 70 | 11.02 | 1.042 | 8.47 | 0.928 |
| 80 | 10.00 | 1.000 | 7.74 | 0.889 |
| 90 | 9.13 | 0.960 | 7.10 | 0.851 |
| 100 | 8.20 | 0.914 | 6.57 | 0.817 |
| Rate constant (min.$^{-1}$) | 7.56 x $10^{-3}$ | | 7.56 x $10^{-3}$ | |
| Fig. 9. | Curve 5. | | Curve 6. | |

## Order in isovaleric acid

The order with respect to isovaleric acid was determined exactly in the same way as in the oxidation of isobutyric acid and found to be unity. The plot of rate constant Vs isovaleric acid concentration is shown in the figure 11 and the data are given in the following tables.

FIG. 10

DEPENDENCE OF RATE CONSTANT ON ISOVALERIC ACID CONCENTRATION

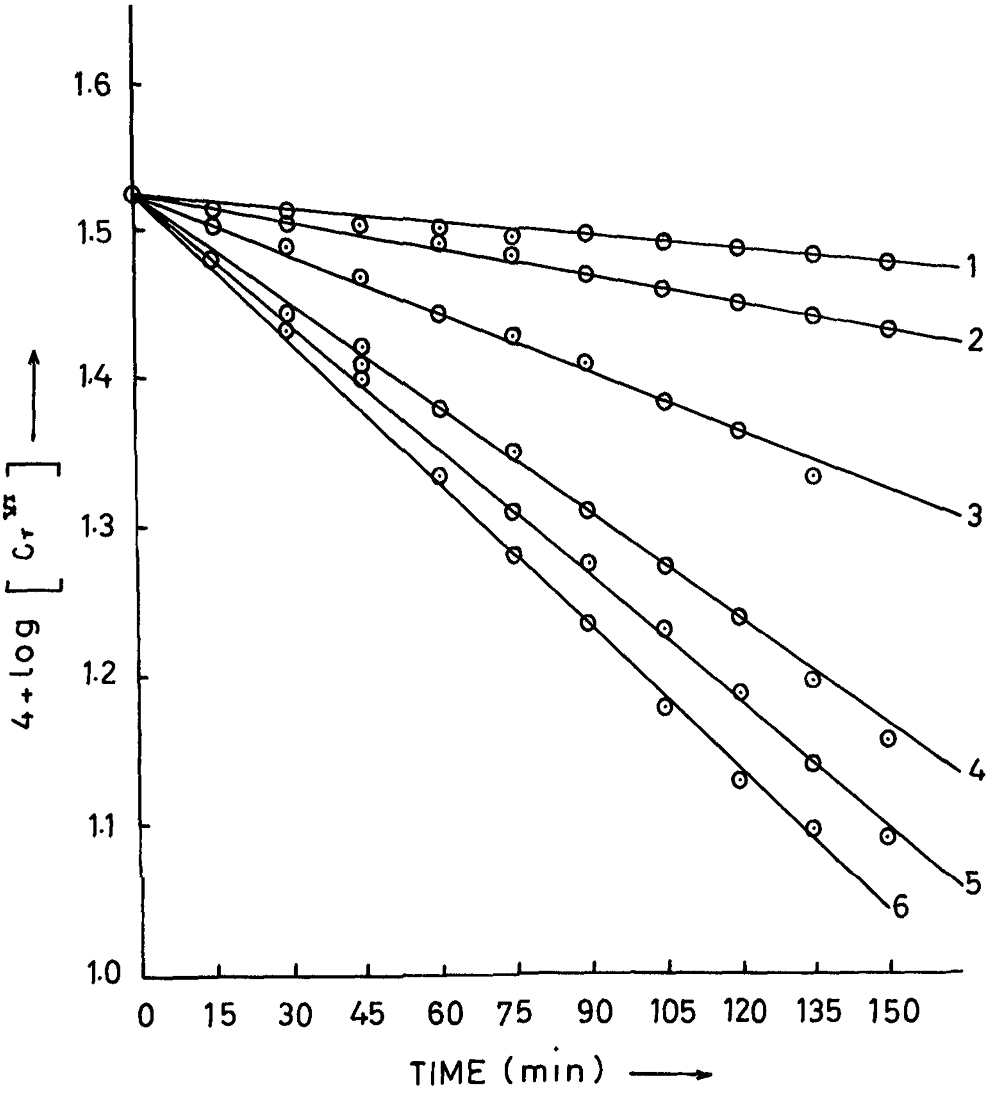


Table - XXIV.

Dependence of rate constant on the concentration of isovaleric acid.

Temp. 75 ± .1°C; $[H_2SO_4] = 5.0M$; $[Cr^{VI}] = 33.33 \times 10^{-4}M$.

| [Isovaleric acid] | $4.0 \times 10^{-2}M$ | | $5.0 \times 10^{-2}M$ | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}](M)$ | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}](M)$ | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 15 | 33.06 | 1.519 | 33.06 | 1.519 |
| 30 | 32.80 | 1.515 | 32.35 | 1.509 |
| 45 | 32.34 | 1.509 | 31.70 | 1.501 |
| 60 | 31.88 | 1.503 | 30.98 | 1.491 |
| 75 | 31.50 | 1.498 | 30.45 | 1.483 |
| 90 | 31.03 | 1.491 | 29.60 | 1.471 |
| 105 | 30.50 | 1.484 | 29.15 | 1.464 |
| 120 | 30.04 | 1.477 | 28.37 | 1.452 |
| 135 | 29.38 | 1.468 | 27.60 | 1.440 |
| 150 | 28.60 | 1.456 | 26.87 | 1.429 |
| Rate constant (min.$^{-1}$) | $1.08 \times 10^{-3}$ | | $1.64 \times 10^{-3}$ | |
| Fig. 10. | Curve 1. | | Curve 2. | |

Table - XXV.

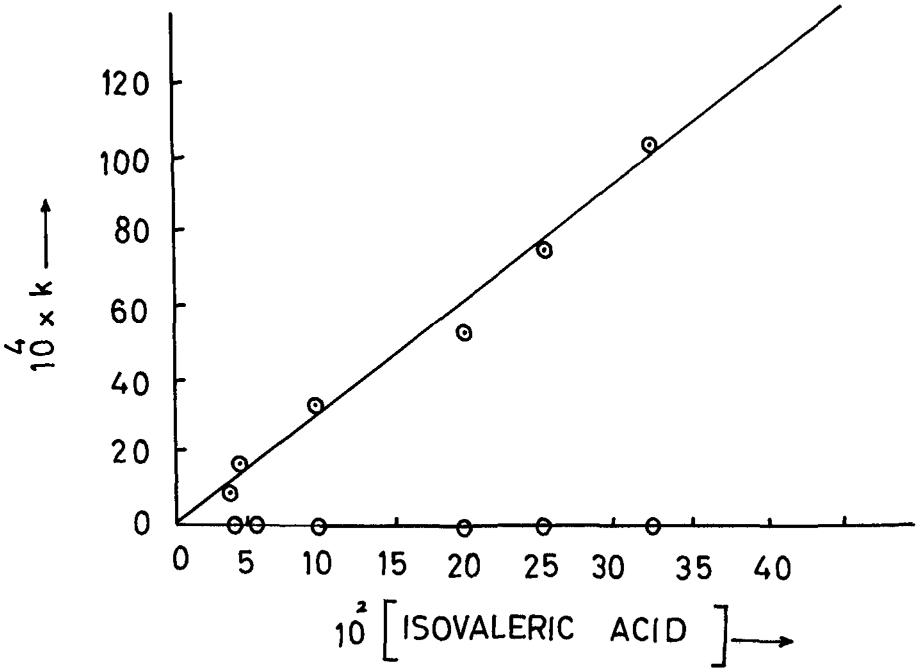
Dependence of rate constant on the concentration of isovaleric acid.

Temp. 70 ± .1°C; $[H_2SO_4] = 5.0M$; $[Cr^{VI}] = 33.33 \times 10^{-4}M$.

| [Isovaleric acid] | $10.0 \times 10^{-2}M$ | | $20.0 \times 10^{-4}M$ | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 15 | 32.13 | 1.507 | 31.00 | 1.491 |
| 30 | 31.28 | 1.495 | 28.50 | 1.454 |
| 45 | 29.56 | 1.470 | 26.98 | 1.431 |
| 60 | 28.37 | 1.452 | 25.40 | 1.404 |
| 75 | 27.17 | 1.434 | 23.10 | 1.363 |
| 90 | 26.12 | 1.417 | 20.83 | 1.318 |
| 105 | 24.40 | 1.387 | 19.17 | 1.282 |
| 120 | 23.34 | 1.368 | 17.32 | 1.239 |
| 135 | 21.70 | 1.336 | 15.67 | 1.195 |
| 150 | 19.64 | 1.293 | 14.08 | 1.148 |
| Rate constant (min.$^{-1}$) | $3.50 \times 10^{-3}$ | | $5.44 \times 10^{-3}$ | |
| Fig. 10. | Curve 3. | | Curve 4. | |

FIRST ORDER DEPENDENCE OF RATE CONSTANT ON ISOVALERIC ACID CONCENTRATION

FIG. 11



## Table - XXVI.

Dependence of rate constant on the concentration of isovaleric acid.

Temp. 75 ± .1°C; $[H_2SO_4] = 5.0M$; $[Cr^{VI}] = 33.33 \times 10^{-4}M$.

| [Isovaleric acid] | $25.0 \times 10^{-2}M$ | | $33.33 \times 10^{-2}M$ | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}](M)$ | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}](M)$ | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 15 | 30.93 | 1.490 | 30.54 | 1.485 |
| 30 | 28.87 | 1.460 | 28.10 | 1.448 |
| 45 | 26.67 | 1.426 | 25.70 | 1.410 |
| 60 | 24.14 | 1.382 | 22.13 | 1.345 |
| 75 | 22.28 | 1.348 | 19.53 | 1.291 |
| 90 | 20.22 | 1.305 | 17.22 | 1.236 |
| 105 | 17.43 | 1.241 | 14.30 | 1.155 |
| 120 | 15.63 | 1.194 | 12.25 | 1.088 |
| 135 | 14.03 | 1.147 | 10.27 | 1.011 |
| 150 | 12.44 | 1.094 | 8.87 | 0.948 |
| Rate constant ($min.^{-1}$) | $7.73 \times 10^{-3}$ | | $10.50 \times 10^{-3}$ | |
| Fig. 10. | Curve 5. | | Curve 6. | |

## Variation of rate constant with acidity

Sulphuric acid was varied from 3.0M to 5M. The rate was found to increase with increasing sulphuric acid content of the reaction mixture. Since sulphuric acid is considered to dissociate into $HSO_4^-$ ions only, sodium bisulphate was used to compensate for the change of ionic strength. The results of acidity variation are reported in the tables below.

FIG. 12

ACIDITY DEPENDENCE OF THE OXIDATION RATE

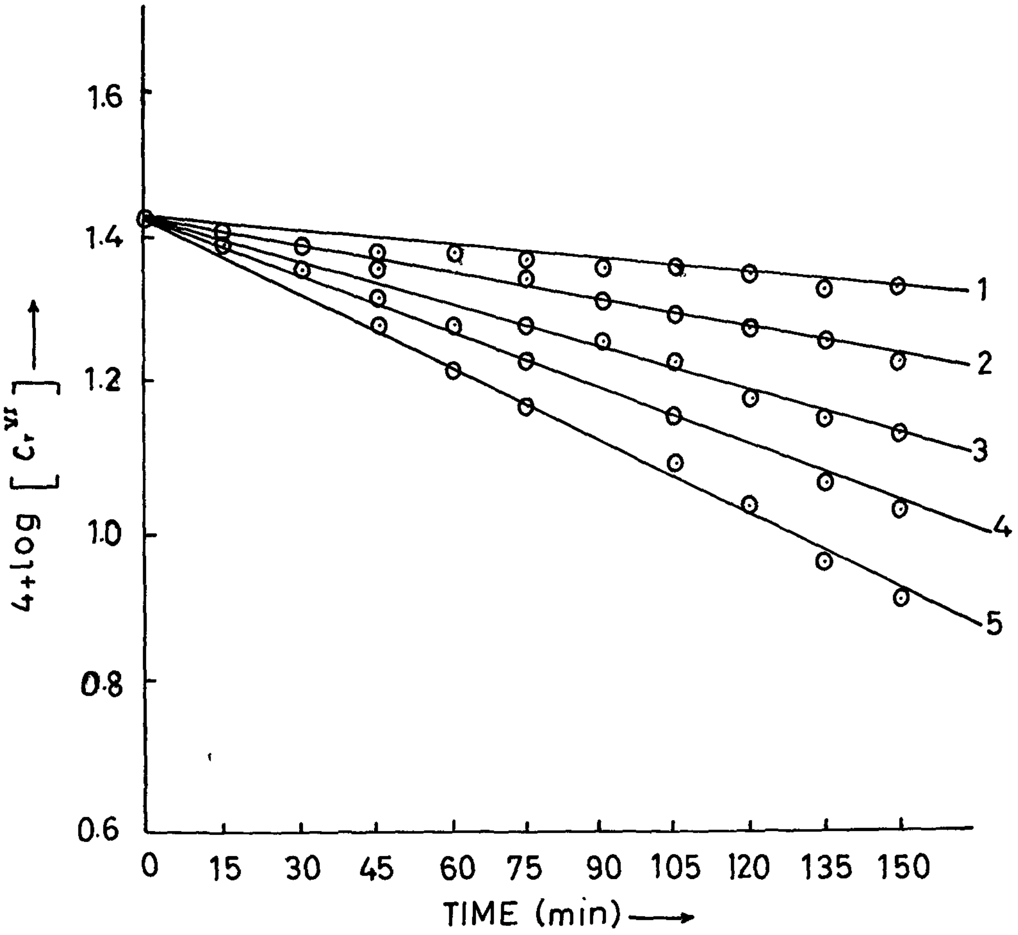


Table - XXVII.

Acidity dependence of the oxidation rate.

Temp. 75 ± .1°C; $[H_2SO_4 + NaHSO_4] = 6.0M$; [Isovaleric acid] = 0.2M; $[Cr^{VI}] = 26.66 \times 10^{-4}M$.

| $[H_2SO_4]$ | 3.0M | | 3.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 15 | 25.90 | 1.419 | 25.80 | 1.411 |
| 30 | 25.46 | 1.406 | 24.20 | 1.383 |
| 45 | 24.63 | 1.391 | 23.50 | 1.371 |
| 60 | 23.74 | 1.375 | 22.00 | 1.342 |
| 75 | 22.70 | 1.356 | 20.30 | 1.307 |
| 90 | 21.23 | 1.327 | 18.95 | 1.277 |
| 105 | 20.10 | 1.303 | 17.40 | 1.240 |
| 120 | 19.30 | 1.286 | 15.53 | 1.191 |
| 135 | 18.37 | 1.264 | 14.18 | 1.151 |
| 150 | 17.06 | 1.232 | 12.43 | 1.094 |
| Rate constant (min.$^{-1}$) | $3.37 \times 10^{-3}$ | | $4.82 \times 10^{-3}$ | |
| Fig. 12. | Curve 1. | | Curve 2. | |

Table - XXVIII.

Acidity dependence of the oxidation rate.

Temp. 75 ± .1°C; [$H_2SO_4$ + $NaHSO_4$] = 6.0M; [Isovaleric acid] = 0.2M; [$Cr^{VI}$] = 26.66 x $10^{-4}$M.

| [$H_2SO_4$] | 4.0M | | 4.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4$[$Cr^{VI}$](M) | 4+log[$Cr^{VI}$] | $10^4$[$Cr^{VI}$](M) | 4+log[$Cr^{VI}$] |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 15 | 25.45 | 1.405 | 24.20 | 1.383 |
| 30 | 24.34 | 1.386 | 23.80 | 1.376 |
| 45 | 23.23 | 1.366 | 21.64 | 1.335 |
| 60 | 21.64 | 1.335 | 19.80 | 1.296 |
| 75 | 19.84 | 1.297 | 17.53 | 1.243 |
| 90 | 17.57 | 1.244 | 15.15 | 1.180 |
| 105 | 15.60 | 1.193 | 13.10 | 1.117 |
| 120 | 14.40 | 1.158 | 11.20 | 1.049 |
| 135 | 12.12 | 1.083 | 9.42 | 0.974 |
| 150 | 10.42 | 1.018 | 7.86 | 0.895 |
| Rate Constant (min.$^{-1}$) | 6.14 x $10^{-3}$ | | 8.37 x $10^{-3}$ | |
| Fig. 12. | Curve 3. | | Curve 4. | |

Table - XXIX.

Acidity dependence of the oxidation rate.

Temp. 75 ± .1°C; $[H_2SO_4 + NaHSO_4]$ = 6.0M; [Isovaleric acid] = 0.2M; $[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| $[H_2SO_4]$ | 5.0M | |
|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log $[Cr^{VI}]$ |
| 0 | 26.66 | 1.426 |
| 15 | 24.57 | 1.390 |
| 30 | 22.43 | 1.350 |
| 45 | 19.70 | 1.294 |
| 60 | 17.20 | 1.235 |
| 75 | 13.94 | 1.144 |
| 90 | 11.40 | 1.056 |
| 105 | 10.27 | 1.011 |
| 120 | 7.47 | 0.873 |
| 135 | 5.38 | 0.731 |
| 150 | 4.18 | 0.621 |
| Rate constant (min.$^{-1}$) | 10.28 x $10^{-3}$ | |

Fig. 12. Curve 5.

Table - XXX.

Effect of acidity on the rate constants.

| $[H^+]$ (M) | $[H^+]^2$ | $k \times 10^3$ ($min.^{-1}$) | $\frac{k}{[H^+]} \times 10^3$ ($l.mole^{-1} min.^{-1}$) | $\frac{k}{[H^+]^2} \times 10^4$ ($l^2.mole^{-2} min.^{-1}$) |
|---|---|---|---|---|
| 3.0 | 9.00 | 3.37 | 1.12 | 3.74 |
| 3.5 | 12.25 | 4.82 | 1.37 | 3.93 |
| 4.0 | 16.00 | 6.14 | 1.53 | 3.83 |
| 4.5 | 20.25 | 8.37 | 1.86 | 4.13 |
| 5.0 | 25.00 | 10.28 | 2.05 | 4.01 |

## Temperature dependence

Reaction was studied at six different temperatures under identical reaction conditions. Activation energy and other thermodynamic parameters were calculated from standard equation described earlier. The values found are:

Activation energy = 11.5 Kcal
Heat of activation = 10.8 Kcal
Entropy of activation = -46.5 eu.

The rate constants at various temperatures are given in the following tables.

FIG. 13

TEMPERATURE DEPENDENCE OF THE OXIDATION RATE

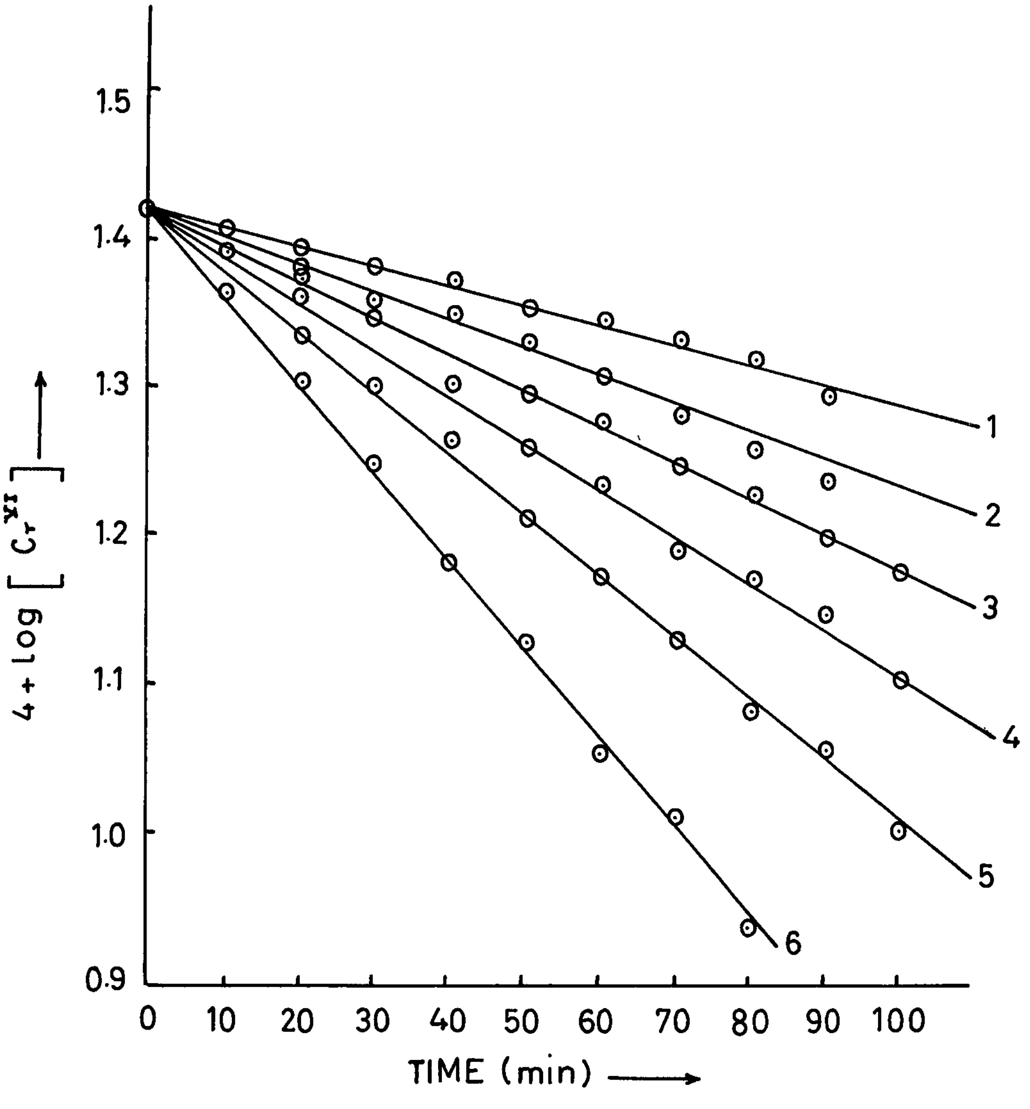


Table - XXXI.

Temperature - dependence of the reaction rate.

$[H_2SO_4]$ = 5.0M; [Isovaleric acid] = 0.1M;
$[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| Temperature | 243°K | | 248°K | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 25.63 | 1.408 | 26.05 | 1.415 |
| 20 | 25.04 | 1.398 | 25.28 | 1.402 |
| 30 | 24.50 | 1.389 | 24.40 | 1.387 |
| 40 | 23.74 | 1.375 | 22.80 | 1.357 |
| 50 | 23.04 | 1.362 | 21.90 | 1.340 |
| 60 | 22.28 | 1.348 | 20.70 | 1.316 |
| 70 | 21.57 | 1.334 | 19.65 | 1.293 |
| 80 | 20.87 | 1.319 | 18.43 | 1.265 |
| 90 | 19.84 | 1.297 | 17.33 | 1.238 |
| 100 | 17.95 | 1.254 | 16.12 | 1.207 |
| Rate constant (min.$^{-1}$) | 3.32 x $10^{-3}$ | | 4.70 x $10^{-3}$ | |
| Fig. 13. | Curve 1. | | Curve 2. | |

Table - XXXII.

Temperature dependence of the oxidation rate.

$[H_2SO_4]$ = 5.0M; [Isovaleric acid] = 0.1M;
$[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| Temperature | 353°K | | 358°K | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 25.70 | 1.410 | 25.58 | 1.408 |
| 20 | 23.98 | 1.380 | 23.87 | 1.378 |
| 30 | 23.12 | 1.364 | 22.50 | 1.352 |
| 40 | 21.87 | 1.340 | 20.41 | 1.310 |
| 50 | 19.95 | 1.300 | 18.70 | 1.272 |
| 60 | 19.23 | 1.284 | 17.30 | 1.238 |
| 70 | 18.03 | 1.256 | 15.84 | 1.200 |
| 80 | 17.14 | 1.234 | 15.13 | 1.180 |
| 90 | 16.14 | 1.208 | 14.32 | 1.156 |
| 100 | 15.34 | 1.186 | 12.76 | 1.106 |
| Rate constant ($min.^{-1}$) | 5.52 x $10^{-3}$ | | 7.36 x $10^{-3}$ | |
| Fig. 13. | Curve 3. | | Curve 4. | |

FIG. 14

ACTIVATION ENERGY

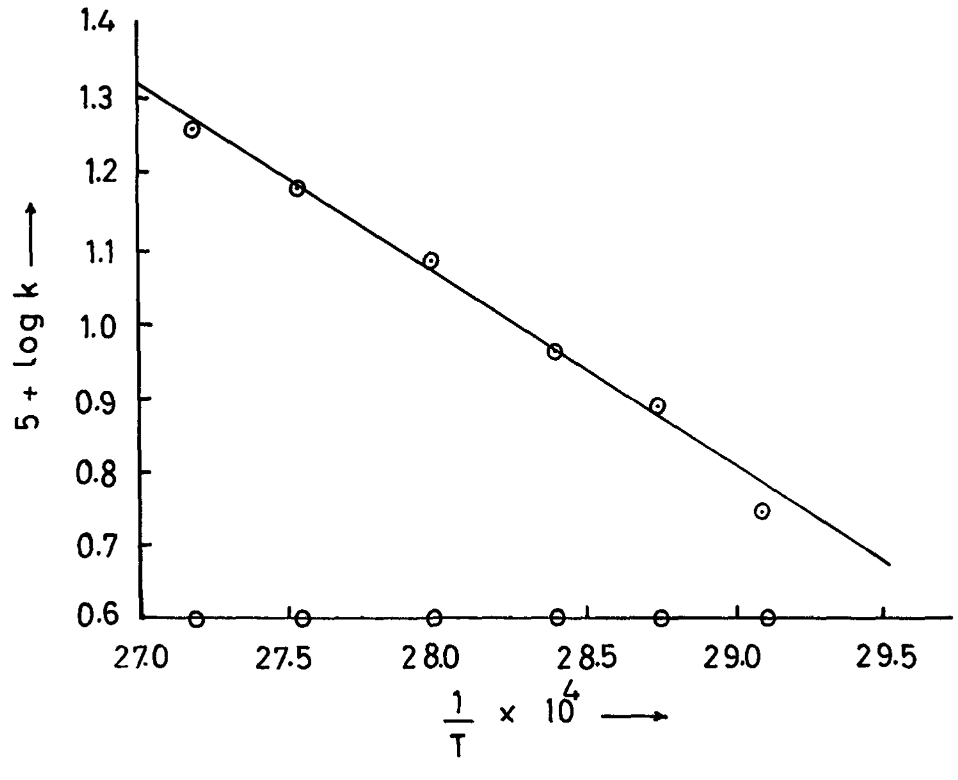


Table - XXXIII.

Temperature dependence of the reaction rate.

$[H_2SO_4] = 5.0M$; [Isovaleric acid] $= 0.1M$;
$[Cr^{VI}] = 26.66 \times 10^{-4}M$.

| Temperature | 363°K | | 368°K | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 24.26 | 1.385 | 23.70 | 1.375 |
| 20 | 22.13 | 1.345 | 20.90 | 1.320 |
| 30 | 20.51 | 1.312 | 17.98 | 1.255 |
| 40 | 18.88 | 1.276 | 15.48 | 1.190 |
| 50 | 16.74 | 1.224 | 13.67 | 1.136 |
| 60 | 15.13 | 1.180 | 11.56 | 1.063 |
| 70 | 13.98 | 1.146 | 10.35 | 1.015 |
| 80 | 12.20 | 1.086 | 9.03 | 0.956 |
| 90 | 11.27 | 1.052 | - | - |
| 100 | 10.30 | 1.013 | - | -. |
| Rate constant (min.$^{-1}$) | $11.50 \times 10^{-3}$ | | $16.12 \times 10^{-3}$ | |

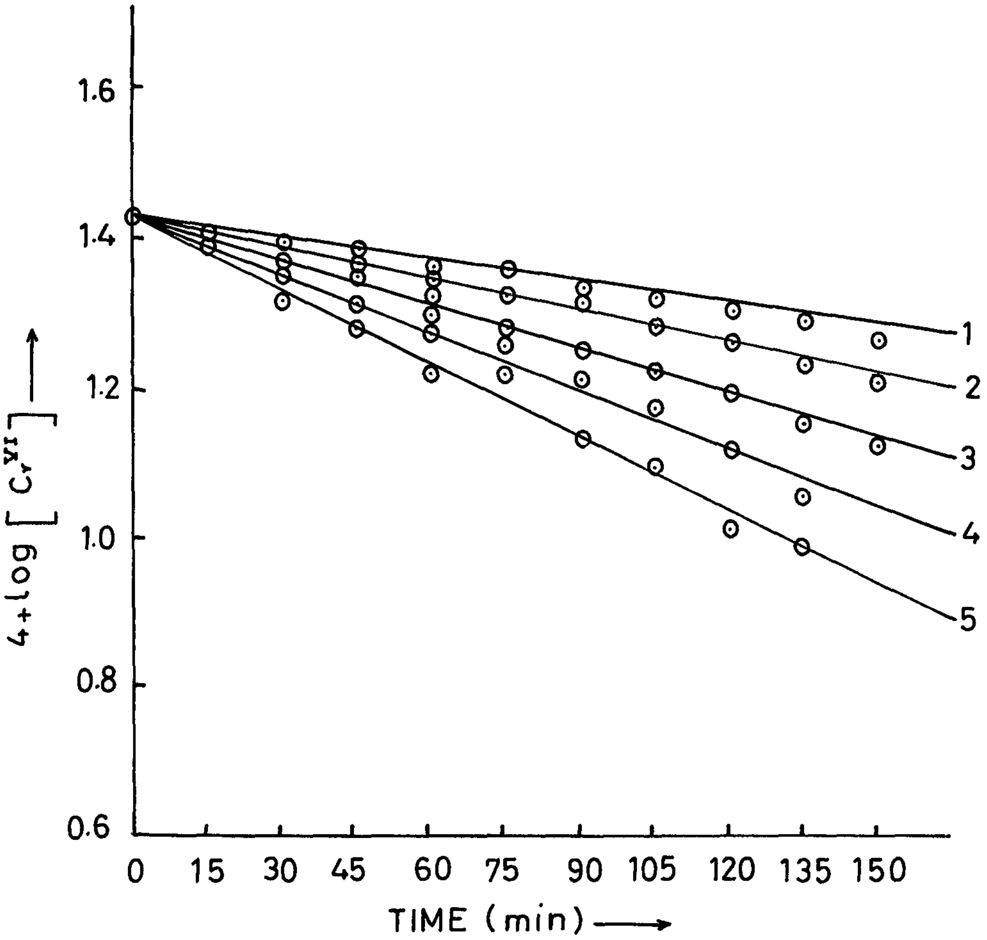
Fig. 13. Curve 5. Curve 6.

## Effect of Ionic Strength

By varying the concentration of sodium perchlorate, the ionic strength of the reaction mixture was regulated. A positive influence is observed. The plot of $0\mu^{1/2}$ Vs. log $k$ fails to give any conclusive results. The rate constants at various ionic strengths are registered below.

FIG. 15

DEPENDENCE OF RATE CONSTANT ON IONIC STRENGTH



## Table - XXXIV.

Effect of ionic strength on the oxidation rate.

Temp.75$\pm$.1°C; $[H_2SO_4]$= 4.5M; [Isovaleric acid]= 0.1M;
$[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| $[NaClO_4]$ | Nil | | 0.5M | |
|---|---|---|---|---|
| Ionic strength | 4.5M | | 5.0M | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 15 | 26.20 | 1.418 | 26.34 | 1.420 |
| 30 | 25.46 | 1.405 | 25.50 | 1.406 |
| 45 | 24.67 | 1.392 | 24.33 | 1.386 |
| 60 | 23.83 | 1.377 | 23.17 | 1.365 |
| 75 | 22.90 | 1.360 | 22.02 | 1.342 |
| 90 | 22.16 | 1.347 | 20.90 | 1.320 |
| 105 | 21.53 | 1.333 | 19.64 | 2.293 |
| 120 | 20.70 | 1.315 | 18.66 | 1.271 |
| 135 | 19.67 | 1.294 | 17.73 | 1.248 |
| 150 | 18.96 | 1.278 | 16.73 | 1.223 |
| Rate constant (min.$^{-1}$) | 2.60 x $10^{-3}$ | | 3.77 x $10^{-3}$ | |
| Fig. 15. | Curve 1. | | Curve 2. | |

Table - XXXV.

Effect of ionic strength on the oxidation rate.

Temp. 75±.1°C; $[H_2SO_4]$ = 4.5M; [Isovaleric acid] = 0.1M

$[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| $[NaClO_4]$ | 1.0M | | 1.5M | |
|---|---|---|---|---|
| Ionic strength | 5.5M | | 6.0M | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 15 | 25.35 | 1.404 | 25.50 | 1.406 |
| 30 | 24.46 | 1.388 | 24.20 | 1.383 |
| 45 | 22.95 | 1.360 | 22.84 | 1.358 |
| 60 | 21.38 | 1.330 | 20.88 | 1.319 |
| 75 | 19.65 | 1.293 | 19.23 | 1.284 |
| 90 | 18.00 | 1.255 | 17.16 | 1.234 |
| 105 | 16.90 | 1.227 | 15.60 | 1.193 |
| 120 | 15.80 | 1.198 | 13.44 | 1.128 |
| 135 | 14.64 | 1.165 | 11.83 | 1.073 |
| 150 | 13.38 | 1.126 | 10.23 | 1.010 |
| Rate constant (min.$^{-1}$) | 5.56 x $10^{-3}$ | | 7.25 x $10^{-3}$ | |
| Fig. 15. | Curve 3. | | Curve 4. | |

## Table - XXXVI.

Effect of ionic strength on the oxidation rate.

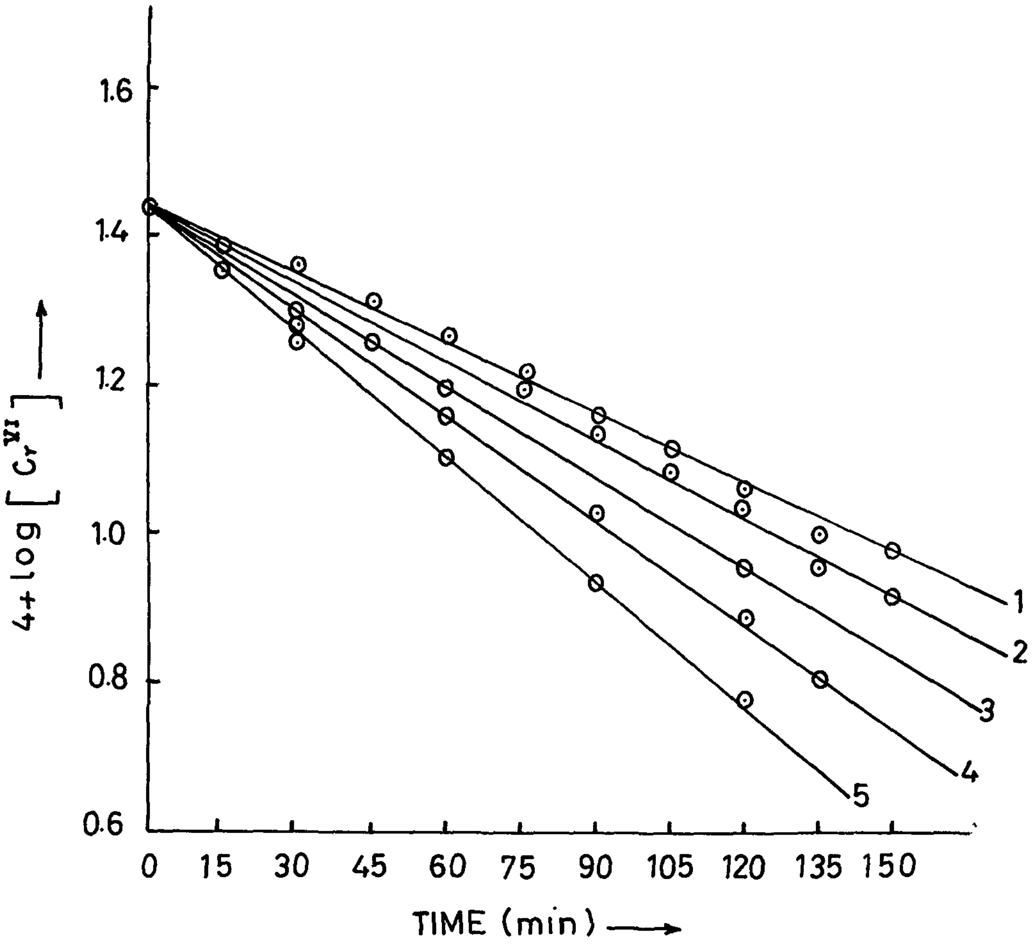
Temp.75$\pm$.1°C; $[H_2SO_4]$ = 4.5M; [Isovaleric acid] = 0.1M; $[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| $[NaClO_4]$ | 2.0M | |
|---|---|---|
| Ionic strength | 6.5M | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 |
| 15 | 24.80 | 1.394 |
| 30 | 23.20 | 1.365 |
| 45 | 21.13 | 1.324 |
| 60 | 19.26 | 1.284 |
| 75 | 17.20 | 1.235 |
| 90 | 15.20 | 1.181 |
| 105 | 13.08 | 1.116 |
| 120 | 11.06 | 1.034 |
| 135 | 8.90 | 0.950 |
| 150 | 6.80 | 0.832 |
| Rate constant (min.$^{-1}$) | 8.46 x $10^{-3}$ | |

Fig. 15. Curve 5.

FIG. 16

EFFECT OF ACETIC ACID ON THE OXIDATION RATE



## Table - XXXVII.

Influence of acetic acid on the oxidation rate.

Temp.75$\pm$.1°C; $[H_2SO_4]$= 5.0M; [Isovaleric acid]= 0.1M;
$[Cr^{VI}]$ = 26.66 x $10^{-4}$M.

| [Acetic acid] | 0.1M | | 0.2M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 15 | 25.07 | 1.399 | 24.80 | 1.394 |
| 30 | 23.34 | 1 .368 | 22.70 | 1.356 |
| 45 | 21.17 | 1.325 | 20.96 | 1.321 |
| 60 | 19.37 | 1.287 | 19.00 | 1.278 |
| 75 | 17.16 | 1.234 | 16.94 | 1.229 |
| 90 | 14.98 | 1.175 | 14.52 | 1.162 |
| 105 | 13.14 | 1.118 | 12.67 | 1.102 |
| 120 | 11.60 | 1.065 | 11.08 | 1.044 |
| 135 | 10.03 | 1.003 | 9.02 | 0.955 |
| 150 | 8.34 | 0.921 | 7.12 | 0.853 |
| Rate constant (min.$^{-1}$) | 8.22 x $10^{-3}$ | | 8.94 x $10^{-3}$ | |
| Fig. 16. | Curve 1. | | Curve 2. | |

Table - XXXVIII.

Influence of acetic acid on the oxidation rate.

Temp. 75$\pm$.1°C; $[H_2SO_4]$ = 5.0M; [Isovaleric acid] = 0.1M;
$[Cr^{VI}] = 26.66 \times 10^{-4}$M.

| [Acetic acid] | 0.5M | |
|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 |
| 15 | 22.85 | 1.359 |
| 30 | 20.53 | 1.312 |
| 45 | 18.36 | 1.263 |
| 60 | 15.92 | 1.202 |
| 75 | 14.02 | 1.146 |
| 90 | 12.10 | 1.083 |
| 105 | 9.94 | 0.997 |
| 120 | 7.83 | 0.893 |
| 135 | 6.34 | 0.802 |
| 150 | 4.50 | 0.653 |
| Rate constant ($min.^{-1}$) | $10.40 \times 10^{-3}$ | |

Fig. 16. Curve 3.

Table - XXXIX.

Influence of acetic acid on the oxidation rate.

Temp. 75±.1°C; $[\mathrm{H_2SO_4}] = 5.0\mathrm{M}$; [Isovaleric acid] = 0.1M;
$[\mathrm{Cr}^{VI}] = 26.66 \times 10^{-4}\mathrm{M}$.

| [Acetic acid] | 0.7M | | 1.0M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[\mathrm{Cr}^{VI}]$(M) | $4+\log[\mathrm{Cr}^{VI}]$ | $10^4[\mathrm{Cr}^{VI}]$(M) | $4+\log[\mathrm{Cr}^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 23.57 | 1.372 | 22.18 | 1.346 |
| 20 | 21.10 | 1.324 | 19.78 | 1.296 |
| 30 | 19.50 | 1.290 | 18.60 | 1.269 |
| 40 | 17.96 | 1.254 | 16.16 | 1.208 |
| 50 | 16.57 | 1.219 | 14.82 | 1.171 |
| 60 | 14.87 | 1.172 | 12.80 | 1.107 |
| 70 | 13.38 | 1.126 | 11.32 | 1.057 |
| 80 | 12.25 | 1.088 | 10.20 | 1.008 |
| 90 | 11.06 | 1.044 | 9.54 | 0.931 |
| 100 | 9.57 | 0.981 | 7.10 | 0.851 |
| Rate constant (min.$^{-1}$) | $11.18 \times 10^{-3}$ | | $12.17 \times 10^{-3}$ | |
| Fig. 16. | Curve 4. | | Curve 5. | |

# Chapter IV

# Kinetics of Oxidation of phenylacetic acid

The oxidation of phenylated fatty acids is important from the biological point of view since it throws light upon the mode of oxidation of fatty acids of related structures in the animal body. Dakin[134,135] studied the oxidation of phenylated fatty acids in vivo and in vitro by hydrogen peroxide. His results afforded the most convincing evidence of the occurrence of $\beta$-oxidation in both the cases showing a close analogy between them. The use of copper as a catalyst in the oxidation of phenyl derivatives of aliphatic acids has been reported by Jones and MacLean[136]. They observed that the ease of oxidation was increased with the increase in the side chain. The special susceptibility of phenylacetic acid to oxidation was ascribed to the fact that $\beta$-oxidation took place at the nuclear carbon atom to which the side chain was attached.

Bacterial oxidation of benzoic and phenylacetic acids by Vibrio[137] was reported to take place by different metabolic routes, but a section of tricarboxylic cycle which enters through $\beta$-ketoglutaric acid was shown to be common to both. Hockenhull[138] demonstrated that the initial oxidation of phenylacetic acid by Penicillium chrysogenum took place in the side chain as dehydrogenation process with the formation of benzaldehyde. Phenylacetaldehyde and hydroxyphenylacetic acid were envisaged as intermediates. Mercuric and iodoacetate ions were observed to inhibit the oxidation. Spiro[139] suggested that $\alpha$-oxidation of fatty acids in the organism was not due to a peculiar oxidation mechanism, but it was limited by the properties of the oxidizable compound which determined the peculiar position of attack.

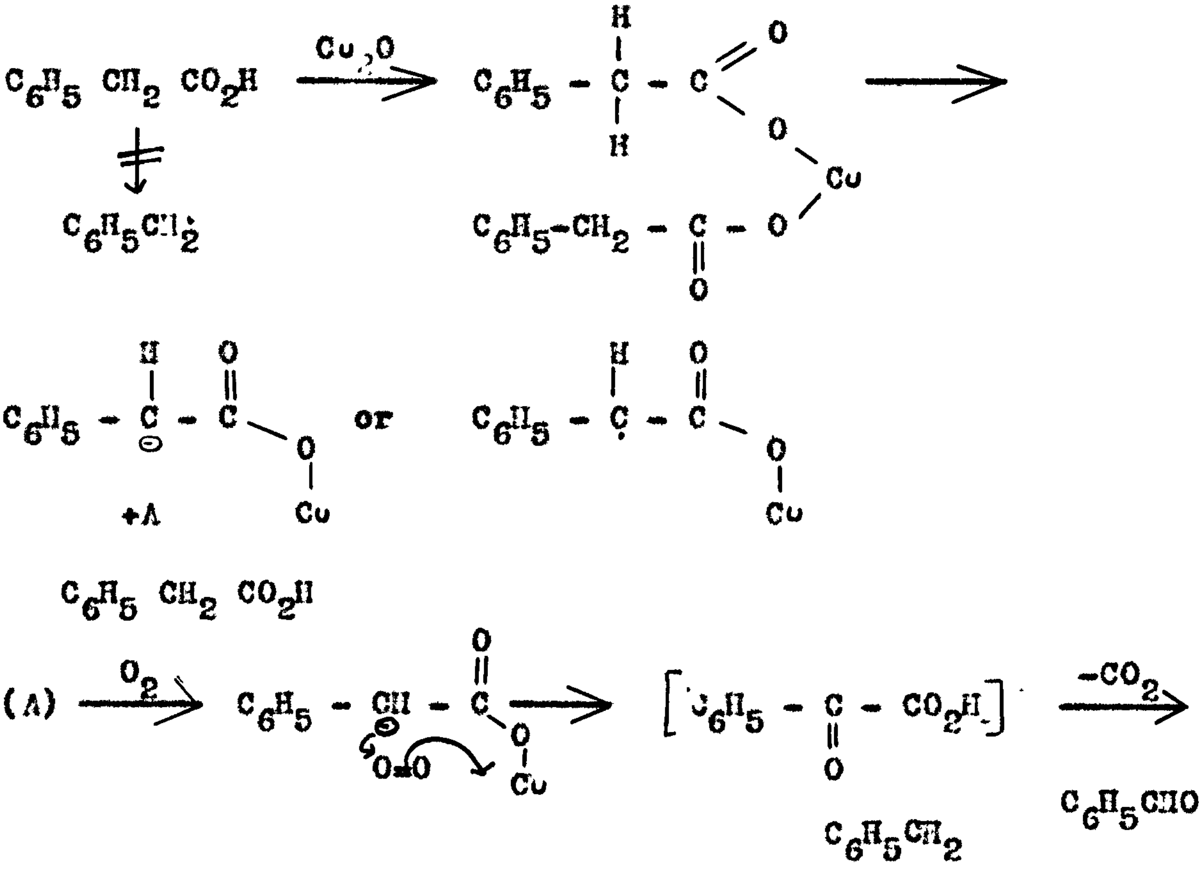
The oxidation of phenylated fatty acids by hot alkaline permanganate was investigated by Przhevalskii[140] who reported that the oxidation took place at the carbon atom next to phenyl group. The hydroxyl group was introduced which was then further oxidized to a carbonyl compound and finally to benzoic acid. The remainder side chain was oxidized to carbon dioxide or to a dibasic acid. Oxidative degradation of carboxylic acids by potassium permanganate has also been reported by Skraup et al[141]. These workers obtained benzoic acid from phenylacetic acid; benzoic and benzoylformic acid from hydrocinnamic and phenylbutyric acids by oxidizing them with one mole of acid and 0.1 mole of potassium permanganate in presence of two equivalents of potassium carbonate. Permanganate oxidation of phenylacetic and phenylpropionic acids in acid, basic and neutral media was carried out by Dimitrov and Stefanova[142]. Formation of pyruvic acid, as identified by gas chromatography, was attributed to the breaking of benzene ring. Use of solid manganese dioxide as an oxidant for the oxidation of organic compounds was reported by El-Sadar[143] who obtained benzaldehyde (50% yield) and carbon dioxide from phenylacetic acid.

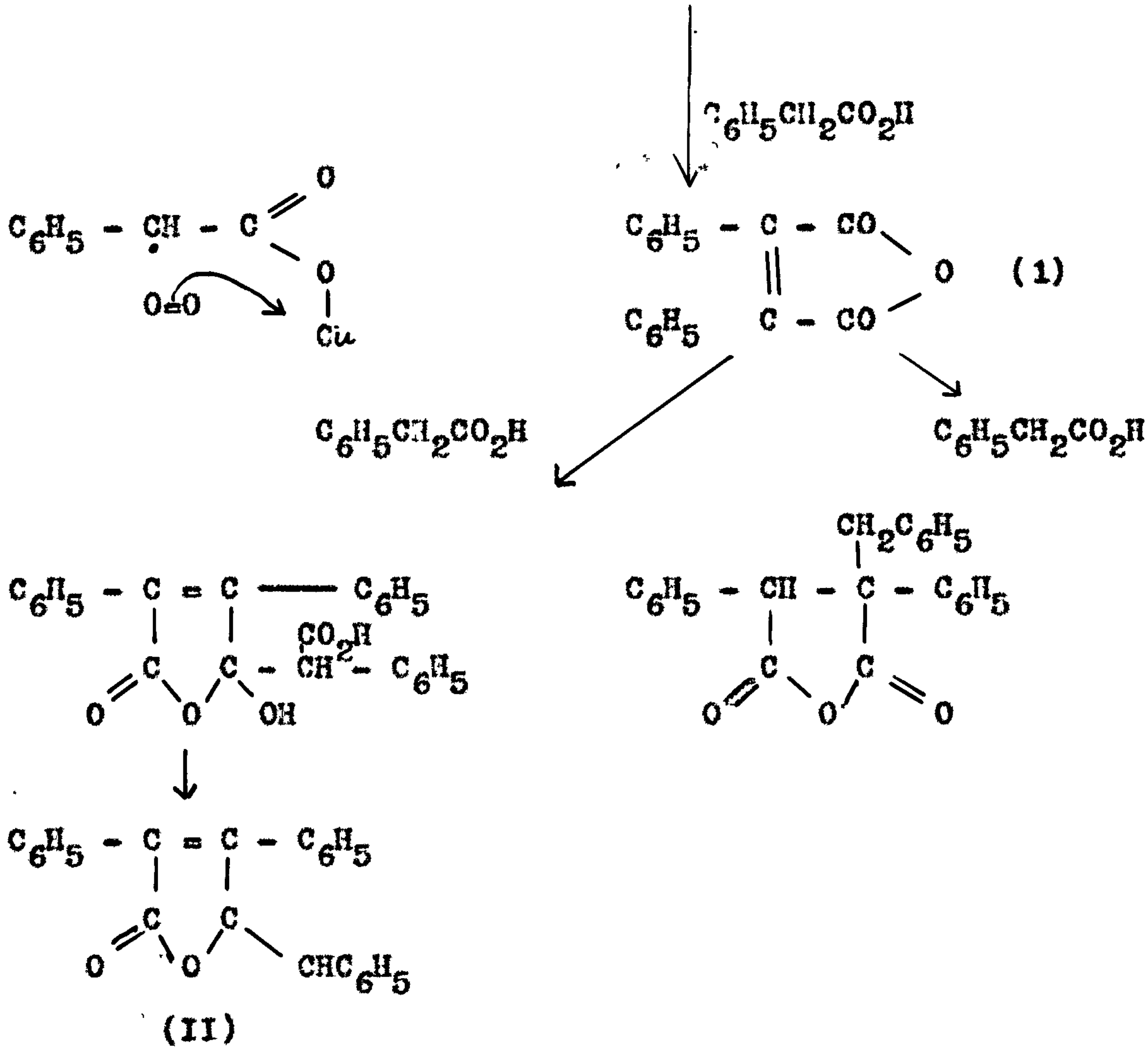
The usual oxidative degradation process in lignin chemistry to vanillin by nitrobenzene was applied to model compounds[144]. It was shown that phenylacetic acid was oxidized to benzoylformic acid. Persulphate oxidation[145] of phenylacetic acid gave diphenylmethane (36% yield) and benzaldehyde. Bacon and Hanna[146] used argentic picolinate as a suitable oxidant for organic compounds in aqueous suspensions. They found that phenylacetic acid was oxidized to benzaldehyde by this reagent. Waters[123] obtained little benzaldehyde from the oxidation of phenylacetic acid by cobaltic salts. Fieser's[147] observations on the alkyl side chain by chromic anhydride strongly suggest that the degradation of an acid side chain proceeds by an initial $\beta$-oxidation followed by decarboxylation to $\beta$-keto acid. The lower homologous acids arise by the similar processes. Hence they concluded that the phenomena of $\beta$-oxidation was not limited to biological oxidations.

only. The schematic representation is as follows:

$$-(CH_2)_9CO_2H \longrightarrow -(CH_2)_7COCH_2CO_2H \longrightarrow$$
$$-(CH_2)_7CO\ CH_3 \longrightarrow -(CH_2)_{1-7}\ CO_2H.$$

Recently[148] oxidative decarboxylation of phenylacetic acid has been shown to proceed through ionic mechanism and not via free radical one. Benzoylformic acid has been postulated as the key intermediate, the formation of which has been illustrated by either radical or ionic mechanism. The reaction has been shown schematically as:





In the present chapter studies on the oxidation of phenylacetic and benzoic acids were conducted in order to get an insight into the mechanism of oxidation of fatty acids by chromic acid.

## Order in Chromic acid

The disappearance of chromic acid followed apparently first order kinetics when it was examined as plots of log $[Cr^{VI}]$ Vs. time. The typical plot is shown in figure 1. It is to be noted that decrease in chromic acid is accompanied by increase in rate constants. The observations at various chromic acid concentrations are tabled below:

FIG. 1
DEPENDENCE OF RATE CONSTANT ON CHROMIC ACID CONCENTRATION

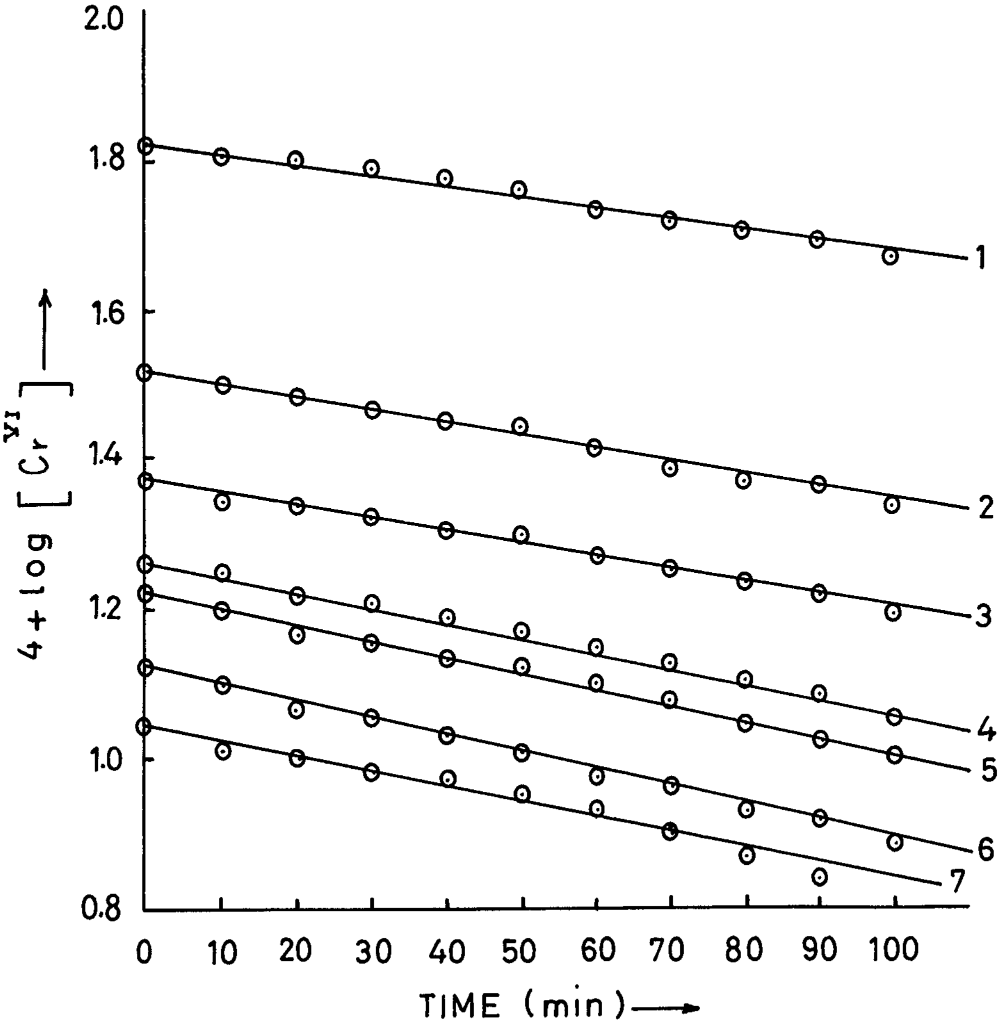


Table - I.

Dependence of rate constant on chromic acid concentration.

Temp.75±.1°C; [$H_2SO_4$]= 5.0M; [Phenyl acetic acid]=$6.6\times10^{-2}$M.

| [Chromic acid] | $66.66\times10^{-4}$M | | $33.33\times10^{-4}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 66.66 | 1.823 | 33.33 | 1.522 |
| 10 | 65.13 | 1.814 | 32.00 | 1.505 |
| 20 | 63.72 | 1.804 | 30.97 | 1.491 |
| 30 | 62.53 | 1.796 | 29.72 | 1.473 |
| 40 | 60.40 | 1.781 | 28.62 | 1.456 |
| 50 | 57.73 | 1.761 | 27.23 | 1.435 |
| 60 | 55.05 | 1.740 | 26.52 | 1.423 |
| 70 | 52.20 | 1.718 | 24.95 | 1.397 |
| 80 | 50.52 | 1.703 | 23.54 | 1.371 |
| 90 | 48.40 | 1.684 | 23.34 | 1.368 |
| 100 | 46.26 | 1.665 | 21.80 | 1.338 |
| Rate constant (min.$^{-1}$) | $4.20\times10^{-3}$ | | $4.27\times10^{-3}$ | |
| Fig. 1. | Curve 1. | | Curve 2. | |

### Table - II.

Dependence of rate constant on chromic acid concentration.

Temp.70±.1°C; $[H_2SO_4]$= 5.0M; [Phenyl acetic acid]=0.6x$10^{-2}$M.

| [Chromic acid] | $23.80 \times 10^{-4}$ | | $18.51 \times 10^{-4}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 23.80 | 1.376 | 18.51 | 1.267 |
| 10 | 22.65 | 1.355 | 17.70 | 1.248 |
| 20 | 21.82 | 1.339 | 16.75 | 1.224 |
| 30 | 21.20 | 1.326 | 16.19 | 1.209 |
| 40 | 20.52 | 1.312 | 15.58 | 1.192 |
| 50 | 20.20 | 1.305 | 14.68 | 1.166 |
| 60 | 18.80 | 1.274 | 14.00 | 1.146 |
| 70 | 18.18 | 1.259 | 13.28 | 1.123 |
| 80 | 17.35 | 1.239 | 12.60 | 1.100 |
| 90 | 16.68 | 1.222 | 13.03 | 1.080 |
| 100 | 15.53 | 1.191 | 11.32 | 1.054 |
| Rate constant (min.$^{-1}$) | $4.14 \times 10^{-3}$ | | $4.60 \times 10^{-3}$ | |
| Fig. 1. | Curve 3. | | Curve 4. | |

Table - III.

Dependence of rate constant on chromic acid concentration.

Temp. 78±.1°C; $[H_2SO_4]$ = 5.0M; [Phenylacetic acid] = $6.6 \times 10^{-2}$M.

| [Chromic acid] | $16.66 \times 10^{-4}$M | | $13.33 \times 10^{-4}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 16.66 | 1.221 | 13.33 | 1.124 |
| 10 | 15.87 | 1.200 | 12.56 | 1.099 |
| 20 | 15.10 | 1.178 | 11.90 | 1.076 |
| 30 | 14.44 | 1.159 | 11.45 | 1.059 |
| 40 | 13.70 | 1.136 | 10.78 | 1.033 |
| 50 | 13.23 | 1.121 | 10.33 | 1.014 |
| 60 | 12.70 | 1.103 | 9.74 | 0.988 |
| 70 | 12.03 | 1.080 | 9.12 | 0.960 |
| 80 | 11.36 | 1.055 | 8.68 | 0.938 |
| 90 | 10.66 | 1.028 | 8.14 | 0.910 |
| 100 | 10.03 | 1.001 | 7.60 | 0.880 |
| Rate constant (min.$^{-1}$) | $4.73 \times 10^{-3}$ | | $4.86 \times 10^{-3}$ | |
| Fig. 1. | Curve 5. | | Curve 6. | |

Table - IV.

Dependence of rate constant on chromic acid concentration.

Temp.75$\pm$.1$^{\circ}$C; [$H_2SO_4$] = 5.0M; [Phenylacetic acid] = 6.6x$10^{-2}$M.

| [Chromic acid] | 11.10 x $10^{-4}$M | |
|---|---|---|
| Time(mins.) | $10^4$[$Cr^{VI}$](M) | 4+log[$Cr^{VI}$] |
| 0 | 11.10 | 1.045 |
| 10 | 10.68 | 1.028 |
| 20 | 10.28 | 1.012 |
| 30 | 9.88 | 0.994 |
| 40 | 9.50 | 0.977 |
| 50 | 9.05 | 0.956 |
| 60 | 8.57 | 0.933 |
| 70 | 8.03 | 0.905 |
| 80 | 7.55 | 0.878 |
| 90 | 7.05 | 0.848 |
| 100 | 6.55 | 0.816 |
| Rate constant (min.$^{-1}$) | 4.73 x $10^{-3}$ | |

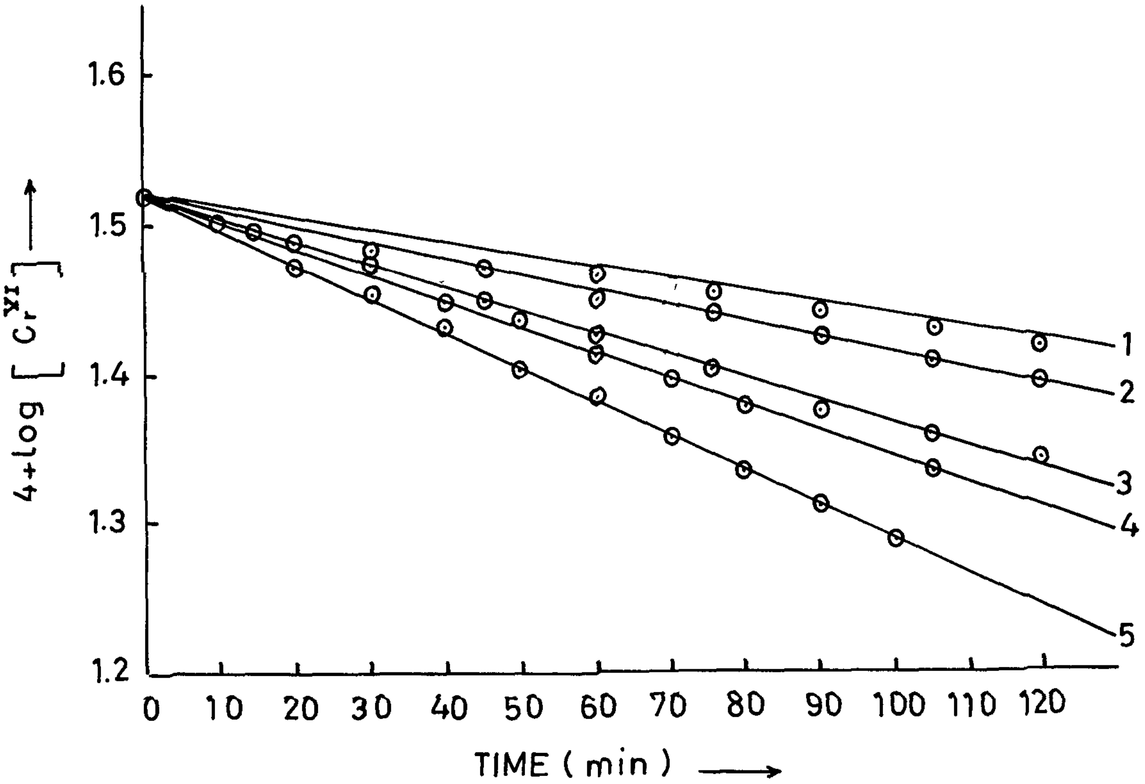
Fig. 1. Curve 7.

## Order in phenylacetic acid

The oxidation of phenylacetic acid by chromic acid was studied at low substrate concentration and could not be varied much because of its poor solubility. However, first order dependence on substrate was estimated from the plot of rate constant Vs. phenylacetic acid concentration. A straight line passing through the origin was obtained. The rate at various concentrations of phenylacetic acid are given in the following tables:

FIG. 2

DEPENDENCE OF RATE CONSTANT ON PHENYLACETIC ACID CONCENTRATION



## Table - V.

Dependence of rate constant on the concentration of phenylacetic acid.

Temp. 70 ± .1°C; $[H_2SO_4]$ = 5.0M; $[Cr^{VI}]$ = $33.33 \times 10^{-4}$ M.

| [Phenylacetic acid] | $4.0 \times 10^{-2}$ M | | $5.0 \times 10^{-2}$ M | |
|---|---|---|---|---|
| Time (mins.) | $10^4[Cr^{VI}]$ (M) | $4 + \log[Cr^{VI}]$ | $10^4[Cr^{VI}]$ (M) | $4 + \log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 15 | 31.88 | 1.503 | 32.20 | 1.507 |
| 30 | 30.93 | 1.490 | 30.86 | 1.489 |
| 45 | 30.10 | 1.478 | 29.98 | 1.476 |
| 60 | 29.47 | 1.470 | 28.97 | 1.462 |
| 75 | 28.53 | 1.455 | 28.16 | 1.450 |
| 90 | 27.77 | 1.443 | 26.98 | 1.430 |
| 105 | 27.08 | 1.432 | 26.20 | 1.418 |
| 120 | 26.26 | 1.419 | 25.25 | 1.402 |
| 135 | 25.56 | 1.407 | 24.50 | 1.390 |
| 150 | 24.87 | 1.395 | 23.60 | 1.372 |
| Rate constant ($min.^{-1}$) | $1.96 \times 10^{-3}$ | | $2.52 \times 10^{-3}$ | |
| Fig. 2. | Curve 1. | | Curve 2. | |

## Table - VI.

Dependence of rate constant on the concentration of phenylacetic acid.

Temp.$70 \pm .1^{\circ}$C; $[H_2SO_4] = 5.0$M; $[Cr^{VI}] = 33.33 \times 10^{-4}$M.

| [Phenylacetic acid] | $6.6 \times 10^{-2}$M | |
|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 |
| 15 | 31.62 | 1.500 |
| 30 | 30.17 | 1.496 |
| 45 | 28.72 | 1.458 |
| 60 | 27.08 | 1.432 |
| 75 | 25.44 | 1.405 |
| 90 | 23.98 | 1.380 |
| 105 | 23.10 | 1.363 |
| 120 | 22.10 | 1.344 |
| 135 | 21.14 | 1.325 |
| 150 | 20.13 | 1.301 |
| Rate constant ($min.^{-1}$) | $3.77 \times 10^{-3}$ | |

Fig. 2. Curve 3.

Table - VII.

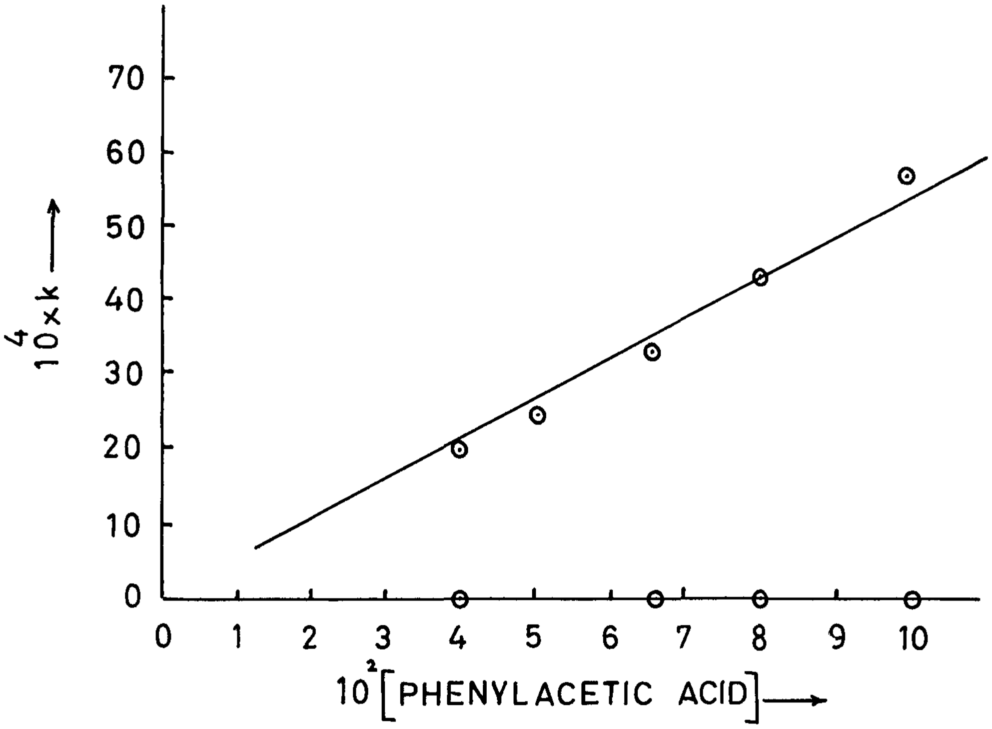
Dependence of rate constant on the concentration of phenylacetic acid.

Temp. 70 ± .1°C; $[H_2SO_4]$ = 5.0N; $[Cr^{VI}]$ = 33.33 x $10^{-4}$M.

| [Phenylacetic acid] | 8.0 x $10^{-2}$M | | 10.0 x $10^{-2}$M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | 4+log$[Cr^{VI}]$ |
| 0 | 33.33 | 1.522 | 33.33 | 1.522 |
| 10 | 32.24 | 1.508 | 31.86 | 1.503 |
| 20 | 30.90 | 1.490 | 30.46 | 1.483 |
| 30 | 29.70 | 1.472 | 29.06 | 1.463 |
| 40 | 28.67 | 1.457 | 27.65 | 1.441 |
| 50 | 27.53 | 1.440 | 25.87 | 1.412 |
| 60 | 26.44 | 1.422 | 24.55 | 1.390 |
| 70 | 25.23 | 1.402 | 23.32 | 1.367 |
| 80 | 23.98 | 1.380 | 22.05 | 1.343 |
| 90 | 22.62 | 1.354 | 20.70 | 1.316 |
| 100 | 21.64 | 1.335 | 19.43 | 1.288 |
| Rate constant (min.$^{-1}$) | 4.28 x $10^{-3}$ | | 5.72 x $10^{-3}$ | |
| Fig. 2. | Curve 4. | | Curve 5. | |

FIRST ORDER DEPENDENCE OF RATE CONSTANT ON PHENYLACETIC ACID CONCENTRATION

FIG. 3



## Variation of rate constant with acidity

No suitable buffer could be prepared for studying the influence of pH on the reaction rate. Nevertheless, hydrogen ion concentration was changed as such by varying the sulphuric acid - sodium bisulphate ratio in the reaction mixture. The concentration of hydrogen ions was calculated on the assumption that the first dissociation of sulphuric acid is complete and second dissociation is negligible. The effect of various concentrations of sulphuric acid on the rate constants are given in the tables. It is observed that the quotients obtained by dividing pseudo first order rate constants by hydrogen ion concentration vary but by the square of hydrogen ion concentration remain constant in each run. It indicates that the reaction is of second order with respect to hydrogen ions.

FIG. 4

ACIDITY DEPENDENCE OF THE REACTION RATE

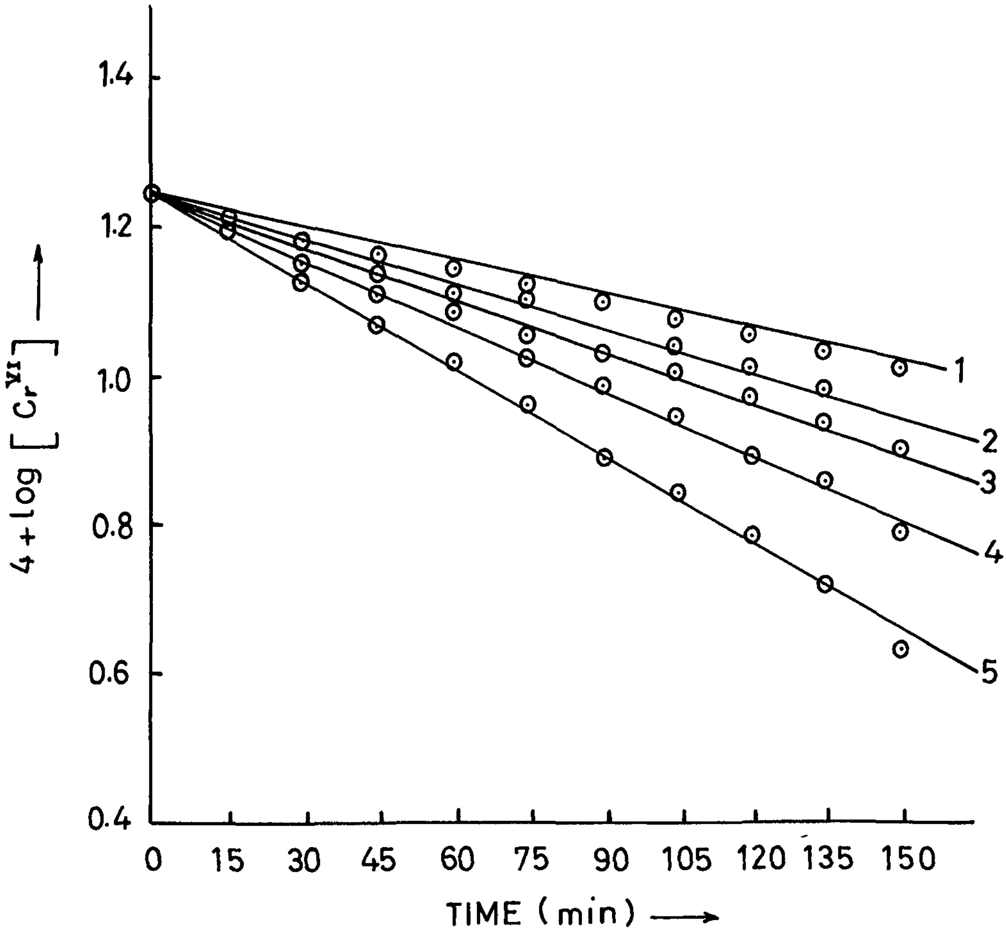


Table - VIII.

Acidity dependence of the oxidation rate.

Temp.70±.1°C; $[H_2SO_4] + [NaHSO_4] = 6.0M$;
$[\text{Phenylacetic acid}] = 6.6 \times 10^{-2}M$;
$[Cr^{VI}] = 26.66 \times 10^{-4}M$.

| $[H_2SO_4]$ | 4.0M | | 4.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 16.66 | 1.221 | 16.66 | 1.221 |
| 15 | 15.75 | 1.197 | 15.48 | 1.189 |
| 30 | 15.12 | 1.180 | 14.70 | 1.167 |
| 45 | 14.46 | 1.160 | 13.95 | 1.144 |
| 60 | 13.64 | 1.135 | 13.08 | 1.116 |
| 75 | 13.05 | 1.115 | 12.55 | 1.098 |
| 90 | 12.38 | 1.093 | 12.10 | 1.083 |
| 105 | 11.80 | 1.071 | 11.36 | 1.055 |
| 120 | 11.13 | 1.046 | 10.70 | 1.024 |
| 135 | 10.56 | 1.023 | 9.93 | 0.997 |
| 150 | 10.20 | 1.012 | 9.34 | 0.970 |
| Rate constant (min.$^{-1}$) | $3.33 \times 10^{-3}$ | | $3.77 \times 10^{-3}$ | |
| Fig. 4. | Curve 1. | | Curve 2. | |

Table - IX.

Acidity dependence of the oxidation rate.

Temp. 70±.1°C; $[H_2SO_4] + [NaHSO_4] = 6.0M$;
$[\text{Phenylacetic acid}] = 6.6 \times 10^{-2}M$;
$[Cr^{VI}] = 16.60 \times 10^{-4}M$.

| $[H_2SO_4]$ | 5.0M | | 5.5M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 16.66 | 1.221 | 16.66 | 1.221 |
| 15 | 15.30 | 1.184 | 15.40 | 1.187 |
| 30 | 14.54 | 1.162 | 14.13 | 1.150 |
| 45 | 13.67 | 1.136 | 12.87 | 1.109 |
| 60 | 12.53 | 1.098 | 11.50 | 1.060 |
| 75 | 11.56 | 1.063 | 10.52 | 1.022 |
| 90 | 10.93 | 1.038 | 9.72 | 0.987 |
| 105 | 10.43 | 1.018 | 8.80 | 0.944 |
| 120 | 9.58 | 0.981 | 7.87 | 0.896 |
| 135 | 8.80 | 0.944 | 7.10 | 0.851 |
| 150 | 7.97 | 0.901 | 6.17 | 0.790 |
| Rate constant (min.$^{-1}$) | $4.82 \times 10^{-3}$ | | $6.47 \times 10^{-3}$ | |
| Fig. 4. | Curve 3. | | Curve 4. | |

### Table - X.

Acidity dependence of the oxidation rate.

Temp. 70±.1°C; $[H_2SO_4] + [NaHSO_4] = 6.0M$;
$[\text{Phenylacetic acid}] = 6.6 \times 10^{-2}M$;
$[Cr^{VI}] = 16.66 \times 10^{-4}M$.

| $[H_2SO_4]$ | 6.0M | |
|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 16.66 | 1.221 |
| 15 | 15.10 | 1.180 |
| 30 | 13.38 | 1.126 |
| 45 | 11.67 | 1.067 |
| 60 | 10.40 | 1.017 |
| 75 | 9.16 | 0.961 |
| 90 | 7.87 | 0.896 |
| 105 | 7.00 | 0.846 |
| 120 | 6.20 | 0.792 |
| 135 | 5.30 | 0.724 |
| 150 | 4.24 | 0.627 |
| Rate constant ($min.^{-1}$) | $8.05 \times 10^{-3}$ | |

Fig. 4. Curve 5.

Table - XI.

Effect of acidity on the rate constant.

| $[H^+]$ (M) | $[H^+]^2$ | $k \times 10^3$ ($min.^{-1}$) | $\frac{k}{[H^+]} \times 10^3$ ($l.mole^{-1} min.^{-1}$) | $\frac{k}{[H^+]^2} \times 10^4$ ($l^2.mole^{-2} min.^{-1}$) |
|---|---|---|---|---|
| 4.0 | 16.00 | 3.33 | 0.83 | 2.08 |
| 4.5 | 20.25 | 3.97 | 0.88 | 1.98 |
| 5.0 | 25.00 | 4.82 | 0.96 | 1.92 |
| 5.5 | 30.25 | 6.47 | 1.17 | 2.13 |
| 6.0 | 36.00 | 8.05 | 1.34 | 2.23 |

## Temperature dependence

The effect of temperature on the oxidation rate was determined under similar reaction conditions. Activation energy, heat of activation and entropy of activation were determined from the formulae mentioned already. Observations recorded under identical conditions but varying temperature are presented in the following tables. The values of activation parameters are:

Energy of activation = 17.9 Kcal
Heat of activation = 17.2 Kcal
Entropy of activation = −28.5 eu.

FIG. 5

TEMPERATURE DEPENDENCE OF THE REACTION RATE

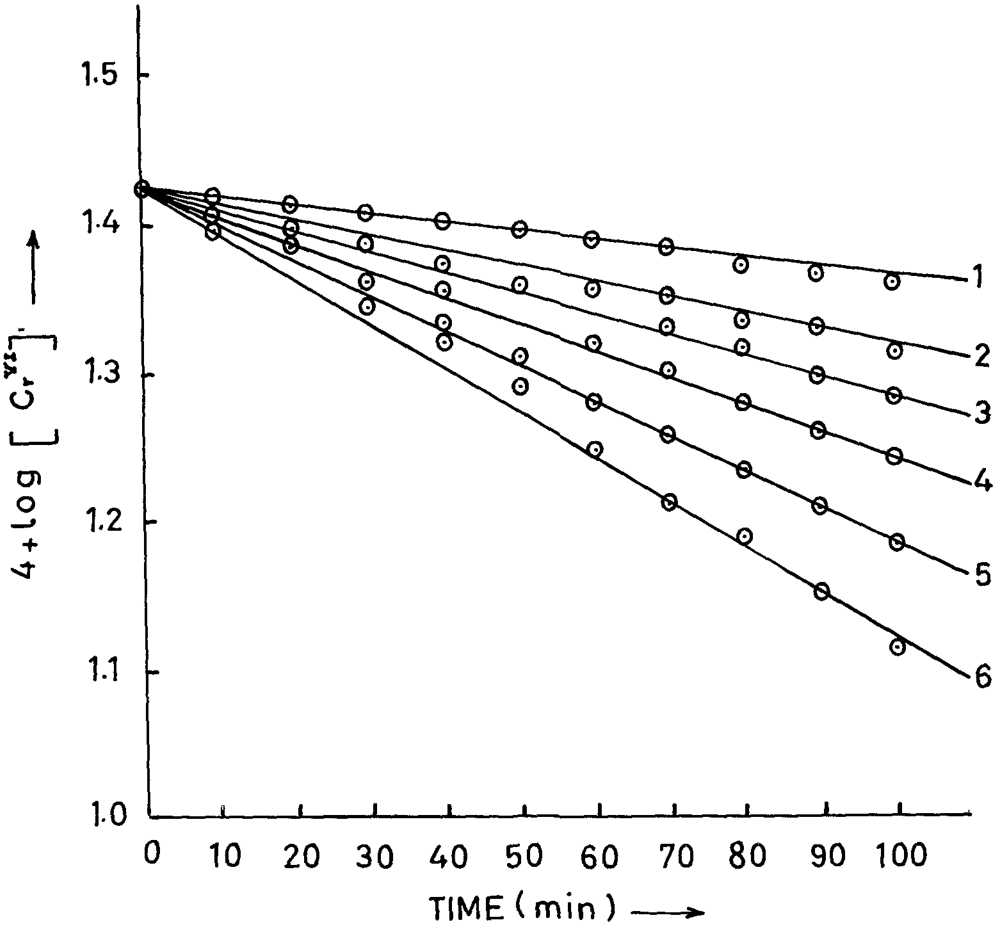


Table - XII.

Temperature dependence of the oxidation rate.

$[H_2SO_4] =$ 5.0M; [Phenylacetic acid] = 5.3 x $10^{-2}$M
$[Cr^{VI}] =$ 26.66 x $10^{-4}$M.

| Temperature | 338°K | | 343°K | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.426 | 26.66 | 1.426 |
| 10 | 26.35 | 1.420 | 26.15 | 1.417 |
| 20 | 26.10 | 1.416 | 25.34 | 1.404 |
| 30 | 25.90 | 1.413 | 24.73 | 1.393 |
| 40 | 25.34 | 1.405 | 23.76 | 1.376 |
| 50 | 24.87 | 1.395 | 23.30 | 1.367 |
| 60 | 24.40 | 1.387 | 22.90 | 1.360 |
| 70 | 24.05 | 1.381 | 22.40 | 1.350 |
| 80 | 23.65 | 1.373 | 21.83 | 1.340 |
| 90 | 23.30 | 1.367 | 21.38 | 1.330 |
| 100 | 22.98 | 1.361 | 20.72 | 1.316 |
| Rate constant (min.$^{-1}$) | 1.53 x $10^{-3}$ | | 2.43 x $10^{-3}$ | |
| Fig. 5. | Curve 1. | | Curve 2. | |

Table - XIII.

Temperature dependence of the oxidation rate.

$[H_2SO_4]$ = 5.0M; [Phenylacetic acid] = $5.3 \times 10^{-2}$M;
$[Cr^{VI}]$ = $26.66 \times 10^{-4}$M.

| Temperature | 348°K | | 353°K | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 25.98 | 1.414 | 25.56 | 1.407 |
| 20 | 25.45 | 1.405 | 24.62 | 1.391 |
| 30 | 24.67 | 1.392 | 23.32 | 1.367 |
| 40 | 23.72 | 1.375 | 21.90 | 1.340 |
| 50 | 23.20 | 1.365 | 20.60 | 1.313 |
| 60 | 22.50 | 1.352 | 19.25 | 1.284 |
| 70 | 21.52 | 1.332 | 18.16 | 1.259 |
| 80 | 20.84 | 1.319 | 17.10 | 1.233 |
| 90 | 20.05 | 1.302 | 16.28 | 1.211 |
| 100 | 19.20 | 1.283 | 15.30 | 1.184 |
| Rate constant (min.$^{-1}$) | $3.55 \times 10^{-3}$ | | $5.33 \times 10^{-3}$ | |
| Fig. 5. | Curve 3. | | Curve 4. | |

FIG. 6

ACTIVATION ENERGY

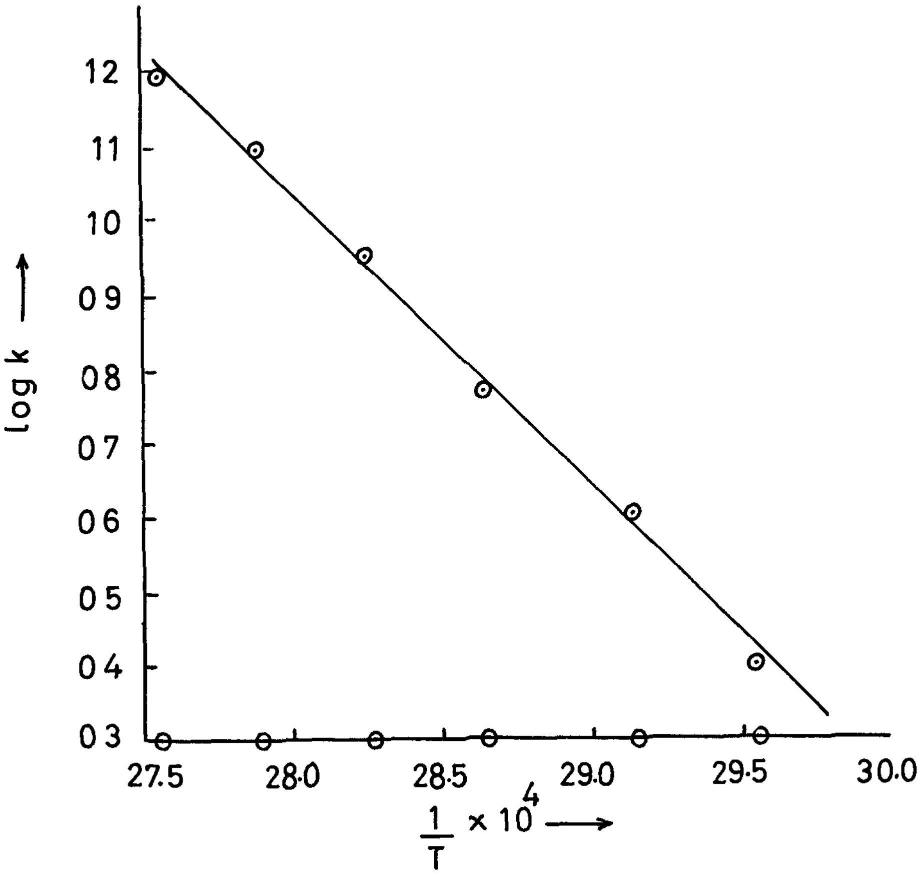


Table - XIV.

Temperature dependence of the oxidation rate.

$[H_2SO_4] = 5.0M$; $[\text{Phenylacetic acid}] = 5.3 \times 10^{-2}M$;
$[Cr^{VI}] = 26.66 \times 10^{-4}M$.

| Temperature | $358^\circ K$ | | $363^\circ K$ | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}](M)$ | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}](M)$ | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 25.53 | 1.407 | 25.14 | 1.400 |
| 20 | 24.20 | 1.383 | 23.67 | 1.374 |
| 30 | 22.70 | 1.356 | 21.68 | 1.336 |
| 40 | 21.10 | 1.324 | 19.70 | 1.294 |
| 50 | 19.57 | 1.291 | 18.13 | 1.258 |
| 60 | 17.82 | 1.251 | 16.10 | 1.206 |
| 70 | 16.44 | 1.215 | 14.37 | 1.157 |
| 80 | 15.32 | 1.185 | 13.35 | 1.125 |
| 90 | 14.07 | 1.148 | 12.08 | 1.082 |
| 100 | 12.90 | 1.110 | 10.56 | 1.023 |
| Rate constant ($min.^{-1}$) | $7.73 \times 10^{-3}$ | | $9.53 \times 10^{-3}$ | |
| Fig. 5. | Curve 5. | | Curve 6. | |

## Effect of ionic strength

The ionic strength of the reaction mixture has been controlled by adding various amounts of sodium perchlorate. Ionic strength of the medium has been calculated on the following assumptions.

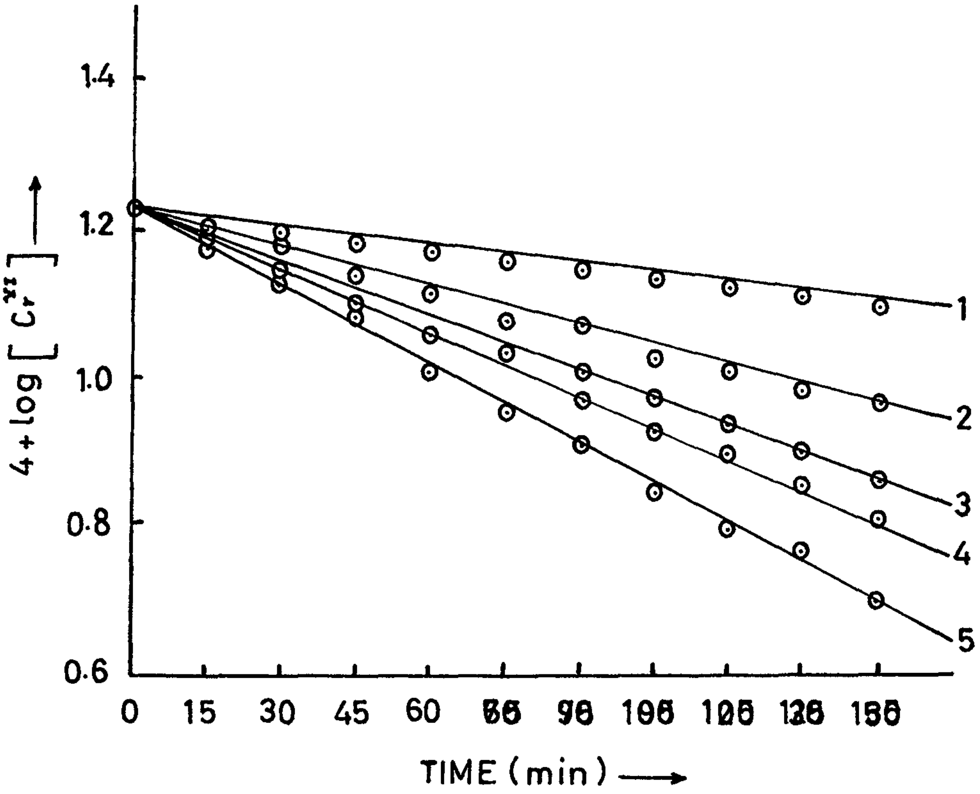
(a) The first dissociation of sulphuric acid is complete and second dissociation is negligible:

(b) Phenylacetic acid and chromic acid do not contribute significantly to the total ionic strength.

The data appear in the following tables:

FIG. 7

DEPENDENCE OF OXIDATION RATE ON IONIC STRENGTH



## Table - XV.

Effect of ionic strength on the reaction rate.

Temp.75±.1°C; $[H_2SO_4] = 4.5M$; [Phenylacetic acid] = $5.3 \times 10^{-2}M$;
$[Cr^{VI}] = 16.66 \times 10^{-4} M$.

| $[NaClO_4]$ | Nil | | 0.5M | |
|---|---|---|---|---|
| Ionic strength | 4.5 | | 5.0 | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 16.66 | 1.221 | 16.66 | 1.221 |
| 15 | 16.20 | 1.209 | 15.23 | 1.182 |
| 30 | 15.82 | 1.199 | 13.80 | 1.140 |
| 45 | 15.40 | 1.187 | 12.88 | 1.110 |
| 60 | 14.92 | 1.173 | 12.08 | 1.082 |
| 75 | 14.46 | 1.160 | 11.76 | 1.070 |
| 90 | 14.04 | 1.147 | 10.82 | 1.035 |
| 105 | 13.72 | 1.137 | 10.23 | 1.010 |
| 120 | 13.33 | 1.125 | 9.90 | 0.996 |
| 135 | 12.94 | 1.112 | 9.60 | 0.982 |
| 150 | 12.50 | 1.096 | 9.25 | 0.966 |
| Rate constant (min.$^{-1}$) | $2.03 \times 10^{-3}$ | | $3.90 \times 10^{-3}$ | |
| Fig. 7. | Curve 1. | | Curve 2. | |

## Table - XVI.

Effect of ionic strength on the reaction rate.

Temp.75$\pm$.1°C; $[H_2SO_4]$= 4.5M; [Phenylacetic acid]= $5.3\times10^{-2}$M; $[Cr^{VI}]$= $16.66 \times 10^{-4}$M.

| $[NaClO_4]$ | 1.0M | | 1.5M | |
|---|---|---|---|---|
| Ionic strength | 5.5M | | 6.0M | |
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 16.66 | 1.221 | 16.66 | 1.221 |
| 15 | 14.58 | 1.163 | 12.27 | 1.154 |
| 30 | 13.36 | 1.126 | 13.00 | 1.114 |
| 45 | 12.30 | 1.090 | 11.92 | 1.076 |
| 60 | 11.42 | 1.058 | 10.84 | 1.035 |
| 75 | 10.85 | 1.035 | 10.29 | 1.012 |
| 90 | 10.03 | 1.001 | 9.54 | 0.979 |
| 105 | 9.24 | 0.965 | 8.40 | 0.924 |
| 120 | 8.74 | 0.941 | 7.97 | 0.901 |
| 135 | 8.08 | 0.907 | 7.22 | 0.858 |
| 150 | 7.50 | 0.874 | 6.70 | 0.826 |
| Rate constant (min.$^{-1}$) | $5.48 \times 10^{-3}$ | | $6.52 \times 10^{-3}$ | |
| Fig. 7. | Curve 3. | | Curve 4. | |

### Table - XVII.

Effect of ionic strength on the reaction rate.

Temp. 75±.1°C; $[H_2SO_4] = 4.5M$;
$[\text{Phenylacetic acid}] = 5.3 \times 10^{-4} M$;
$[Cr^{VI}] = 16.66 \times 10^{-4} M$.

| | |
|---|---|
| $[NaClO_4]$ | 2.0M |
| Ionic strength | 6.5M |

| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
|---|---|---|
| 0 | 16.66 | 1.221 |
| 15 | 13.90 | 1.143 |
| 30 | 11.34 | 1.054 |
| 45 | 10.48 | 1.020 |
| 60 | 9.44 | 0.975 |
| 75 | 8.50 | 0.930 |
| 90 | 7.98 | 0.902 |
| 105 | 6.86 | 0.836 |
| 120 | 6.08 | 0.784 |
| 135 | 5.72 | 0.758 |
| 150 | 4.90 | 0.690 |

| | |
|---|---|
| Rate constant (min.$^{-1}$) | $8.86 \times 10^{-3}$ |

Fig. 7. Curve 5.

FIG. 8

EFFECT OF ACETIC ACID ON THE RATE CONSTANT

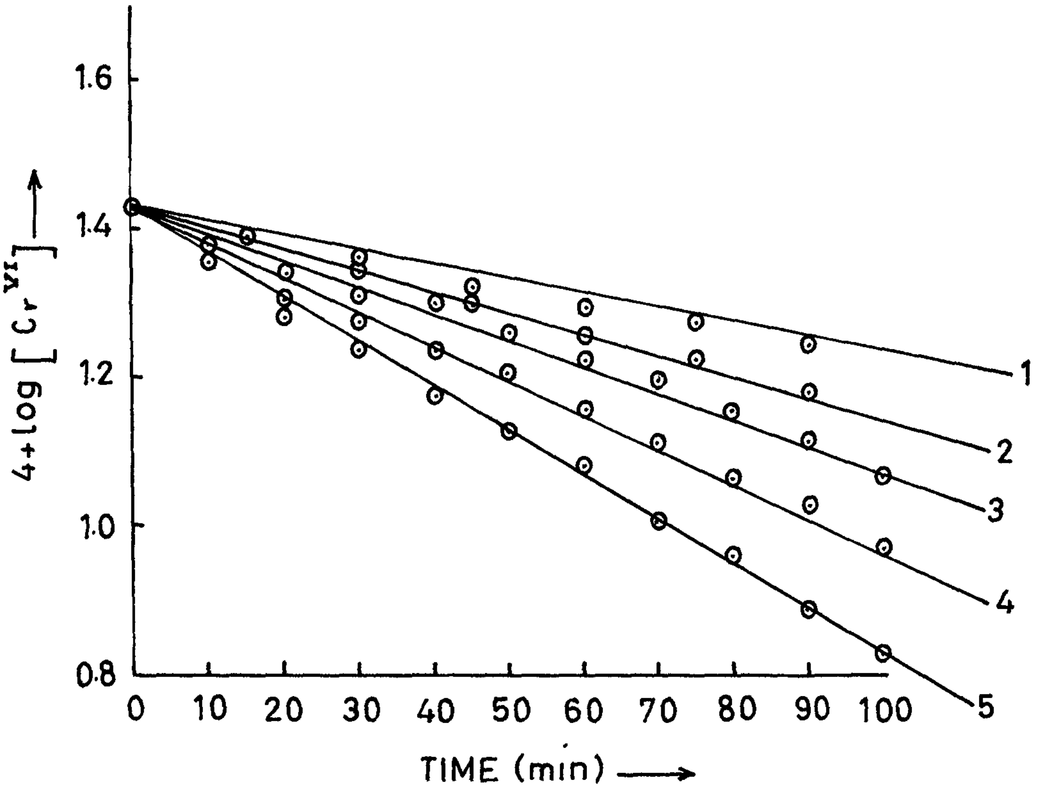


Table - XVIII.

Influence of acetic acid on the reaction rate.

Temp.75±.1°C; [$H_2SO_4$]= 5.0M; [Phenylacetic adid]= $5.3x10^{-2}$M;
[$Cr^{VI}$] = $26.66 \times 10^{-4}$M.

| [Acetic acid] | 0.1M | | 0.2M | |
|---|---|---|---|---|
| Time(mins.) | $10^4$[$Cr^{VI}$](M) | 4+log[$Cr^{VI}$] | $10^4$[$Cr^{VI}$](M) | 4+log[$Cr^{VI}$] |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 15 | 24.90 | 1.396 | 24.98 | 1.397 |
| 30 | 23.03 | 1.362 | 22.96 | 1.361 |
| 45 | 21.66 | 1.335 | 21.46 | 1.331 |
| 60 | 20.23 | 1.306 | 19.95 | 1.300 |
| 75 | 19.13 | 1.281 | 18.72 | 1.272 |
| 90 | 17.42 | 1.241 | 17.66 | 1.247 |
| 105 | 16.38 | 1.214 | 16.43 | 1.215 |
| 120 | 14.78 | 1.170 | 15.03 | 1.177 |
| 135 | 14.07 | 1.148 | 13.80 | 1.140 |
| 150 | 12.73 | 1.104 | 12.18 | 1.085 |
| Rate constant (min.$^{-1}$) | $5.20 \times 10^{-3}$ | | $5.44 \times 10^{-3}$ | |
| Fig. 8. | Curve 1. | | Curve 2. | |

Table - XIX.

Influence of acetic acid on the reaction rate.

Temp. 75 ± .1°C; [$H_2SO_4$] = 5.0M;
[Phenylacetic acid] = 5.3 x $10^{-2}$M;
[$Cr^{VI}$] = 26.66 x $10^{-4}$M.

| [Acetic acid] | 0.8M | |
|---|---|---|
| Time(mins.) | $10^4$[$Cr^{VI}$](M) | 4+log[$Cr^{VI}$] |
| 0 | 26.66 | 1.425 |
| 15 | 24.57 | 1.390 |
| 30 | 22.25 | 1.347 |
| 45 | 20.12 | 1.304 |
| 60 | 17.90 | 1.253 |
| 75 | 16.50 | 1.217 |
| 90 | 15.02 | 1.176 |
| 105 | 13.33 | 1.124 |
| 120 | 12.37 | 1.092 |
| 135 | 10.96 | 1.039 |
| 150 | 9.62 | 0.982 |
| Rate constant (min.$^{-1}$) | 6.90 x $10^{-3}$ | |

Fig. 8. Curve 3.

Table - XX.

Influence of acetic acid on the reaction rate.

Temp.75$\pm$.1°C; $[H_2SO_4]$= 5.0M; [Phenylacetic acid]= $5.3 \times 10^{-2}$M;
$[Cr^{VI}]$= $26.66 \times 10^{-4}$M.

| [Acetic acid] | 0.7M | | 1.0M | |
|---|---|---|---|---|
| Time(mins.) | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ | $10^4[Cr^{VI}]$(M) | $4+\log[Cr^{VI}]$ |
| 0 | 26.66 | 1.425 | 26.66 | 1.425 |
| 10 | 23.38 | 1.368 | 23.54 | 1.371 |
| 20 | 22.12 | 1.344 | 20.32 | 1.308 |
| 30 | 20.25 | 1.306 | 18.26 | 1.261 |
| 40 | 18.88 | 1.276 | 17.35 | 1.240 |
| 50 | 18.08 | 1.257 | 16.04 | 1.205 |
| 60 | 16.80 | 1.225 | 14.48 | 1.161 |
| 70 | 15.86 | 1.200 | 13.08 | 1.116 |
| 80 | 14.64 | 1.165 | 11.77 | 1.070 |
| 90 | 13.33 | 1.125 | 10.70 | 1.030 |
| 100 | 11.82 | 1.072 | 9.30 | 0.968 |
| Rate constant (min.$^{-1}$) | $7.73 \times 10^{-3}$ | | $9.20 \times 10^{-3}$ | |
| Fig. 8. | Curve 4. | | Curve 5. | |

# CHAPTER V

# DISCUSSION

The kinetics of oxidation of lower fatty acids by chromic acid closely resembles that of hydrocarbons by the same oxidant. The trend in reactivity of the methyl, methylene and methine groups has been found to be similar in both the reactions. The introduction of phenyl group has the same effect as in the case of hydrocarbons. From the similarity in the rates of oxidation of hydrocarbons and fatty acids, conclusion is drawn that the reaction possesses important features of carbonium ions.

From the preliminary experiments it is observed that acetic and pivalic acids are not attacked by chromic acid. It indicates that neither methyl group nor carboxyl group is oxidized by this oxidant. The resistivity of these groups towards chromic acid oxidation has also been demonstrated by Hickinbottom[149] and Rocek[93]. This clearly indicates that methylene and methine groups of the aliphatic acids are oxidized.

The reaction rate depends upon the first power of Cr(VI), the first power of substrates, but the dependence of rate constant on hydrogen ion concentration is of second order. It is seen that as the concentration of Cr(VI) is decreased, the first order rate constant increases. But the increase is not to an extent such that a higher order term in Cr(VI) may be defined. Similar effect was observed by Novick and Westheimer[15] in the oxidation of isopropyl alcohol and by Kemp and Waters[98] in the oxidation of formic acid and formaldehyde. The explanation put forward by Westheimer that it is due to the hydrolysis of the dichromate ion

$$Cr_2O_7^{=} + H_2O \rightleftharpoons 2\ HCrO_4^{-}$$

seems to be the correct one.

Rocek and Krupicka[26] showed that in strong sulphuric acid solutions, the rate of chromic acid oxidation of isopropyl alcohol follows $H_o$, since the water molecule does not participate in the transition state. Westheimer[41] showed that $H_o$ is not the correct acidity function to be used in describing the protonation of the acid chromate ion and the $H_-$ function should be used. The latter increases more rapidly with decreasing water concentration in the solvent than does $H_o$ since both proton and acid chromate ion will be hydrated whereas the neutral product chromic acid will have a considerable degree of hydration. Lee and Stewart[150] introduced a new function $H_- + \log a_{H_2O}/a_{HA}$ and showed that it gave a much better fit to the ionization data than the simple acidity functions $H_o$ or $H_-$. By comparing the values of these functions, it is seen that the value of new function decreases more rapidly than $H_-$. The values of these functions at higher temperatures are not reported in the literature but it has been determined[67] that a very small but systematic drift is found in the relationship between acidity function and acid concentration with changing temperature. However, the plots of logarithm of rate constants against new acidity function yielded a straight line but the slope was quite high. The high slope may be due to the use of unvalid acidity functions.

It has been shown that the oxidation of organic substrates by Cr(VI) depends upon its particular species whose stability and structure depends upon the acidity of the medium. Chromic acid is a fairly strong acid ($k_1 = 0.18$, $k_2 = 3.2 \times 10^{-7}$) and in dilute aqueous solutions the following equilibria have been reported[151-153].

(a) $H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^-$

(b) $HCrO_4^- \rightleftharpoons H^+ + CrO_4^{=}$

(c) $2HCrO_4^- \rightleftharpoons Cr_2O_7^{=} + H_2O$

(d) $HCr_2O_7 \rightleftharpoons H^+ + Cr_2O_7$

(e) $H_2Cr_2O_7 \rightleftharpoons H^+ + HCr_2O_7^-$

The dimerization equilibrium (C) is of great importance. In dilute acidic aqueous solutions, at concentrations greater than 0.05M, the dichromate ion (and its protonated species) is the predominant species and at lower concentrations, the monomer (and its protonated species) predominates[152]. It has also been confirmed[12] that dichromate ion is a far weak oxidising agent than acid chromate ion. Very little, however, is known about the chromium species in the strong acidic medium.

It has been suggested by many workers that electron deficient cations such as $H\overset{+}{Cr}O_3$ and $H_3\overset{+}{Cr}O_4$ are the most probable species[26,154,155]. Since the concentration of sulphuric acid used is comparable to that used formerly, it can safely be concluded that the protonated species as shown above are the effective oxidizing agent in our system. .

It is seen that increase in ionic strength increases the rate of oxidation. Interpretation of these data seems to be difficult as there may be many factors which may cause a change in rate with changing ionic strength. The acid chromate-dichromate equilibrium is a function of ionic strength for two reasons. First, increasing ionic strength will favour the formation of a divalent ion and secondly, a divalent ion will have a higher ion pair association constant than a univalent ion. Both of these effects cause the equilibrium to shift towards the dichromate ion as the ionic strength increases. This would correspondingly decrease the rate of reaction. It is contrary to our findings and hence this explanation is untenable. The decrease in rate constant with increasigg ionic strength indicates a reaction between oppositely charged ions. But increase in rate with increasing ionic strength is consistant with a reaction between neutral molecule and charged species[156]. It seems reasonable because the reacting aliphatic acid molecule is undoubtelly a neutral molecule and hexavalent chromium is a cationic species $HCrO_3^+$. Therefore step (2) of the reaction mechanism is favoured by increasing ionic strength.

The influence of chain length on the rate of oxidation of fatty acids was determined and the observed order of reactivity followed the sequence propionic < butyric < valeric. This is the order of reactivity expected on the basis of Rocek and Krupicska's mechanism[26]. The increase in the rate constant with increasing carbon chain may be due to the greater number of methylene groups or it may be due to the nucleophilicity of larger alkyl groups, a situation similar to that found earlier for the chromic acid oxidation of alcohols[33]. It is also known[51,133,147,156], that carboxyl group greatly inhibits the chromic acid oxidation of carbon chain. Rocek[93] carried out the qualitative investigation of the carboxyl group effect and attempted to express this influence on the basis of his kinetic data. We also found that the order of reactivity of fatty acids is in agreement with Rocek's observation. As the carbon chain increases, the inductive effect of carboxyl group diminishes and hence the increase in oxidation rate with increasing chain length takes place.

It is well known that branching in the $\beta$-position to the reaction centre has a very pronounced effect on the reaction velocities and can cause changes in the rate constants of many orders of magnitude[157]. The results on the oxidation of branched chain acids show that the replacement of one hydrogen by one methyl group increases the rate by 20 times. This is consistant with the fact that methyl groups which are electron releasing make the methylene group more negative and thus facilitate the attack by electrophilic species $HCrO_3^+$. The high rates of oxidation of branched chain acids can also be accounted in the same way.

In order to follow the effect of benzene ring on the oxidation rate of aliphatic acids benzoic and phenylacetic acid were taken. Benzoic acid was hardly oxidized but phenylacetic acid was oxidized about 25 times faster than propionic acid. The increase of the reaction rate cannot however, be attributed to the oxidation of benzene ring which is hardly affected by chromic acid as evidenced by the unreactivity of benzoic acid which is formed as the end-product.

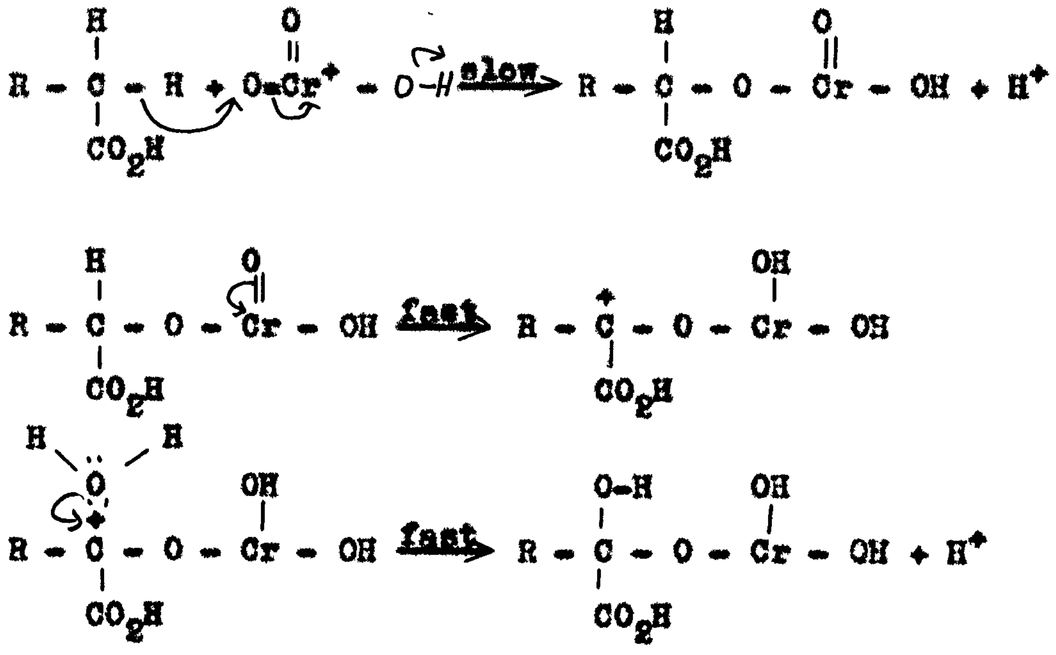
The rate of chromic acid oxidation of fatty acids in the presence of manganous or cerous ions was found difficult to measure. However, experiments were performed with various concentrations of manganese (II) and cerium (III) ions. The rates were highly irregular and, therefore, no satisfactory conclusion could be drawn. The fact is that there are many complications which are responsible for these irregular results. Firstly, various manganese salts obscures the end point of an iodometric titration (perhaps by catalysing the air oxidation of $I^-$). Secondly, the analytical procedure determines both the Cr(VI) concentration and the concentration of manganese species of oxidation states higher than two. Several attempts were made to find an analytical procedure which would distinguish between Cr(VI) and higher oxidation states of manganese and cerium. But no such procedure could be evolved. It was however, found that the amount of chromic acid consumed in the reaction mixture to which no manganese (II) or cerium (III) ions had been added, was more than that to which these ions had been added. It indicated that some retardation by these ions was caused.

On the basis of the results which have been obtained the rate law may be written as

$$-\frac{d(Cr^{VI})}{dt} = k[\text{Fatty acid}][Cr^{VI}][H^+]^2.$$

The following mechanism which is consistant with the above rate law, involves the direct transfer of methylene hydrogens as hydride ions to the oxidising agent.

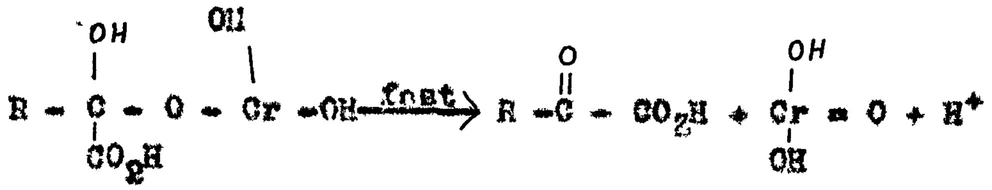
(1) $HCrO_4^- + 2H^+ \rightleftharpoons H\overset{+}{C}rO_3 + H_2O$



(2) $R-\overset{H}{\underset{CO_2H}{C}}-H + O=\overset{O}{\overset{\|}{Cr^+}}-O-H \xrightarrow{slow} R-\overset{H}{\underset{CO_2H}{C}}-O-\overset{O}{\overset{\|}{Cr}}-OH + H^+$

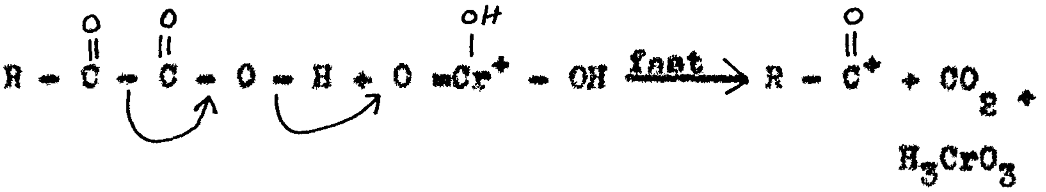
(3) $R-\overset{H}{\underset{CO_2H}{C}}-O-\overset{O}{\overset{\|}{Cr}}-OH \xrightarrow{fast} R-\overset{+}{\underset{CO_2H}{C}}-O-\overset{OH}{Cr}-OH$

(4) $\overset{H_2\ddot{O}}{}\ R-\overset{+}{\underset{CO_2H}{C}}-O-\overset{OH}{Cr}-OH \xrightarrow{fast} R-\overset{O-H}{\underset{CO_2H}{C}}-O-\overset{OH}{Cr}-OH + H^+$

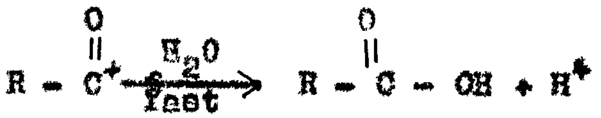
(5) 

$$R - \overset{OH}{\underset{CO_2H}{C}} - O - \overset{OH}{Cr} - OH \xrightarrow{fast} R - \overset{O}{\overset{\|}{C}} - CO_2H + \overset{OH}{\underset{OH}{Cr}} = O + H^+$$

(6) $H_2CrO_3 + HCrO_3^+ + H^+ \xrightleftharpoons{fast} CH_2CrO_3$

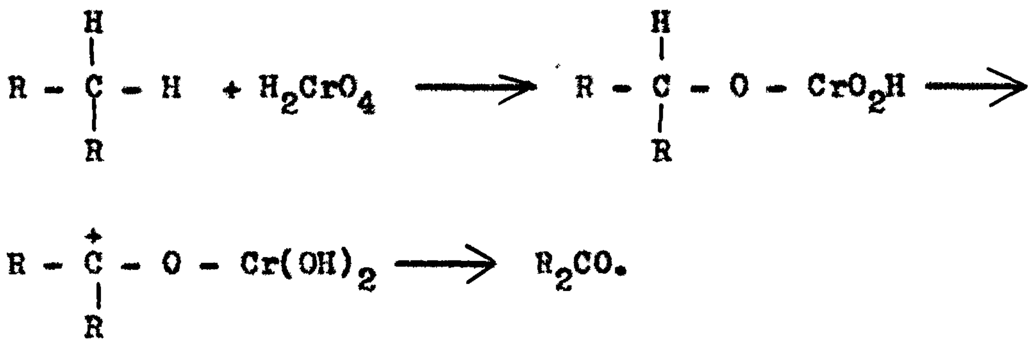
(7) 

$$R - \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{C}} - O - H + O = \overset{OH}{Cr^+} - OH \xrightarrow{fast} R - \overset{O}{\overset{\|}{C}}{}^+ + CO_2 + H_3CrO_3$$

(8) 

$$R - \overset{O}{\overset{\|}{C}}{}^+ \xrightarrow[fast]{H_2O} R - \overset{O}{\overset{\|}{C}} - OH + H^+$$

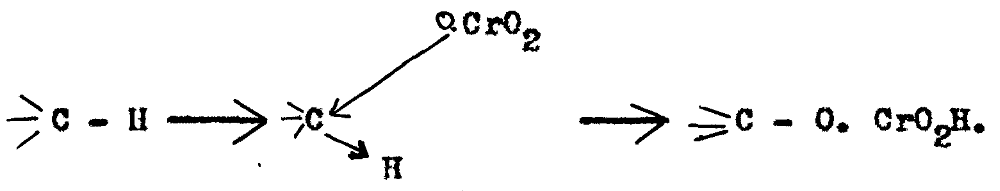
Hares and Roock[158] reported that the oxidation of methylene group was a two stage process. In the first stage a partially developed carbonium ion is formed (by hydride ion transfer); the second step is the reaction of this species with Cr(IV) compound already formed in the first stage. In our reaction mechanism equations (2) and (3) show the formation of carbonium ion from the fatty acid molecule. The formation of carbonium ions in the chromic acid oxidation of organic compounds has been confirmed by Necsoiu[159]. It is reasonable to assume equation (2) as the rate determining step since it involves the abstraction of hydride ion. (generally hydride shifts are relatively slow processes). A mechanism very similar to this has been postulated by Foster and Hickinbottom[149] for the chromic acid, oxidation of methylene group in the saturated hydrocarbons.



$$R-\underset{R}{\overset{H}{C}}-H + H_2CrO_4 \longrightarrow R-\underset{R}{\overset{H}{C}}-O-CrO_2H \longrightarrow$$

$$R-\underset{R}{\overset{+}{C}}-O-Cr(OH)_2 \longrightarrow R_2CO.$$

The intermediate $>C-O.CrO_2H$ postulated as common to these oxidations was assumed to arise by abstraction of a hydride ion to give a carbonium ion capable of combining with $\overset{+}{HCrO_3}$. It is suggested that the intermediate $>C-O.CrO_3H$ may also be formed by direct attack of chromium trioxide on the carbon.



When the carbonium ion has been formed it picks up a water molecule from the solvent to give the complex compound shown in equation (4). This complex subsequently breaks down to give keto acid and a compound of tetravalent chromium. The fate of this intermediate (as shown in eqn.6) is similar to that previously postulated[1,99,160]

. The hydride abstraction mechanism in our system is strengthened by the fact that groups which release electrons, would be expected to facilitate such a reaction and are observed to enhance the oxidation rate. The keto acid is cleaved to give $R - \overset{\overset{O}{\|}}{C}{}^{+}$ and carbon dioxide. $R - \overset{\overset{O}{\|}}{C}{}^{+}$ reacts with water rapidly forming the lower acid. The cleavage of keto acid can not be caused by direct attack of chromic acid on the keto acid molecule but must result from the action of some unstable intermediate containing chromium in an unusual valence state. The evidence for it was obtained by adding manganese or cerous ions to the reaction mixture. These ions are not oxidized by chromic acid itself but the earlier work[160] shows that these ions react rapidly according to the equations

$$Cr^{IV} + Mn^{II} \longrightarrow Cr^{III} + Mn^{III}$$

$$Cr^{IV} + Ce^{III} \longrightarrow Cr^{III} + Ce^{IV}.$$

Furthermore, an unstable intermediate containing pentavalent chromium also occurs during chromic acid oxidations[160] but arises only from tetravalent chromium by way of reaction (6). Therefore, when $Mn^{++}$ or $Ce^{+++}$ sweeps away tetravalent chromium from solution, it removes pentavalent chromium as well. Hence no cleavage of keto acid takes place.

As the reaction under study is very complicated, no significance can be attached to the thermodynamic parameters. However, these functions have been calculated and are tabulated below.

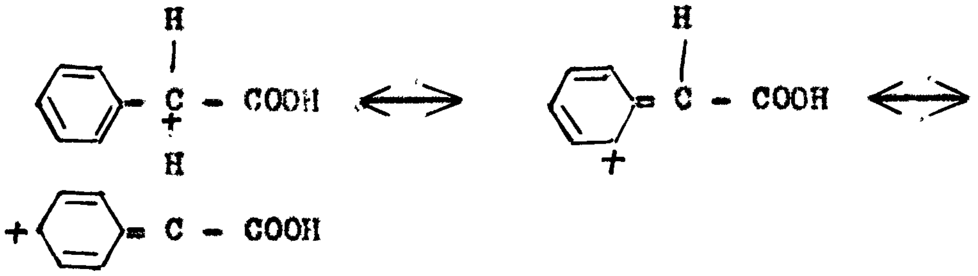
| Acid | E (Kcal/mole) | $\Delta F^{\ddagger}$ (Kcal/mole) | $\Delta H^{\ddagger}$ (Kcal/mole) | $\Delta S^{\ddagger}$ ( eu.) |
|---|---|---|---|---|
| Propionic acid | 17.0 | 27.2 | 16.3 | - 30.8 |
| Butyric acid | 18.4 | 26.9 | 17.7 | - 26.1 |
| Valeric acid | 20.7 | 26.7 | 20.0 | - 19.1 |
| Isobutyric acid | 14.7 | 27.3 | 14.0 | - 37.5 |
| Isovaleric acid | 11.5 | 27.2 | 10.8 | - 46.5 |
| Phenylacetic acid | 17.9 | 27.3 | 17.2 | - 28.4 |

It is seen that the value of $\Delta F^{\ddagger}$ is the same in all the acids. But the values of energy of activation E and $\Delta H^{\ddagger}$, however, increase with the increase in chain length. These values are comparatively low for branched chain acids. It is well known that if $\Delta S^{\ddagger}$ is positive, the formation of activated complex is more probable and the reaction is fast while negative entropy of activation indicates slow reactions. A comparison of $\Delta S^{\ddagger}$ values for straight chain acids justifies the observed order of reactivity, valeric $>$ butyric $>$ propionic.

The high rates of oxidation in the presence of acetic acid can be explained by assuming that in the solvents containing acetic acid, most of the chromic acid is present as an acetyl derivative $CH_3COOCrO_3H$ or its conjugate acid $CH_3COO\ CrO_3H_2^+$ with an oxidizing power considerably higher than that of even chromic acid or chromacidium ion. It is evident that the replacement of a hydroxyl hydrogen by an acetyl group would considerably decrease the electron density on the central chromium atom and increase its electrophilic reactivity and hence the greater oxidizing power.

Another explanation which seems attractive is that the reaction mechanism involves the transient formation of carbonium ions. The length of the life of a carbonium ion depends upon the nucleophilic properties of a solvent. It has been reported[161] that increasing acetic acid concentrations stabilize a carbonium ion. Thus a greater concentration of acetic acid should favour a mechanism that leads to such an intermediate. It has also been reported (Hall and Spengeman, reported at the Kansas City meeting of the A.C.S. April, 1936) on the basis of more extensive data, that a solution of sulphuric acid in glacial acetic acid is much more acidic than that of the same sulphuric acid concentration in water.

The high rate of oxidation of phenylacetic acid is also consistent with our mechanism because phenyl group stabilizes the carbonium ion due to resonance.



The reaction which is the subject of the present study had to be followed in a medium of considerable complexity. It is, therefore, unlikely that any suggested reaction scheme will be susceptible to rigorous analysis.

# BIBLIOGRAPHY

1. Hampton, J., Leo, A., and Westheimer, F.H.
J. Am. Chem. Soc., 78, 306 (1956).

2. Cawley, J.J., and Westheimer, F.H.
ibid., 85,177 (1963).

3. Mosher, W.A., and Langerak, E.O.
ibid., 71, 286 (1949).

4. Heidig, H.A., Funck, D.L., Wrich, R., Baker, R.,
and Kreiser, W.,
ibid., 72, 4617 (1950).

5. Bowden, K., Heilborn, I.M., Jones, E.R.H., and
Weedon, B.C.L.
J. Chem. Soc., 1946, 39.

6. Bowman, M.I., Moore, C.E., Deutsch, H.R., and
Hartman, J.L.
Trans. Kentucky Acad. Sci, 14, 33 (1953).

7. Feiser, L.F.,
J. Am. Chem. Soc., 75, 4386 (1953).

8. Poos, G.I., Arth, G.E., Buyler, R.E., and Sarett, L.H.
J. Am. Chem. Soc., 75, 422 (1953).

9. Holum, J.R.,
J. Org. Chem., 26, 4814 (1961).

10. Mosher, W.A., and Preiss, O.M.
J. Am. Chem. Soc., 75, 5605 (1953).

11. Oppenauer, R.V., and Oberrauch, H.
Anales. Asoc. Quim., Arg., 37, 246 (1949).

12. Leo, A., and Westheimer, F.H.
J. Am. Chem. Soc., 74, 4383 (1952).

13. Anbar, M., Dostrovsky, I., Samuel, D., and Yoffe, A.D.
J. Chem. Soc., 1954, 3603.

14. Zeiss, H.H., and Mathews, C.N.
J. Am. Chem. Soc., 78, 1694 (1956).

15. Westheimer, F.H., and Novick, A.
J. Chem. Phys., 11, 506 (1943).

16. Cohen, M., and Westheimer, F.H.
ibid., 74, 4383 (1952).

17. Kuivilu, H.G., and Beeker, W.J.
ibid., 74, 5329 (1952).

18. Antony, V., and Chatterjee, A.K.
Z. Anorg. Allgem. Chem., 280, 110 (1955).

19. Schreiber, J., and Eschenmosher, A.
Helv. Chim. Acta., 38, 1529 (1955).

20. Kwart, H., and Francis, P.S.
J. Am. Chem. Soc., 77, 4907 (1955).

21. Rocek, J., and Krupicka, J.
Coll. Czech. Chem. Commun., 23, 2068 (1958).

22. Chaterjee, A.C., and Antony, V.
Z. Physik, Chem. (Leipzig), 210, 103 (1959).

23. Krauss, H.L., Z. Naturforsch, 136, 199 (1958).

24. Klamiong, U.,
Acta. Chim. Scand. 11, 1313 (1957) 12, 576 (1958).

25. Rocek, J., Westheimer, F.H., Eschenmosher, A.,
Moldovanyi, L., and Schreiber, J.
Helv. Chim. Acta., 45, 2554 (1962).

26. Rocek, J., and Krupicka, J.
Chem. and Ind. (Lond.), 1668 (1957).

27. Westheimer, F.H., and Chang, Y.W.
J. Phy. Chem., 63, 438 (1959).

28. Kwart, H., and Francis, P.S.
J. Am. Chem. Soc., 77, 4907 (1955).

29. Graham, G.T.E., and Westheimer, F.H.
ibid., 80, 3030 (1958).

30. Cawley, J.T., and Westheimer, F.H.
Chem. and Ind. (London), 656 (1960).

31. Lansbury, P.T., Pattison, U.A., and Diehl, J.W.
Chem. and Ind. (London), 653 (1962).

32. Sager, F.,
J. Am. Chem. Soc., 78, 4970 (1950).

33. Rocek, J.
Coll. Czech. Chem. Comm., 23, 833 (1957).
25, 375 (1960).

34. Slack, R., and Waters, W.A.
J. Chem. Soc., 594 (1949).

35. Chatterjee, A.K., and Mukherjee, S.K.,
Z. Physik Chem. (Leipzig), 207, 372 (1957);
208, 281, (1958); 210, 166 (1959).

36. Chang, Y.W., and Westheimer, F.H.
J. Am. Chem. Soc., 82, 1401 (1960).

37. Criegee, R., Kraft, L., and Rank, R.
Ann., 507, 159 (1933).

38. Buist, G.J., and Bunton, C.A.
J. Chem. Soc., 4580 (1957).

39. Rocek, J., and Westheimer, F.H.
J. Am. Chem. Soc., 84, 2241 (1962).

40. Lucchi, E.
Boll. Sci. Fac Chim. Ind. Bologna, 208, 333, (1940);
Gazz. Chim. Ital., 71, 729, 752 (1941).

41. Wiberg, K.B., and Hill, T.
J. Am. Chem. Soc., 80, 3022 (1958).

42. Wiberg, K.B., and Stewart, R.
ibid., 77, 1786 (1955).

43. Rocek, J.,
Tetrahedron Letters, No. 5, 1 (1959).

44. Chatterjee, A.K., and Mukherjee, S.K.
J. Am. Chem. Soc., 80, 3600 (1958).

45. Kemp, T.J., and Waters, W.A.
Proc. Roy. Soc., A274, 480 (1963).

46.(a) Bell, R.P., B. Darwent, B.D.B.,
Trans. Faraday, Soc., 46, 34 (1950).

46.(b) Bell, R.P., and Clunie, J.C.
ibid., 48, 439 (1952).

46.(c) Bell, R.P., Rand, M.H., and (Miss) Wynne-Jones, K.M.A.
ibid., 52, 1093 (1956).

47. Bell, R.P., and Rand, M.H.
Bull. Soc. Chim., 115, 115 (1955).

48. Fuson, R.C., Advanced Organic Chemistry.
John Willey & Sons. Inc., New York, N.Y. 1954, p.366.

49. Merz, J.H., and Waters, W.A.
Diss. Farad. Soc., No. 2, 186 (1947).

50. Wiberg, K.B., and Richardson, W.H.
J. Am. Chem. Soc., 84, 2800 (1962).

51. Petit, G.
Bull. Soc. Chim. France., 12, 568 (1945).

52. Umeda, K., and Tarama, K.I.
Nippon Kagaku Zasshi, 83, 1216 (1962).

53. Best, P.A., Lettler, J.S., and Wabes, W.A.
J. Chem. Soc., 1962, 822; Littler, J.S., ibid, 1962, 827, 832.

54. Wiberg, K.B., and Gatzke, A.L.
Unpublished results.

55. Rocek, J., and Rielh, Sr.A. Private Communication.

56. Guyot, J., and Simon, L.J.
Compt. rend. Acad. Sci., 170, 736 (1920).

57. Goves, C.E.
Ann., 167, 357 (1873).

58. Beilstein, F., and Kurbatow, A.
Ann., 202, 215 (1880).

59. Wendland, R., and LaLonde, J.
Org. Syn. Coll., Vol. IV, 757 (1963).

60. Abell, R.D.,
J. Chem. Soc., 1951, 1379.

61. Fittig, R., Ahrens, W., and Mattheides, L.
Ann., 147, 15 (1868).

62. Slack, R., and Waters, W.A.
J. Chem. Soc., 1948, 1666.

63. Ogata, Y., and Akimoto, H.
J. Org. Chem., 27, 294 (1962).

64. Brandenberger, S.G., Maas, L.W., and Dvoretzky, I.,
J. Am. Chem. Soc., 83, 2146 (1961).

65. Friedman, L., Fishel, D.L., and Schechter, H.
J. Org. Chem., 30, 1453 (1965).

66. Evans, K.B., and Evans, R.J.
Tetrahedron, 8, 313 (1960).

67. Paul, M.A., and Long, F.A.
Chem. rev., 57, 1 (1957).

68. Behr, A.
Ber., 5, 277 (1872).

69. Blitz, H.
Ann., 296, 219 (1897).

70. Bockemuller, W., and Janssen, R.
Ann., 542, 166 (1939).

71. Barbier, P., and Locquin, R.
Compt. rend. Acad. Sci., 156, 1443 (1913).

72. Wieland, H., Schlichting, and Jacobi, R.
Z. Physiol. Chem., 161, 80 (1926).

73. Berlin, A.A., Davankov, A.D., and Kalliopin, L.E.
J. Appl. Chem. USSR., 18, 217 (1945).

74. Hickinbottom, W.J., and Wood, D.G.M.
Nature, 168, 33 (1951).

75. Hickinbottom, W.J., Hogg, D.R., and Wood, D.G.M.
J. Chem. Soc., 1954, 4400.

76. Hickinbottom, W.J., Peters, D., and Wood, D.G.M.
J. Chem. Soc., 1955, 1360.

77. Zeiss, H.H., and Zwanzig, F.R.
Chem. and Ind. (London), 545, 1956.
J. Am. Chem. Soc., 79, 1733 (1957).

78. Davis, M.A., and Hickinbottom, W.J.
J. Chem. Soc., 1958, 2205.

79. Elks, J., Evans, R.M., Longe, A.G., and Thomas, G.H.
J. Chem. Soc., 1954, 451.

80. Mares, F., and Rocek, J.
Coll. Czech. Chem. Comm., 26, 2370 (1960).

81. Rock, J. and Mares, F.
ibid, 24, 2741 (1959).

82. Rocek, J.
ibid, 22, 1509 (1957).

83. Kourim, P., and Tykva, R.
ibid., 26, 2511 (1961).

84. Fieser, L.F.,
J. Am. Chem. Soc., 70, 3237 (1948).

85. Bredt, J., and Pinten, P.
J. Prakt. Chem., 115, 45 (1927).

86. Sager, W.F., and Brodley, A.,
J. Am. Chem. Soc., 78, 1187 (1956).

87. Sager, W.F.
ibid., 78, 4970 (1956).

88. Rocek, J.
Coll. Czech. Chem. Commun., 23, 833 (1958).

89. Wiberg, K.B., and Eisenthal, R.
Tetrahedron., Vol. 20, 1151-61 (1964).

90. Rocek, J.
Tetrahedron Letters, 135 (1962).

91. Snethlage, H.C.S., R
Rec. Trav. Chim., 59, 111 (1940).

92. Azanares, J.I., and Raga, J.B.V.
Anales. Real. Soc. Espan. Fis. Quim. (Madrid)
Ser, B50, 545, 656 (1954).

93. Mares, F., and Rocek, J.
Coll. Czech. Chem. Commun., 26, 2389 (1961).

94. Kreulen, D.J.W., and Ter. Horst, D.T.J.
Rec. Trav. Chim., 59, 1165 (1940).

95. Snethlage, H.C.S.
ibid., 60, 877 (1941).

96. Mahajani, A.V., and Bhattacharya, A.K.
Proc. Natl. Acad. Sci. India, sect A23(2) 65 (1954).

97. Pungor, E., and Trompler, J.
J. Inorg. Nucl. Chem., 5, 123 (1957).

98. Mahajani, A.V.
Proc. Natl. Acad. Sci. India, sect. A26(1), 49(1957).

99. Westheimer, F.H.
Chem. rev., 45, 419 (1949).

100. Chapman, E.T., and Smith, M.H.
J. Chem. Soc., 20, 173 (1867).

101. Coninck, W.O.De.,
Chem. Zentr., 1906, 1, 449.

102. Beilstein, F., and Wiegand, E.
Ber., 17, 840 (1884).

103. Bakore, G.V., and Narain, S.
J. Chem. Soc., 1963, 3419.

104. Kwart, H., and Francis, P.S.
J. Am. Chem. Soc., 77, 4907 (1955).

105. Tocher, M.
J. Chem. Edn., 35, 207 (1958).

106. Hetch., and Grungweig.
Ber., XI, 1053 (1878).

107. Dakin, H.D.
J. Biol. Chem., 4, 77 (1908).

108. Dakin, H.D.
ibid., 4, 91, 227 (1908).

109. Dakin, H.D.
Am. Chem. J., 44, 41-48 (1910).

110. Chutterbuck, P.W., and Raper, H.S.,
Biochem. J., 19, 385 (1925).

111. Allen, R.H., and Witzemann, E.J.
J. Am. Chem. Soc., 63, 1922 (1941).

112. Ogata, Y., and Sawaki, Y.
Tetrahedron, 21, 3381 (1965).

113. Hatcher, W.H., and Hill, A.C.
Trans. Roy. Soc. Can. Sect(III)(3), 23 (1929).

114. Berezin, I.V. Ugarova, N.N.,Panish, A.M., and
Khrolova, O.R.
Zh. Fiz. Khim., 39(2), 369 (1965).

115. Csanyi, L.J.
Acta. Chim. Acad. Sci. Hungary., 21, 35-40 (1959).

116. Foster, L.M., and Payne, J.H.,
J. Am. Chem. Soc., 63, 223-25 (1941).

117. Kline, L.
Biochem. Z., 220, 117 (1930).

118. Dimitrov, D., and Natan, V., Godishnik
Khim. Technol Inst., 8(2), 127 (1961).

119. Neunhoeffer, O., and Raths, J.
J. Prakt. Chem., (4), 2, 84 (1955).

120. Deupre, J.F., and Lyons, R.E.
Proc. Indiana, Acad. Sci., 46, 101 (1937).

121. Fleury, P., and Boisson, R.
J. Pharm. Chim., 30, 307, 16 (1939).

122. Morette, A., and Gaudefroy, G.
Compt. rend., 237, 1523 (1953).

123. Clifford, A.A., and Waters, W.A.
J. Chem. Soc., 1965, 2796.

124. Polonovski, M.
Compt. rend., 178, 576 (1924).

125. Polonovski, M., and Lindenberg, A.
ibid., 209, 546 (1939).

126. Sully, B.D.
J. Chem. Soc., 1942, 366.

127. Feigl, F., 'Spot Tests in Organic analysis'
Elsvier Publishing Company, 1960., pp. 369, 121.

128. Kenyon, J., and Symons, M.C.R.
J. Chem. Soc., 1953, 2129.

129. Podo, J.S.P., and W.A. Waters.
ibid., 1956, 717.

130. Beckwith, A.L.J., and Goodrich, J.E.
Aust. J. Chem., 18, 1023 (1965).

131. Bacon, R.G.R., and Bott, R.W.
Chem. and Ind., 1953, 1285.

132. Fichter, F., and Heer, J.
Helv. Chim. Acta., 18, 1276 (1935).

133. Cason, J. Fessenden, S., and Agre, C.L.
Tetrahedron, 7, 289 (1959).

134. Dakin, H.D.
J. Biol. Chem., 4, 419 (1908).

135. Dakin, H.D.
ibid., 4, 424 (1908).

136. Jones, R.O., and MacLean, I.S.,
Biochem. J., 29, 1877 (1935).

137. Dagley, S., Fewster, M.E., and Happold, F.C.
J. Bact., 63, 327-36 (1952).

138. Hockenhull, D.J.D., Walker, A.D., Wilkin, G.D.,
and Winder, F.G.
Biochem. J., 50, 605 (1952).

139. Spiro, K.
Helv. Chim. Acta., 4, 459 (1921).

140. Prazheval'skii, D.S.
J. Russ. Phys. Chem. Soc., 49, 567-72 (1917-18).

141. Skraup, S., and Schwanberger, E.
Ann., 462, 135-58 (1928).

142. Dimitrov, D., and Stefanova, A.D., Godishnik
Khim. Technol Inst., 11(2), 159 (1964).

143. Barakat, M.Z., Wahab, M.F.A., and El-Sadar, M.M.
J. Chem. Soc., 1956, 4685.

144. Kratzl, K., Hoyos, F.E., and Silbernagel, H.
Montash. Chem., 91, 219-26 (1960).

145. Horii, Z., and Sakurai, K.
J. Pharm. Soc. Japan, 77, 1-2 (1957).

146. Bacon, R.G.R., and Hanna, W.J.W.
Proc. Chem. Soc., 1959, 305.

147. Nakanishi, K., and Fieser, L.F.
J. Am. Chem. Soc., 74, 3910 (1952).

148. Watanabe, T., Furukawa, N., and Oal, S.
Bull. Chem. Soc., Japan., 41, 242 (1968).

149. Foster, G., and Hickinbottom, W.J.
J. Chem. Soc., 1960, 680.

150. Lee, D.J., and Stewart, R.,
J. Am. Chem. Soc., 86, 3022 (1965).

151. Neuss, J.D., and Rieman, W.
J. Am. Chem. Soc., 56, 2238 (1934).

152. Tong, J.Y.P., and King, E.L.
ibid., 75, 6180 (1953).

153. Baily, N., Carrington, A., Lott, K.A.K., and Symons, M.C.R.
J. Chem. Soc., 1960, 290.

154. Levitt, L.S.
J. Org. Chem., 1297 (1955).

155. Waters, W.A.
Qvart, rev., 12, 277 (1958).

156. Snethlage, H.G.S.
Rec. Trav. Chim., 56, 873 (1937).

157. Ingold, C.K., 'Structure and Mechanism in Organic Chemistry'.
Cornell Univ. Press. Ithaca, 1953.

158. Mares, F., and Rocek, J.
Coll. Czech. Chem. Commun., 26, 2355 (1961).

159. Necsoiu, I., and Nenitzescu, C.D.
Chem. & Ind., 1960, 377.

160. Watanabe, W., and Westheimer, F.H.
J. Chem. Phys., 17, 61 (1949).

161. Dostrovsky, I., and Samuel, D.
J. Chem. Soc., 1954, 658.