

THE KINETICS AND MECHANISMS

OF

CHLOROHYDRIN FORMATION.

by

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P R E F A C E

The reaction between a halogen or hydrogen halide and an olefinic substance is one of the fundamental reactions of organic chemistry. It is not surprising, therefore, that considerable attention has been given to the kinetics of the electrophilic and nucleophilic addition of halogens or hydrogen halides to olefins under the influence of both thermal and photochemical activation (1 - 6). The factors most likely to influence the rate of the reaction viz., the nature of the olefin and its substituent groups, the particular halogen or hydrogen halide employed, the temperature, the influence of catalysts and the powerful solvent effects have all been investigated in detail with the result that this seemingly straightforward class of reactions has been shown to possess considerable complexity.

On the other hand, the kinetics of the reactions of hypohalous acids, and in particular hypochlorous acid, with olefins has received rather scant attention. In some ways this is remarkable in view of the fact that the formation of chlorohydrins by this reaction has been known for at least seventy years when Erlenmeyer and Müller (7) and Melikov (8,9) investigated the addition of hypochlorous acid to the isomeric crotonic acids. Perhaps the most important contribution to our knowledge of reactions of this kind is due to Bloomfield and co-workers (10,11) who, while investigating the addition of olefinic acids and esters towards hypochlorous acid and ethyl hypochlorite, isolated,

identified and estimated the relative amounts of the isomeric chlorohydrins formed in this reaction.

At about the same time, Shilov and collaborators began an investigation of the kinetics of the reactions involving the addition of hypochlorous acid to olefinic compounds and during the past eighteen years, a series of papers from this source have been published (12 - 20). It is unfortunate that these investigators should have studied the catalytic effect of added chloride ion, usually from hydrochloric acid, in the majority of their reaction systems as the intervention of molecular chlorine formed in this way would seriously interfere with the true nature of hypochlorous acid additions. The results of early work by Shilov et al. (14) on the addition ~~to~~ ethene, indicated that the addition of chlorine to the double bond was about 100,000 times greater than that of hypochlorous acid, yet it was only in later papers (18 - 20) that this complicating factor seemed to be fully appreciated. However, during their early work they concluded that the addition reaction was a complex one and could not be described by a simple bimolecular or termolecular process. It seemed, therefore, that a detailed investigation of the kinetics of chlorohydrin formation was desirable and would prove a profitable and useful subject for research.

In 1949, during a period of study leave in New Zealand, Mr. G.C. Israel, then of this Department, with Professor F.G. Soper and Mr. J.K. Martin of the University of Otago, investigated the reaction between allyl alcohol and hypochlorous acid in aqueous

solution at 25° , (21). These workers found that the values of the specific rate constants were influenced by changes in pH of the reaction system. Israel (22) re-investigated this reaction at 25° in the presence of acetic acid - sodium acetate buffers of constant pH and when work was subsequently commenced in this Department, buffered solutions of constant pH were employed in all the reactions studied.

To avoid the complicating effect of the external buffer, the earliest work carried out by the present author was on crotonic acid buffered by its sodium salt in aqueous solution (23). The successful development of a velocity equation for this reaction led to the investigation of the reaction of hypochlorous acid with other $\alpha\beta$ -unsaturated acids viz., tiglic and β : β -dimethylacrylic acids. In each case the solution was buffered internally by the appropriate amount of the sodium salt of the acid.

The observation by Bloomfield et al. (11) that $\alpha\beta$ -unsaturated esters reacted with hypochlorous acid more slowly than the corresponding acids, prompted a continuance of the kinetic study involving the use of external acetic acid - sodium acetate buffers. Mr. K.D. Reeve (formerly of this Department, now Scientific Officer, Department of Supply) investigated this reaction using ethyl crotonate (24, 25) and this work was then extended by the author to ethyl tiglate and the ethyl and methyl esters of acrylic acid.

These investigations form the substance of this thesis.

Considerable attention has been given to the derivation of satisfactory velocity equations and to the detailed evaluation

of the specific rate constants occurring in this reaction. In general, these velocity equations contain two or more specific rate constants each with its own activation energy. It is, therefore, useless to ascribe any single rate constant to complex reactions of this kind and to attempt to describe the reaction in terms of such a constant and the hypothetical activation energy associated with it.

This thesis has been divided into six Parts and a Mathematical Appendix as listed in the Table of Contents. In discussing the results of each Part, the principle followed has been to include only those points appropriate to that Part in isolation. A discussion of the results of each Part in relation to one another is given in Part 6. The use of () brackets to denote concentrations in place of the customary [] brackets has been adopted because the number of concentration terms in the text is very large and no square brackets were available on the typewriter. In the graphs, however, the conventional square brackets for concentrations have been used. To avoid confusion between literature references, physical constants and equation numbers, all references to the Bibliography have been designated thus : (24).

The whole of this work was carried out by the author in the University of Tasmania in the period February 1951 to April 1953. It was supervised by Mr. G.C. Israel until his departure from this Department in November, 1951; in October, 1952 the Faculty of Science appointed Dr. J.A. Allen to act as nominal supervisor for the remainder of the term.

ACKNOWLEDGMENTS.

The general guidance and interest of Professor E.E. Kurth in whose Department this work was carried out, deserves a special expression of gratitude.

The author is indebted to his former supervisor, Mr. G.C. Israel, who suggested this topic and whose helpful advice, interest and discussions have been of the utmost value. Grateful acknowledgment for valuable discussions in the early stages of this investigation must be extended to a former colleague, Mr. K.D. Reeve. It is a pleasure to acknowledge my indebtedness to Dr. J.A. Allen whose helpful criticisms and encouragement in the final stages of this work have been invaluable.

The author is also indebted to Mr. T.S. McMahon and staff of the Photographic Section of the University of Tasmania for photographing the graphs included in this thesis, while the financial assistance received from the University of Tasmania in the form of a Commonwealth Research Grant is greatly appreciated.

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D. F. Braw.

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P A R T I

METHODS OF STUDYING HYPOCHLOROUS ACID ADDITION REACTIONS.

In studying the kinetics of a reaction there is no simple way of measuring the specific reaction rate directly. Usually the concentration of a reactant or a product is determined at various times and by plotting some suitable function of the concentration against time, a rate equation is obtained. The reaction between hypochlorous acid and an ethenic compound in buffered solution may be represented by the equation,



so that the kinetics of the reaction may be investigated by measuring the change with time in the concentration of hypochlorous acid, olefin or chlorohydrin in the reaction system.

There are two general methods of approaching this problem. The first is to find some easily measured physical property of the reaction system which varies in a regular and determinable manner with the concentration of one of the three principal substances involved. The second method is to sample the reaction system after various time intervals, quench the reaction and analyse the mixture chemically for one of the reactants or products. As physical methods are more direct and have the advantages of ease and accuracy, a survey of possible methods of this kind was first made.

Conductometric and potentiometric methods were ruled out because of the necessity for working in buffered solutions at pH values at which hypochlorous acid is dissociated to the extent of about 0.1 per cent. A polarographic method in which readings of the diffusion current at the half wave potential of an electro-reducible reactant or product may be used as a measure of the

concentration of the particular substance involved was investigated. Examination of the literature gave no details of the determination of hypochlorous acid by this method and the present investigation along these lines proved to be valueless. The hypochlorous acid reacted with the mercury to give brown mercuric oxychloride; for this reason the usual mercury pool was dispensed with and the quiescent electrode connection established via an agar/0.1 N potassium nitrate bridge. The polarograph - Tinsley Type S10600 with pen recorder - did not give reproducible curves for hypochlorous acid. The readings indicated that a continuous change was taking place in the cell and this may be attributed to the reaction between the mercury of the dropping electrode and the hypochlorous acid solution.

Since this work, a paper on the reaction of hypochlorous acid and sodium hypochlorite at the dropping mercury electrode (26) has appeared. A double polarographic wave for a pure 10^{-4} molar hypochlorous acid solution was obtained and was shown to represent the product of a simple chemical reaction at the mercury surface. The cathodic double wave obtained for 10^{-4} molar hypochlorous acid in 0.1 molar potassium nitrate of pH 5.5 was reproducible, but the results lost significance at potentials more positive than 0.35 volts owing to the interference from the anodic dissolution wave of mercury. The half wave potentials for the two steps were given as +0.298 and +0.122 volts respectively.

Although olefinic compounds are not all electroreducible (27), unsaturated acids containing a carboxyl group conjugated with

the double bond usually have this property. Schwaer (28), however, reported that crotonic acid was not reduced at the dropping mercury cathode and in either case, the study of the addition reaction polarographically would be hindered by the reaction of the hypochlorous acid with the mercury of the electrode.

Attempts to study the reaction by examination of the ultra-violet absorption spectra also proved unsatisfactory for the following reasons. Temperature control, an essential in kinetic work, would be difficult in the Unicam S.P.500 Photoelectric Quartz Spectrophotometer that was available. Experiments with ethyl tiglate showed that the wave length for maximum absorption occurred at about 215m μ with a maximum extinction coefficient of between 9,500 and 10,000, but large deviations from Beer's law were found and the accuracy of the instrument is questionable in the 200 - 215m μ wavelength range. A trial reaction between hypochlorous acid and thethyl tiglate in the presence of an acetic acid - sodium acetate buffer showed that the density changed in an irregular manner by only 2 per cent after thirty minutes. Moreover, concentrations which are sufficiently low for a measurable density reading do not permit the reaction to proceed at a measurable rate.

Ungnade and Ortega (29) reported that substituted acrylic acids and esters exhibit maximum absorption at wavelengths between 210 and 225 m μ . They found, for example, that β : β -dimethylacrylic acid exhibited maximum absorption at a wavelength of about 216, 217 m μ with an extinction coefficient at this wavelength of between 5,130 and 10,000. The wavelength of maximum absorption for crotonic acid

has been reported by other workers (30) as occurring at 208 mμ.

Experiments showed that hypochlorous acid itself gave an 'apparent' maximum at a wavelength of 220 mμ but dilution with water in the proportions 1:4 shifted this wavelength to 203 mμ. A consideration of these facts together with the knowledge that the reacting solution was a complex mixture containing olefin, hypochlorous acid, chlorhydrin, and in some cases, an acetic acid-sodium acetate buffer, led to the abandonment of this method for following the decrease in olefin concentration as the reaction proceeded.

The possibility of carrying out the reaction in a dilatometer was investigated, but it was found that this method was unsuitable for these relatively fast reactions. It took several minutes for thermal equilibrium to be established after mixing the reactants and since the half life period for the hypochlorous acid in some of the reactions was less than three minutes, this method had to be rejected. A dilatometer experiment for the relatively slow reaction between ethyl tiglate and hypochlorous acid gave a smooth curvilinear relation between the capillary rise and time, but the significance of the gradient is unknown.

The failure of the possible physical methods of studying these reactions necessitated the use of a method involving the 'quenching' of samples of the reaction mixture at various times and the subsequent analysis of the samples. In the reaction under investigation, the easiest reactant or product to analyse chemically is hypochlorous acid. This very weak acid liberates iodine from an acidified solution of potassium iodide and hence the discharge

of samples taken from the reaction flask into such a solution at recorded times, with subsequent titration using sodium thiosulphate solution and a starch indicator, would give a record of the decrease in the concentration of hypochlorous acid with time. This quenching with acidified potassium iodide has been used by other workers e.g. Blanksma (31), Shilov and Kanyaev (13), and more recently by Israel, Martin and Soper (21). Experiments showed that the iodine liberated in this manner did not react in the presence of potassium iodide and acetic acid with any of the unreacted olefin even after twenty four hours.

So that the interpretation of the experimental data would be rendered as simple as possible, five or six velocity determinations were made in each "Series". Throughout each series the hypochlorous acid concentration was kept constant while the concentration of olefin, in the case of the olefinic acids, or either the ester or the acetic acid-sodium acetate buffer, in the case of the unsaturated esters, was varied in a suitable manner. The general method for finding the initial reaction rate and the initial concentration of hypochlorous acid for each run will be presented in this Part, while the actual derivation of the velocity equation and the justification for using initial data will be discussed under the appropriate sections concerning that particular olefin.

A hypochlorous acid solution of required strength was prepared by the dilution of a 0.1 - 0.2 molar stock solution that was stored in a dark bottle in a refrigerator at 0° - 5° . (See Section 2.1). The strength, pH and purity of this diluted hypochlorous acid solution was checked before use and 15 ml. of this

solution pipetted into each of six or seven 50 ml. capacity standard flasks, one being used as a blank check solution. In the case of the olefinic acids, a stock solution of the acid buffered by its sodium salt to a pH of 4.73 was diluted suitably into five or six 50 ml. capacity standard flasks, each containing a different olefin concentration. In the case of the esters where an external acetic-acid - sodium acetate buffer was used, both the ester and the buffer solution were diluted as required into the same 50 ml. capacity standard flask. Alternatively, placing the buffer solution in with the hypochlorous acid solution had no effect on the reaction rate. The reaction vessel, a 300 ml. capacity conical flask fitted with a ground glass stopper, and the 50 ml. flasks described above were immersed in a constant temperature water bath for at least an hour before use and tests showed that this was at least twice the time needed for thermal equilibrium to be established. Temperature control to within $\pm 0.01^{\circ}$ was possible at both 25° and 35° using a Sunvic E.A.2/T Electronic Relay in conjunction with a mercury-toluene thermoregulator.

To start the reaction, the two standard flasks containing hypochlorous acid and olefin respectively were poured simultaneously into the reaction flask. (see Mathematical Appendix C). The time for half delivery was taken as zero time and the reaction flask was stoppered and well shaken. At suitable time intervals from five to seven samples were withdrawn using a 10 ml. calibrated pipette and delivered into a 150 ml. flask containing 20 ml. of a 2 per cent A.R. potassium iodide solution and 5 ml. of a 5N A.R.

acetic acid solution. The iodine so liberated was titrated with a suitably prepared A.R. sodium thiosulphate solution. It has been shown (32) that adjustment of the strength of the sodium thiosulphate solution so that approximately 10-20 ml. initial titres were obtained, led to greater accuracy. These sodium thiosulphate solutions, which were standardised for each series by the iodate-iodide method, showed no signs of decomposition when containing 0.05 gm. per litre of anhydrous A.R. sodium carbonate. Previous work (32) had also shown that the addition near the end-point of about 0.7 ml. of an 0.5 per cent potato starch solution gave an end-point change that enabled concordant titres to be obtained.

It remained now to find some method of extracting the initial concentration of hypochlorous acid and the initial reaction rate from this time-titre data. The following method due to Israel^{etal.} (21) was adopted. If a linear, or a near-linear plot of some function of the titre against time could be found, then the extrapolation of this graph to zero time together with the determination of the gradient of the tangent to this graph in the initial stages (see Figures 1 and 2) would yield the desired quantities. Investigations showed that the logarithm of the titre proved to be a suitable function and it has been derived (see Mathematical Appendix A) that,

$$V_0 = -2.303 \times \text{gradient} \times (\text{HOCl})_0$$

where

$$V_0 = -d(\text{HOCl})_0/dt = \text{initial velocity in mol.lit.}^{-1} \text{ min.}^{-1}.$$

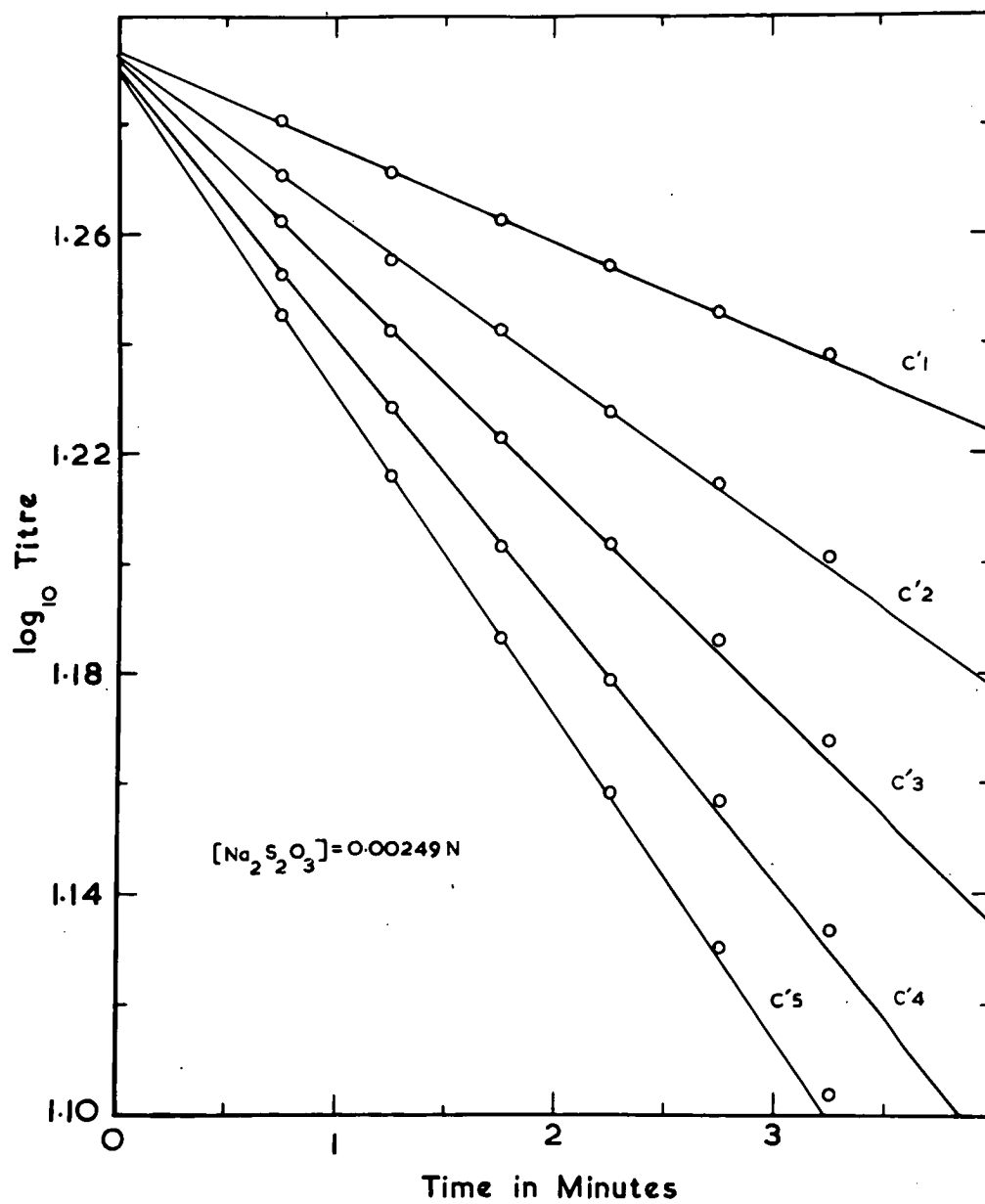


Figure 1

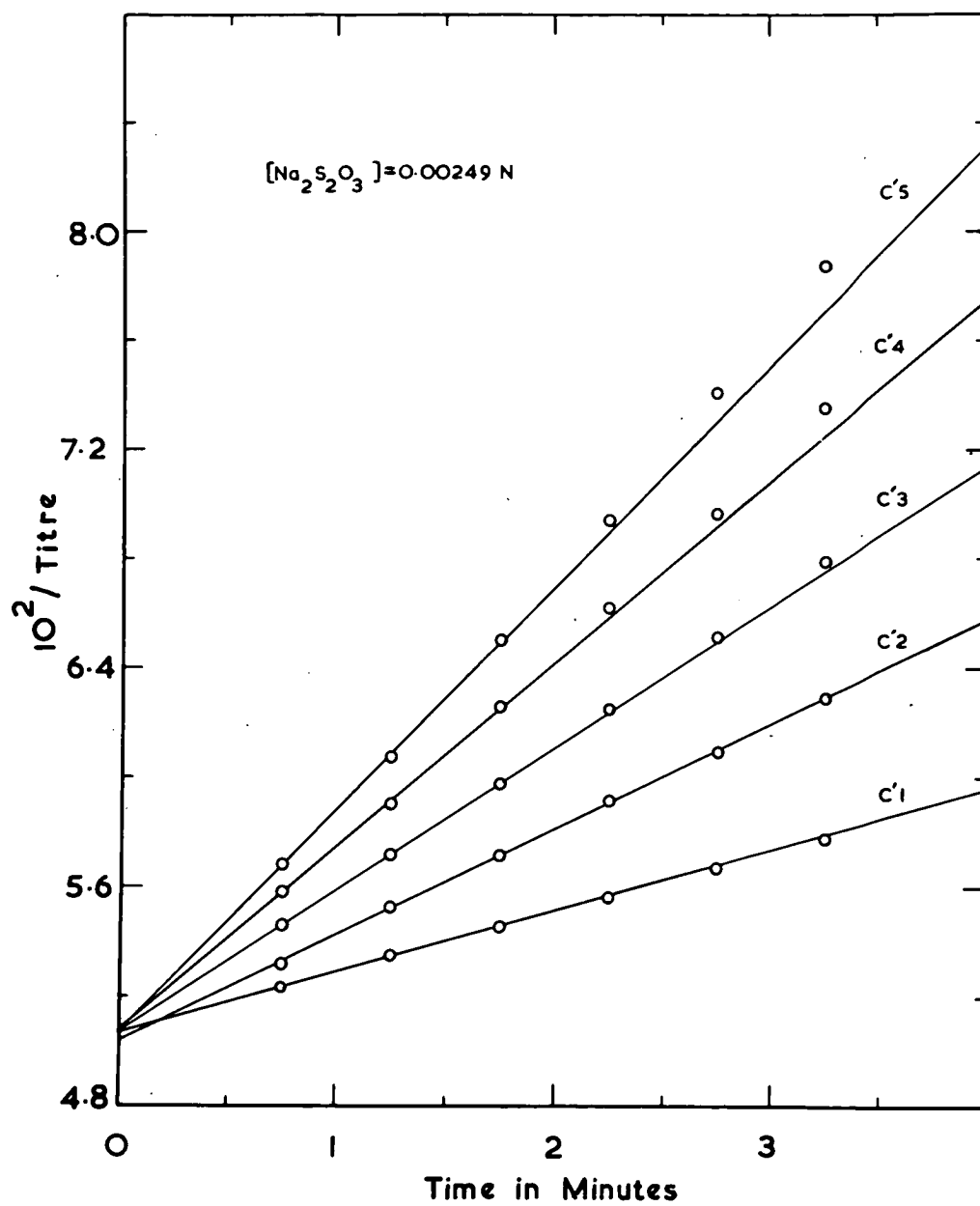


Figure 2

gradient = initial gradient of the log titre - time graph
in minutes⁻¹.

$(\text{HOCl})_0$ = Initial concentration of hypochlorous acid in
in moles litre⁻¹.

Having found a method of studying the rate of addition of hypochlorous acid to ethenic compounds, the derivation of a velocity equation and its significance could now be undertaken. This work applied to specific olefins will be considered in Parts 2 - 5.

P A R T 2

THE REACTION BETWEEN HYPOCHLOROUS ACID AND CROTONIC ACID

at 25° and 35°.

2.1. Introduction.

The kinetics of the addition of hypochlorous acid to crotonic acid were studied by Shilov and Kanyaev (12, 13) who were ^{un}able to derive a definite kinetic equation to express the rate of the reaction accurately. These workers observed that in the absence of other substances, the addition of hypochlorous acid to crotonic acid in aqueous solutions from 0.003 to 0.05 molar proceeded approximately according to the third order equation,

$$- d(\text{HOCl})/dt = k (\text{HOCl})^2 (\text{CH}_3\text{CH}:\text{CH}.\text{COOH}) \dots\dots\dots \text{Equ. (2:1)}$$

where

$$k = 38.3 \times 10^3 \text{ at } 0^\circ.$$

They found that the reaction velocity was approximately proportional to the concentration of crotonic acid, increased as the pH decreased, and was not affected by the presence of neutral salts up to a concentration of 0.01 molar. For relatively high concentrations of crotonic acid, the reaction velocity was found to be approximately proportional to the concentration of Hypochlorous acid but for relatively low concentrations of crotonic acid, the reaction velocity varied as the square of the hypochlorous acid concentration.

The investigation of the kinetics of the reaction between allyl alcohol and hypochlorous acid by Israel, Martin and Soper (21) and the reinvestigation of this reaction in solutions buffered by acetic acid-sodium acetate buffers of constant pH by Israel (22) resulted in the derivation of the velocity equations (2:2) and (2:3) respectively, viz.,

$$V = k_2^{\text{I}} (\text{HOCl}) (\text{C}_3\text{H}_5.\text{OH}) + k_2^{\text{II}} (\text{HOCl})^2 \dots\dots\dots \text{Eqn. (2:2)}$$

$$\begin{aligned}
 V = & k_2^{\text{I}}(\text{HOCl})(\text{C}_3\text{H}_5\text{OH}) + k_2^{\text{II}}(\text{HOCl})^2 + k_3^{\text{II}}(\text{HOAc})(\text{HOCl})^2 \\
 & + k_2^{\text{III}}(\text{HOCl})(\text{HOAc}) \dots\dots\dots \text{Eqn(2:3)}
 \end{aligned}$$

In view of these results, the investigation of the reaction between hypochlorous acid and crotonic acid in solutions of pH 4.73 was commenced as it was thought that an analogous velocity equation might be obtained. If such a multi-term equation were found, the change of order - with respect to hypochlorous acid - with concentration found by Shilov et al. (loc.cit.) could be explained by the varying contributions of the individual terms to the overall reaction rate in the different concentration ranges.

Crotonic acid possessed the majority of the properties necessary for a kinetic study, viz.,

- (i) It had a solubility of 8 per cent in water at room temperature.
- (ii) It was easily purified and was stable to atmospheric oxidation.
- (iii) With a dissociation constant of 2.03×10^{-5} (33,34) it had a good buffer capacity at a pH of 4.73.
- (iv) Preliminary experiments (32) revealed that its reactivity was such that it was neither too fast nor too slow for a kinetic investigation.

The addition of hypochlorous acid to crotonic acid from the organic view-point has long been known to yield a mixture of isomeric chlorhydrins (7) which are soluble in water without decomposition. Michael (35) reported that 74 per cent of the product was α -chloro- β -hydroxy-butanoic acid with the alternative β -chloro- α -hydroxy-butanoic acid as the remaining 26 per cent while

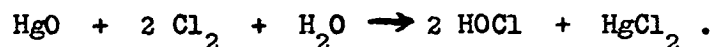
Bloomfield et al. (11) who investigated in some detail the products of the reactions between hypochlorous acid and olefinic acids, stated that stable chlorohydrins were formed at a reasonably fast rate.

Earlier work by the author (32) on this reaction did not result in a satisfactory velocity equation and this may have been caused by the presence of small amounts of mercuric ions in the hypochlorous acid solution. The work described below was performed using mercury-free solutions of hypochlorous acid as it was learnt that mercuric oxide was appreciably soluble in hypochlorous acid solution. (36).

Preparation and purification of hypochlorous acid.

Hypochlorous acid solutions may be prepared by passing chlorine gas into an aqueous suspension of a metallic oxide and recovering the hypochlorous acid by distillation. Alternatively, a non-aqueous suspension of a metallic oxide is shaken with chlorine, the suspension filtered and the soluble chlorine monoxide extracted with water. A most satisfactory method of preparing a stock hypochlorous acid solution of strength 0.1 to 0.2 molar was used in the present work as follows:

Chlorine gas was passed into an aqueous suspension of 150 gm. of yellow mercuric oxide in 500 ml. of distilled water at $0 - 5^{\circ}$. This suspension was agitated frequently and when saturated with chlorine, gassing was ceased, and the flask stoppered and well shaken with the mercuric oxide in order to dissolve as much of the free chlorine as possible. This reaction is given by the equation,



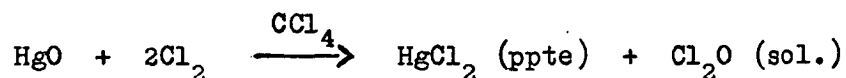
This yellow aqueous solution containing hypochlorous acid , mercuric chloride, mercuric hypochlorite, mercuric oxide, and possibly some mercuric oxychloride was distilled in an all-glass apparatus under reduced pressure in the dark. The condenser water was cooled to 5-10° and the receiver flask was immersed in an ice-salt bath at about -10°. The distilling flask was heated carefully using an electric heating mantle so that the external temperature of the flask did not exceed 40° while the still head temperature remained in the 20-25° range using a pressure of about 15-20 mm.Hg. To prevent loss of chlorine monoxide, no air leak was used; instead, the flask was loosely packed with glass wool and by using the usual Claisen head fitted with an additional splash head, frothing and bumping were overcome. It usually took from five to six hours for 200 ml. of 0.4 molar hypochlorous acid to distil after discarding a small initial fraction.

This method gave hypochlorous acid solutions ranging in strength from 0.2 to 0.9 molar, but to retard decomposition, it was advantageous to dilute the solution with distilled water to 0.1 - 0.2 molar before storing in a blackened bottle in the refrigerator. Hypochlorous acid solutions prepared in this way were practically colourless and had a sweet sickly smell. Silver nitrate gave no immediate precipitate but an opalescence developed on standing. After thirty minutes a copious white precipitate of silver chloride had developed in accordance with the recent findings of Shilov (20)

who reported that silver salts accelerate the decomposition of hypochlorous acid. The pH of a 0.017 molar solution of hypochlorous acid was measured as 4.0 whereas the theoretical value based on a dissociation constant of 6×10^{-8} is 4.5. This, and similar deviations in pH were probably caused by the small amounts of chloric acid present.

A modification of this method was also used. Instead of distilling the crude hypochlorous acid solution obtained after gassing is completed, this solution was allowed to stand at 5° overnight and then filtered. The filtrate was quickly treated with freshly precipitated bismuth hydroxide, filtered, re-treated similarly with bismuth hydroxide and the final filtrate was stored as in the first method. No bismuth could be found in solution. It was found that freshly precipitated bismuth hydroxide eliminated the chloride and free chlorine content of the hypochlorous acid more efficiently than did bismuth oxide which ~~is~~^{was} an alternative to mercuric oxide.

For the non-aqueous method (36), the basic reaction is



and a stock solution of chlorine monoxide dissolved in carbon tetrachloride was prepared as follows:

200 gm. of yellow mercuric oxide was added to 600 gm. of carbon ~~tetrachloride~~^{tetrachloride} ~~disulphide~~ in a conical flask placed in an ice bath. Chlorine was passed slowly through the suspension for one hour during which the flask was frequently agitated. The reddish brown solution

was well shaken with mercuric oxide, filtered, and the extraction of a small portion with distilled water gave a colourless aqueous layer with strength 0.35 molar and pH 3.53. The addition of silver nitrate did not give an immediate precipitate of silver chloride.

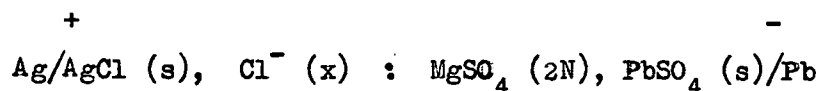
While this method was capable of yielding very concentrated solutions of hypochlorous acid, particularly free from mercury and practically free from chloride, by the simple extraction of a solution of chlorine monoxide in carbon tetrachloride with water, it suffered from the disadvantage that this aqueous extract usually smelt slightly of chlorine. For this reason it was always treated at least twice with freshly precipitated bismuth hydroxide and filtered. Examination showed that neither bismuth nor chloride ions was present in this treated extract and hence this preparative method furnished a source of hypochlorous acid for many of the series studied.

In view of the catalytic activity of any chloride ions present in the hypochlorous acid solution, methods for the detection of chloride in the presence of hypochlorous acid had to be investigated. It will be remembered that the silver nitrate test was not entirely satisfactory in this case, except where no immediate precipitate was obtained.

A literature search revealed that very little polarographic work had been performed with chloride estimation and none at all in the presence of hypochlorous acid. The method of Revenda (37) was tried and whereas reproducible results were obtained

for solutions (without hypochlorous acid) containing from 5-100 p.p.m. of chloride ion, both pure hypochlorous acid and hypochlorous acid to which potassium chloride has been added gave unintelligible results. Consecutive polarographic runs using the same cell solution gave different polarograms indicating that a reaction was taking place in the cell and this method was abandoned.

An estimate of the chloride content was attempted using the electrometric method of Scott (38) involving the construction and calibration of the cell,



The sulphate electrode was constructed in the manner described by Scott, while the Ag/AgCl, Cl⁻ electrode was prepared by making a silver-coated platinum electrode the anode in a 0.5 molar sodium chloride solution and passing a current of 0.5 milliamps overnight. Solutions containing known amounts of sodium chloride were prepared and the E.M.F. of the cell with each of these solutions was measured using a Leeds and Northrup electrometer. The plot of the logarithm of the concentration against e.m.f. showed a linear relation and the results obtained are listed in Table I.

TABLE I

(a) Calibration of Cell:

p.p.m. NaCl	E.M.F. (millivolts)
1000	633
100	684
50	701
10	734
1	780
Distilled water	794

TABLE I (contd)

(b) Test:

Test solution	E.M.F. (mV)	p.p.m. NaCl (calc)
0.03 M HOCl	764	2.1
0.06 M HOCl	794	less than 1
0.8 p.p.m. NaCl in 0.06 M HOCl	740	7.6
8.0 p.p.m. NaCl in 0.06 M HOCl	786	less than 1

No consistent or reproducible results could be obtained by this method probably because the hypochlorous acid interferes with the reversibility of the Ag/AgCl electrode.

Purification of Crotonic Acid.

Trans-crotonic acid from B.D.H. (m.p. 69°) was recrystallised from petroleum ether ($80-100^{\circ}$). 50 gm. of crude crotonic acid were dissolved in 300 ml. of petroleum ether at 45° and the main crop of dried crystals yielded 46 gm. of white needles (m.p. $71.5-72^{\circ}$). A further recrystallisation from petroleum ether raised the melting point slightly to 72° (cf. Beilstein, Heilbron m.p. 72°).

For the purpose of maintaining the reacting solution at a pH close to 4.73 and to avoid the catalytic effects caused by the addition of an external buffer (cf. Israel (22)) a solution of crotonic acid and/sodium crotonate in which $(R.COO^{-})/(R.COOH) = 1.096$, where $R = CH_3.CH:CH$. was prepared. Since for crotonic acid, $pK_a = 4.69$, (33,34) and a buffer of pH 4.73 was required the Henderson equation

$$pH = pK_a + \log \frac{(R.COO^{-})}{(R.COOH)}$$

could be used without serious error. The standard buffer solution was made up as follows:

3.4420 gm. of recrystallised crotonic acid were dissolved in about 500 ml. of distilled water and 103.5 ml. of 0.202 N carbonate-free sodium hydroxide added. The solution was diluted accurately to 1000 ml. and at 19° the pH. was 4.72 (theor. 4.73). In this solution,

$$\begin{aligned}
 (\text{R.COOH}) + (\text{R.COO}^-) &= 3.4420/86.05 \\
 &= 0.0400 \text{ moles litre}^{-1} \\
 \text{and} \quad (\text{R.COO}^-) &= \frac{103.5 \times 0.202}{1000} \\
 &= 0.0209 \text{ moles litre}^{-1}
 \end{aligned}$$

Unlike acetic acid - acetate buffers, this solution kept well and no mould was visible even after storage for twelve months at room temperature in the dark. All sodium hydroxide solutions were standardised against 0.0899 N hydrochloric acid using methyl red indicator, this acid having been previously standardised against twice recrystallised borax.

For the experiments on the effect of variation of pH, the crotonic acid-crotonate buffers were prepared in the following manner:

A 0.2 molar solution of crotonic acid and a 0.186₄ N carbonate-free sodium hydroxide solution were prepared and five buffers whose pH values were inside the high buffer capacity range of the pH-neutralisation curve for crotonic acid were made up according to Table II.

TABLE II

No.	Vol. 0.186 N NaOH	Vol. 0.2 M Crotonic acid	$\frac{(\text{R.COO}^-)}{(\text{R.COOH})}$	Theor pH	Act pH
1	26.82 ml.	100 ml.	1:3	4.21	4.21
2	35.77	100	1:2	4.39	4.40
3	53.65	100	1:1	4.69	4.70
4	71.53	100	2:1	4.99	5.00
5	80.47	100	3:1	5.17	5.19

These volumes were mixed and diluted to 500 ml. accurately so that in all five cases,

$$(\text{R.COOH}) + (\text{R.COO}^-) = 0.04 \text{ moles litre}^{-1}$$

From Pitzer's equation for the variation of the dissociation constant of weak acids with temperature, (see Mathematical Appendix F) and the known value for the dissociation constant at 25° viz., 2.03×10^{-5} , the dissociation constant at 35° was calculated as 2.05×10^{-5} .

The value of pK_a remained unchanged at 4.69 so that buffer solutions of the same composition were used in the experiments at both 25 and 35°.

2.2. Experimental Results and Derivation of the Velocity Equation.

Using the experimental method described in Part 1, the seven series A - G were investigated at 25° and the ten series A' - J' similarly studied at 35°. The results are summarised in Tables III and VI and the following explanatory points should be noted regarding these Tables.

To avoid unnecessary repetition of results, both the observed and the calculated velocities are listed in these Tables even though, as yet, the velocity equation has not been stated. In a few cases the calculated velocities quoted in Tables III and VI differ slightly (not greater than $\pm 0.1 \text{ mol.lit.}^{-1} \text{ min.}^{-1}$) from the value calculated using the velocity equation because an additional decimal place was retained for all the data used in the original derivation of the velocity equation but omitted from Tables III and VI as its accuracy could not be guaranteed.

The pH values listed were those measured after seven minutes of reaction in the case of Table III and after five minutes of reaction in the case of Table VI, and were only included in these Tables to give some indication of the pH in the reacting solution and to show that a variation from the ideal did exist. An explanation for this variation will be discussed in Section 2.4.

To distinguish between results obtained at 25° and 35°, all the series numbers, constants, etc. (except in the final velocity equation) determined at 35° will carry a dash as a superscript.

The following units have been adopted throughout:

Concentration : moles litre⁻¹

Time : minutes

Velocity : moles litre⁻¹ minute⁻¹.

TABLE III

Initial pH = 4.73 Temperature = 25 ± 0.01°

Run	(HOCl) ₀ x 10 ³	(RCOOH) ₀ + (RCOO ⁻) ₀ x 10 ³	V ₀ x 10 ⁵		pH
			obs.	calc.	
A1	1.00	2.00	1.6	1.5	4.60
A2	0.99	4.00	2.6	2.6	4.65
A3	0.99	6.00	3.6	3.7	4.69
A4	0.99	8.00	4.8	4.7	4.69
A5	0.99	10.00	5.8	5.8	4.65
A6	0.99	12.00	7.1	6.9	4.65
B1	1.90	2.00	3.8	3.9	4.68
B2	1.89	4.00	6.0	6.3	4.71
B3	1.90	8.00	11.3	11.1	4.70
B4	1.89	10.00	13.6	13.5	4.69
B5	1.89	12.00	15.8	15.8	4.69
C1	2.96	2.00	7.9	7.9	4.50
C2	2.96	4.00	12.8	12.3	4.55
C3	2.96	8.00	21.4	21.0	4.57
C4	2.95	10.00	25.8	25.3	4.59
C5	2.95	12.00	30.4	29.7	4.57
D1	3.01	2.00	8.4	8.1	-
D2	3.00	4.00	12.5	12.6	-
D3	2.97	8.00	20.8	21.2	-
D4	3.00	10.00	25.6	25.9	-
D5	2.97	12.00	30.0	30.2	-
E1	3.10	2.00	8.0	8.6	4.52
E2	3.11	4.00	13.4	13.3	4.63
E3	3.09	8.00	22.1	22.5	4.67
E4	3.08	10.00	27.0	27.0	4.70
E5	3.08	12.00	30.4	31.6	4.70

TABLE III (contd.)

Run	$(\text{HOCl})_0$	$(\text{RCOOH})_0 + (\text{RCOO}^-)_0$	V_0		pH
No.	$\times 10^3$	$\times 10^3$	$\times 10^5$		
			obs.	calc.	
F1	3.90	2.00	13.0	12.6	4.44
F2	3.90	4.00	19.5	19.1	4.54
F3	3.91	8.00	34.1	32.2	4.54
F4	3.90	10.00	40.6	38.6	4.58
F5	3.90	12.00	47.2	45.2	4.60
G1	4.33	2.00	14.6	15.1	4.06
G2	4.30	4.00	22.2	22.4	4.18
G3	4.31	8.00	36.9	37.6	4.30
G4	4.30	10.00	44.3	45.0	4.33
G5	4.29	12.00	50.8	52.3	4.40

The concentration of hypochlorous acid was kept constant in each Series so that the dependence of the velocity on the olefin concentration could be investigated first. Figure 3 shows the plot of the velocity against the total olefin concentration for various hypochlorous acid concentrations. For the sake of clarity, only five of the seven Series studied are shown as an examination of Table III will reveal that the three Series C, D, and E have very close initial hypochlorous acid concentrations.

Examination of Figure 3 shows that there is a linear relation between the velocity and the total olefin concentration, and also that there is a term in the velocity equation independent of the olefin concentration. Since in all the experiments the ratio $(\text{R.COO}^-)_0 / (\text{R.COOH})_0$ where $\text{R} = \text{CH}_3\text{.CH:CH.}$, was constant and equal to 1.096, this result may be expressed by an equation of the

form
$$V_0 = k (\text{R.COOH})_0 + V_{\text{res}} \dots\dots\dots \text{Eqn (2:4)}$$

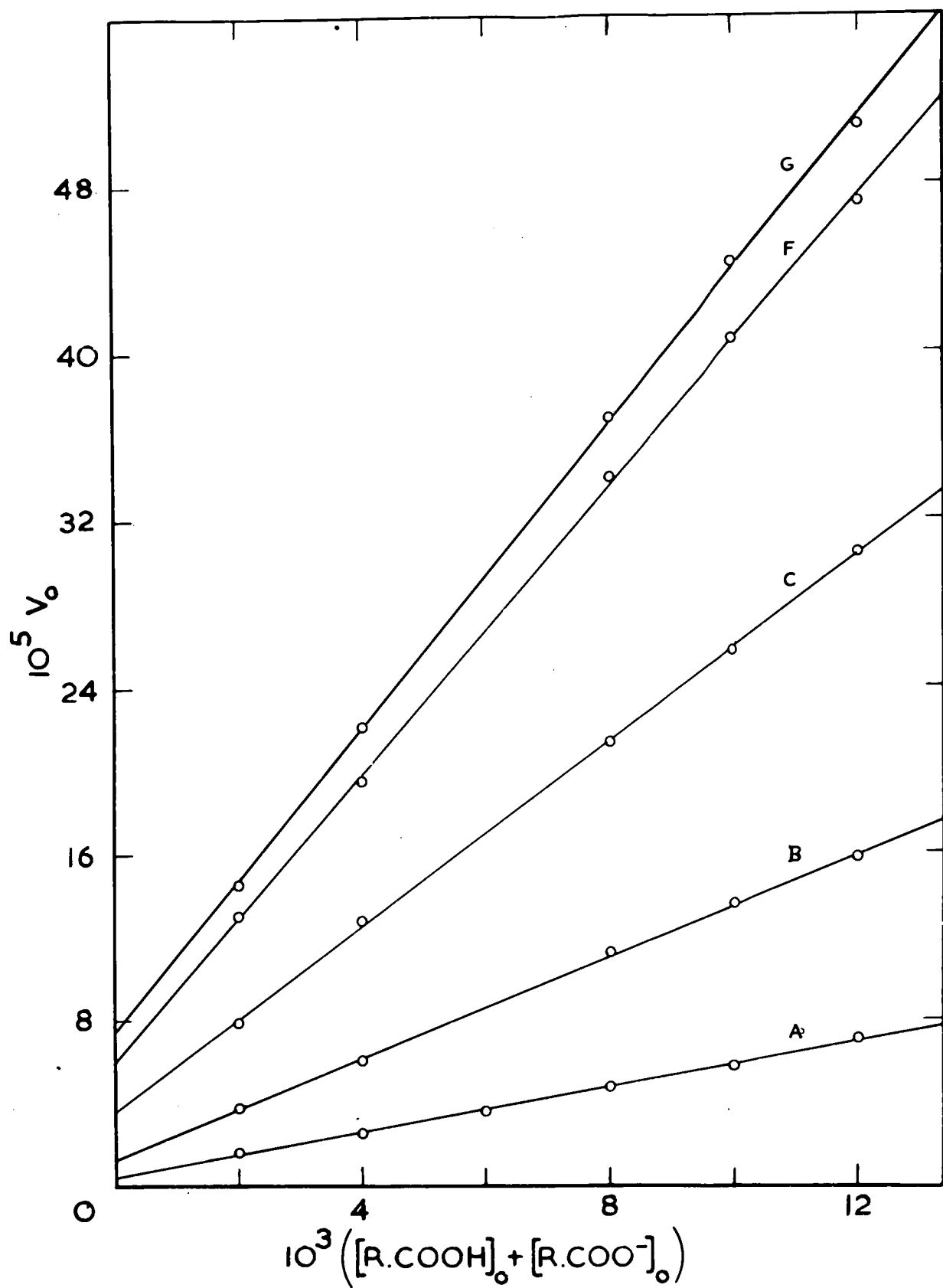


Figure 3

The gradient, $k/2.096$, and the ordinate intercept, V_{res} , were calculated for each of the Series A - G using the method of least squares and the results are listed in Table IV.

TABLE IV

Series No.	$(\text{HOCl})_0$ $\times 10^3$ mol.lit. ⁻¹	Gradient $\times 10^2$ min. ⁻¹	V_{res} $\times 10^5$ mol.lit. ⁻¹ min. ⁻¹
A	0.99	0.55	0.42
B	1.89	1.32	1.32
C	2.95	2.23	3.60
D	2.99	2.16	3.89
E	3.09	2.25	3.90
F	3.90	3.45	6.00
G	4.30	3.65	7.46

The value of $(\text{HOCl})_0$ quoted in this Table is the mean value for that particular Series.

From Figure 3 and Table IV it is clear that both k and V_{res} vary with the concentration of hypochlorous acid and these variations are shown graphically in Figures 4 and 5.

Figure 4 shows that the residual velocity, V_{res} , varies as the square of the initial hypochlorous acid concentration and the line of best fit calculated by the method of least squares is

$$V_{res} = 4.01 (\text{HOCl})_0^2 + 0.055 \times 10^{-5} \quad \text{Eqn. (2:5)}$$

The constant term in this equation is negligible by comparison with the observed velocities and thus the equation reduces to

$$V_{res} = k_2^{II} (\text{HOCl})_0^2 \quad \text{Eqn. (2:6)}$$

where $k_2^{II} = 4.0 \text{ lit.mol.}^{-1} \text{ min.}^{-1}$

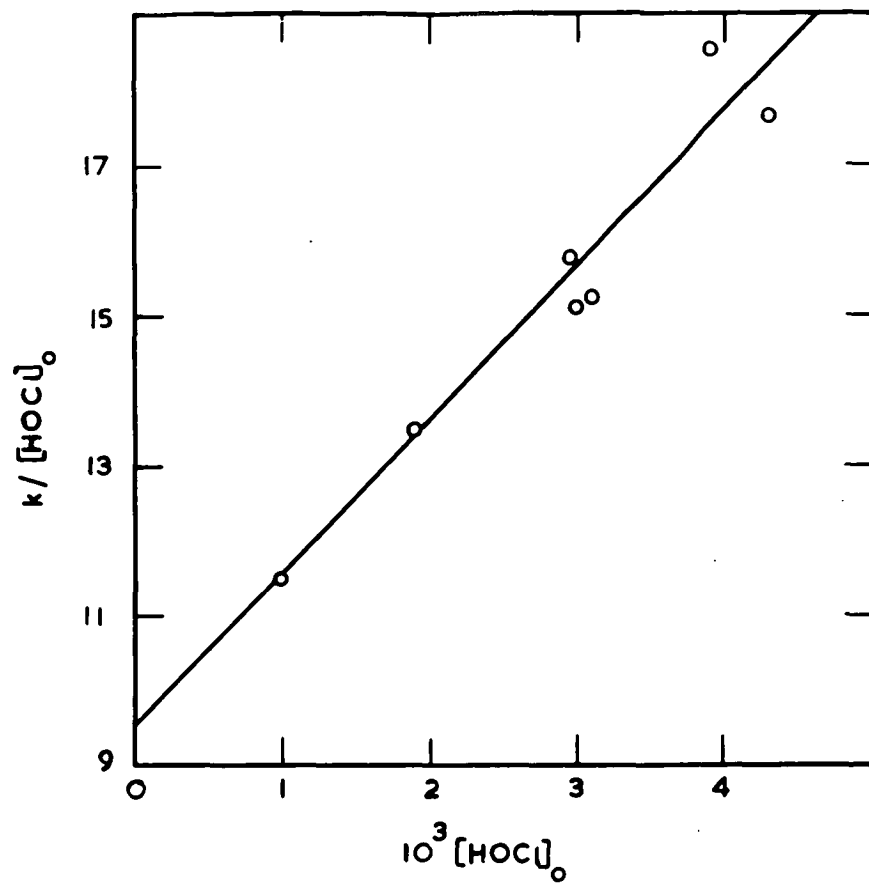


Figure 5

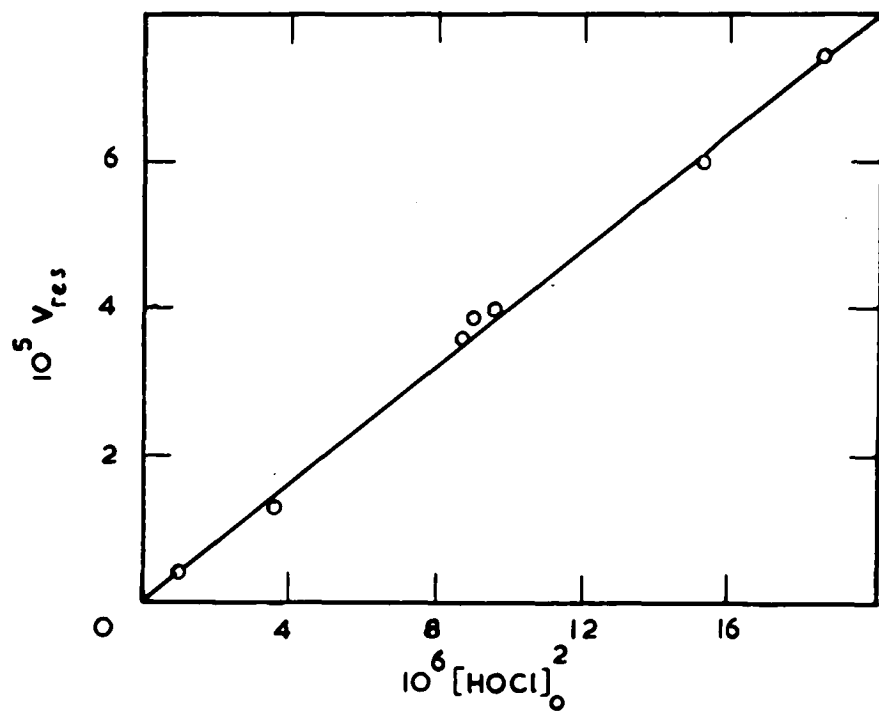


Figure 4

In Figure 5, $k/(\text{HOCl})_0$ is plotted against the initial hypochlorous acid concentration. The equation to the line of best fit is

$$k/(\text{HOCl})_0 = 9.46 + 2.06 \times 10^3 (\text{HOCl})_0 \dots\dots\dots \text{Eqn}(2:7)$$

$$\text{i.e.} \quad k = 9.46(\text{HOCl})_0 + 2.06 \times 10^3 (\text{HOCl})_0^2 \dots \text{Eqn.}(2:8)$$

Thus by inserting Eqns.(2:6) and (2:8) in (2:4) we get the complete velocity equation

$$\begin{aligned} V_0 = & 4.5(\text{HOCl})_0 (\text{RCOOH})_0 + 2.06 \times 10^3 (\text{HOCl})_0^2 (\text{RCOOH})_0 \\ & + 4.01 (\text{HOCl})_0^2 \dots\dots\dots \text{Eqn.}(2:9) \end{aligned}$$

Modification of the first term in Eqn.(2:9) using the fact that $(\text{RCOO}^-)/(\text{RCOOH})_0 = 1.096$ yields Eqn.(2:10) and the reason for this change will be given in the Discussion, Section 2.4. Thus

$$\begin{aligned} V_0 = & 4.5(\text{HOCl})_0 \{ (\text{RCOOH})_0 + (\text{RCOO}^-)_0 \} + 2.1 \times 10^3 (\text{HOCl})_0^2 (\text{RCOOH})_0 \\ & + 4.0(\text{HOCl})_0^2 \dots\dots\dots \text{Eqn.}(2:10) \end{aligned}$$

In general form this equation is

$$\begin{aligned} V = & k_2^{\text{I}} (\text{HOCl}) \{ (\text{RCOOH}) + (\text{RCOO}^-) \} + k_3^{\text{II}} (\text{HOCl})^2 (\text{RCOOH}) \\ & + k_2^{\text{II}} (\text{HOCl})^2 \dots\dots\dots \text{Eqn.}(2:11) \end{aligned}$$

$$\begin{aligned} \text{Where} \quad k_2^{\text{I}} &= 4.5 \text{ lit.mol.}^{-1} \text{ min.}^{-1} \\ k_3^{\text{II}} &= 2.1 \times 10^3 \text{ lit.}^2 \text{ mol.}^{-2} \text{ min.}^{-1} \\ k_2^{\text{II}} &= 4.0 \text{ lit.mol.}^{-1} \text{ min.}^{-1} \end{aligned}$$

$$\text{And} \quad \text{R} = \text{CH}_3 \cdot \text{CH} : \text{CH}.$$

The significance of these specific rate constants will be discussed in Section 2.4.

That equation (2:10) is a reasonably accurate interpretation of the initial course of the reaction is confirmed by the agreement between the values of the initial velocity calculated from it and the observed values. (See Table III).

An analysis of the deviations of the calculated velocities from the observed velocities revealed the following information:-

32 per cent of the calculated velocities have \leq 1 per cent error

70 per cent of the calculated velocities have \leq 3 per cent error

92 per cent of the calculated velocities have \leq 5 per cent error

The average error, disregarding the sign of the deviation was 2.4 per cent, while if the sign of the deviation was included in the average, the error was -0.3 per cent.

So far it has been assumed that ^{the} velocity equation based upon initial reaction data represents the rate at any stage of the reaction. The fundamental method of checking the validity of this assumption would be to integrate the velocity equation based on initial data and evaluate the logarithm of the hypochlorous acid concentration. If the plot of this function against time corresponded with the experimentally determined log titre vs. time curve at all points on the curve, then our generalisation would be completely justified. To reduce the very large number of calculations required to do this, the following method was adopted:-

Since the logarithm of the titre vs. time curves were all smooth and nearly linear it would appear that the initial reaction was not unusual and that the reaction proceeded via this same mechanism throughout. If the time for a certain percentage decrease in the concentration of hypochlorous acid

as calculated from the integration of the initial velocity equation (2:10) compares favourably with the time for that percentage decrease evaluated from the experimental logarithm of the titre vs. time curves in a number of arbitrary series, then we can safely assume that this initial velocity equation is representative of the velocity at any stage of the reaction.

The integration of the general velocity equation obtained for crotonic acid is given in the Mathematical Appendix D. Substitution in this equation gave the results listed in Table V.

TABLE V

Run. No.	$t_{1/10}$ (min.)		$t_{1/5}$ (min.)	
	obs.	calc.	obs.	calc.
B3	1.7 ₃	1.7 ₃	3.7 ₅	3.7 ₂
C3	1.4 ₄	1.5 ₂	-	-
C4	1.1 ₈	1.2 ₆	2.5 ₆	2.7 ₉
D2	2.5 ₅	2.6 ₆	-	-
D5	1.0 ₄	1.0 ₆	2.2 ₂	2.3 ₇
F4	1.0 ₀	1.0 ₉	2.1 ₇	2.2 ₁

In view ^{of the} _^ satisfactory equation developed for the addition of ^h hypochlorous acid to crotonic acid at 25°, this reaction was studied in an analogous manner at 35°. If it could be shown that the reaction followed a mechanism similar to that expressed by the general equation (2:11), then the specific rate constants for the separate terms could be compared with a view to calculating the activation energies for these stages in this temperature interval.

Figure 6 shows the plot of the initial velocity against the total olefin concentration for constant hypochlorous acid concentration for eight of the ten series studied. Table VI shows the kinetic data obtained from the runs at 35° and includes the two series K' and L' which were carried out to study the effect of large concentrations of hypochlorous acid and crotonic acid respectively. These series were not used in the development of the velocity equation as graphs showed that although the L' series having crotonic acid in excess was similar to the A' - J' Series, the K' Series for which hypochlorous acid was the dominant reactant, differed markedly from this general pattern. (Subsequent evaluation of the calculated velocity for the K' and L' Series supported these findings as wide deviations were found for the K' Series). The reason for the omission of the G' and I' Series from Figure 6 was for clarity as Table VI shows that these Series were very similar to the F' and J' Series respectively.

TABLE VI

Initial pH = 4.73		Temperature = 35 ± 0.01°			
Run	(HOCl) ₀	(RCOOH) ₀ + (RCOO ⁻) ₀	V ₀		pH
No.	x 10 ³	x 10 ³	x 10 ⁵		
			obs.	calc.	
A'1	1.54	2.00	4.3	4.7	4.46
A'2	1.54	4.00	7.5	7.8	4.50
A'3	1.53	6.00	10.5	10.8	4.50
A'4	1.53	8.00	13.8	13.9	4.50
A'5	1.53	10.00	16.8	16.5	4.50
B'1	1.96	2.00	6.7	6.9	4.47
B'2	1.96	4.00	10.9	11.2	4.51
B'3	1.95	6.00	14.7	15.3	4.55
B'4	1.95	8.00	18.9	19.6	4.55
B'5	1.95	12.00	26.9	28.0	4.53

TABLE VI (contd.)

Run	$(\text{HOCl})_0$	$(\text{RCOOH})_0 + (\text{RCOO}^-)_0$	V_0		pH
No.	$\times 10^3$	$\times 10^3$	$\times 10^5$		
			obs.	calc.	
C'1	2.44	2.00	9.8	9.9	4.57
C'2	2.44	4.00	16.2	15.6	4.60
C'3	2.44	6.00	22.1	21.3	4.60
C'4	2.43	8.00	27.5	26.9	4.63
C'5	2.42	10.00	32.7	32.6	4.63
D'1	2.84	2.00	12.7	12.7	4.30
D'2	2.81	4.00	19.5	19.5	4.40
D'3	2.81	6.00	26.5	26.6	4.44
D'4	2.81	8.00	33.9	33.6	4.41
D'5	2.81	10.00	40.7	40.5	4.46
E'1	3.04	2.00	13.8	14.2	4.46
E'2	3.03	4.00	21.7	22.0	4.54
E'3	3.03	6.00	30.3	29.9	4.55
E'4	3.03	8.00	38.2	37.6	4.60
E'5	3.03	10.00	47.7	45.6	4.63
F'1	3.46	2.00	17.5	17.8	4.22
F'2	3.45	4.00	27.6	27.1	4.34
F'3	3.45	6.00	37.4	36.6	4.41
F'4	3.44	8.00	45.9	45.8	4.43
F'5	3.41	10.00	53.8	54.5	4.46
G'1	3.48	2.00	17.7	17.9	-
G'2	3.45	4.00	27.5	27.1	-
G'3	3.45	6.00	37.6	36.6	-
G'4	3.45	8.00	47.6	46.1	-
G'5	3.45	10.00	56.4	55.4	-
H'1	3.98	2.00	22.3	22.6	4.04
H'2	3.96	4.00	34.4	34.1	4.21
H'3	3.94	6.00	45.6	45.3	4.28
H'4	3.94	8.00	57.0	56.9	4.32
H'5	3.94	10.00	67.7	68.4	4.36
I'1	4.44	2.00	26.9	27.5	3.90
I'2	4.45	4.00	43.6	41.5	4.15
I'3	4.42	6.00	55.7	54.8	4.20
I'4	4.42	8.00	70.7	68.6	4.28
I'5	4.39	10.00	79.2	81.3	4.33

TABLE VI (contd.)

Run	$(\text{HOCl})_0$	$(\text{RCOOH})_0 + (\text{RCOO}^-)_0$	V_0		pH
No.	$\times 10^3$	$\times 10^3$	$\times 10^5$		
			obs.	calc.	
J'1	4.64	2.00	26.7	29.7	3.87
J'2	4.64	4.00	43.7	44.5	4.14
J'3	4.64	6.00	59.3	59.3	4.27
J'4	4.63	8.00	74.6	74.0	4.30
J'5	4.63	10.00	88.4	88.8	4.34
K'1	10.00	2.00	84.1	121.3	3.12
K'2	10.07	4.00	169.5	176.1	3.00
K'3	10.08	6.00	252.7	229.6	2.99
L'1	2.42	12.00	38.8	38.2	-
L'2	2.42	16.00	52.6	49.6	-
L'3	2.40	20.00	66.0	60.2	-

As previously, the ratio $(\text{RCOO}^-)_0 / (\text{RCOOH})_0$ where $R = \text{CH}_3\text{CH:CH}$. was kept constant and equal to 1.096 and hence the linear relations shown in Figure 6 can be expressed by the equation,

$$V_0 = k' (\text{RCOOH})_0 + V'_{\text{res}} \quad \text{..... Eqn. (2:12)}$$

The gradient, $k'/2.096$, and the ordinate intercept, V'_{res} , were calculated for the ten Series by the method of least squares and are listed in Table VII. The value of $(\text{HOCl})_0$ quoted in this Table is the mean value for that particular Series.

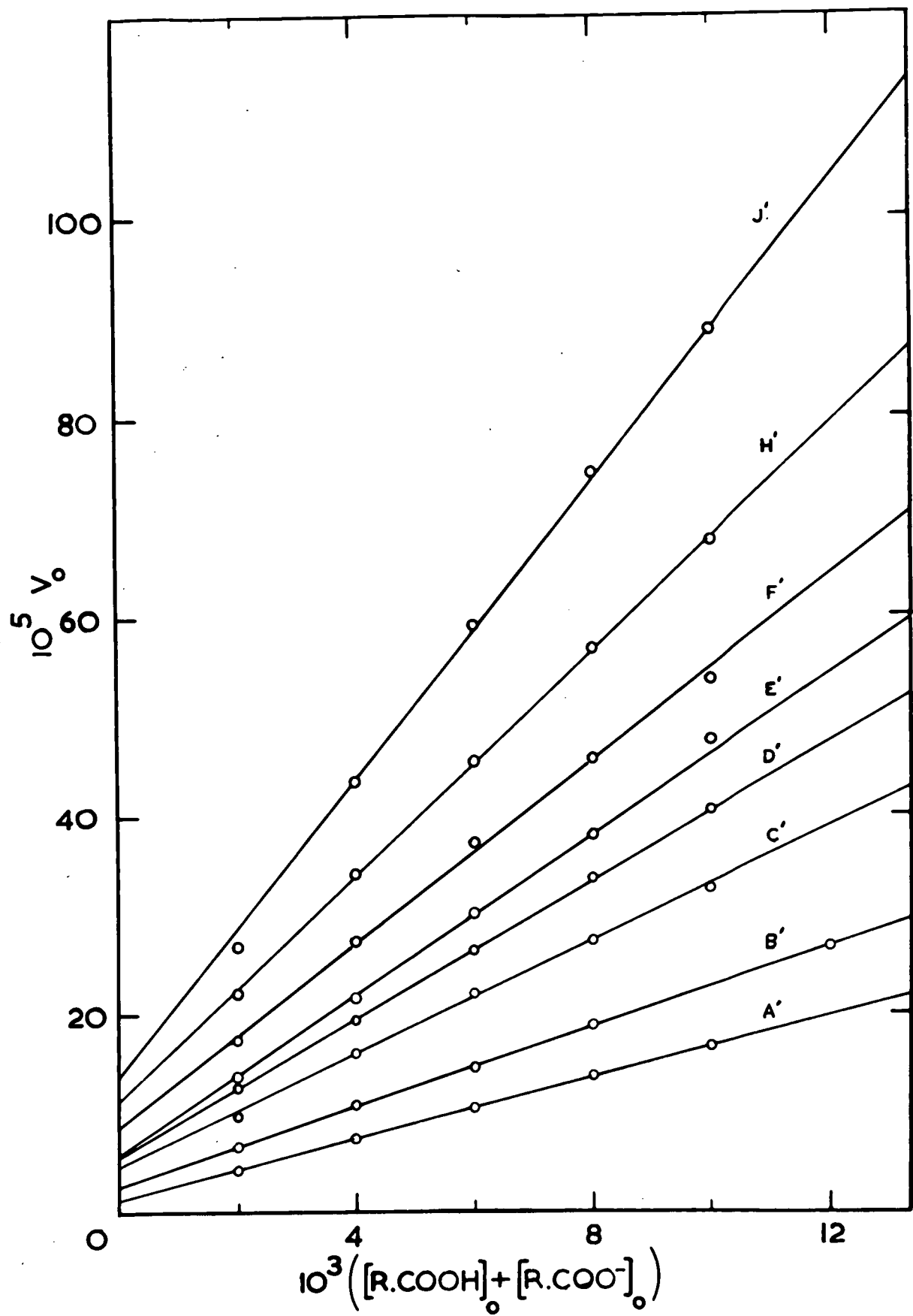


Figure 6

TABLE VII

Series	$(\text{HOCl})_0$ $\times 10^3$ mol.lit. ⁻¹	Gradient $\times 10^2$ min. ⁻¹	V'_{res} $\times 10^5$ mol.lit. ⁻¹ min. ⁻¹
A'	1.53	1.57	1.20
B'	1.95	2.02	2.70
C'	2.43	2.87	4.47
D'	2.82	3.52	5.52
E'	3.03	4.22	5.05
F'	3.44	4.54	9.20
G'	3.45	4.87	8.13
H'	3.95	5.66	11.50
I'	4.43	6.58	15.71
J'	4.64	7.72	12.26

The residual velocity, V'_{res} , has been plotted against the square of the initial hypochlorous acid concentration in Figure 7, for which the method of least squares gives the equation to the line of best fit as,

$$V'_{\text{res}} = 6.89 (\text{HOCl})_0^2 + 0.02 \times 10^{-5} \dots\dots\dots \text{Eqn. (2:13)}$$

Neglecting the constant term which is small in comparison with the observed velocities, we obtain the equation,

$$V'_{\text{res}} = k_2^{\text{II}} (\text{HOCl})_0^2 \dots\dots\dots \text{Eqn. (2:14)}$$

$$\text{where } k_2^{\text{II}} = 6.9 \text{ lit. mol.}^{-1} \text{ min.}^{-1}$$

In Figure 8, $k'/(\text{HOCl})_0$ is plotted against the initial concentration of hypochlorous acid. Application of the method of least squares gives the equation to the line of best fit as,

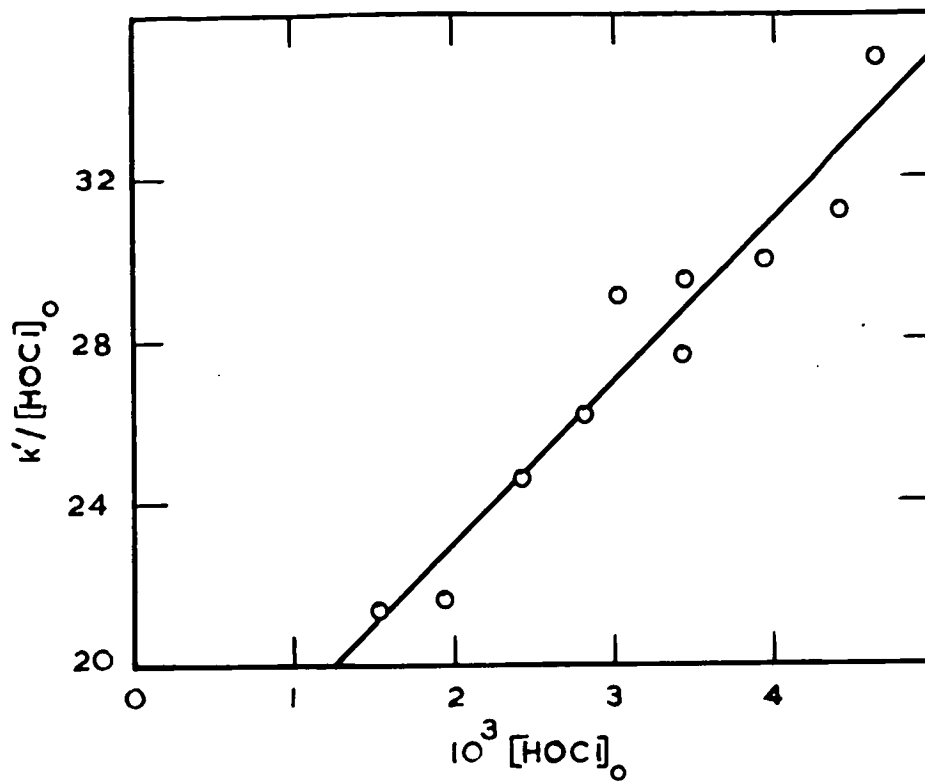


Figure 8

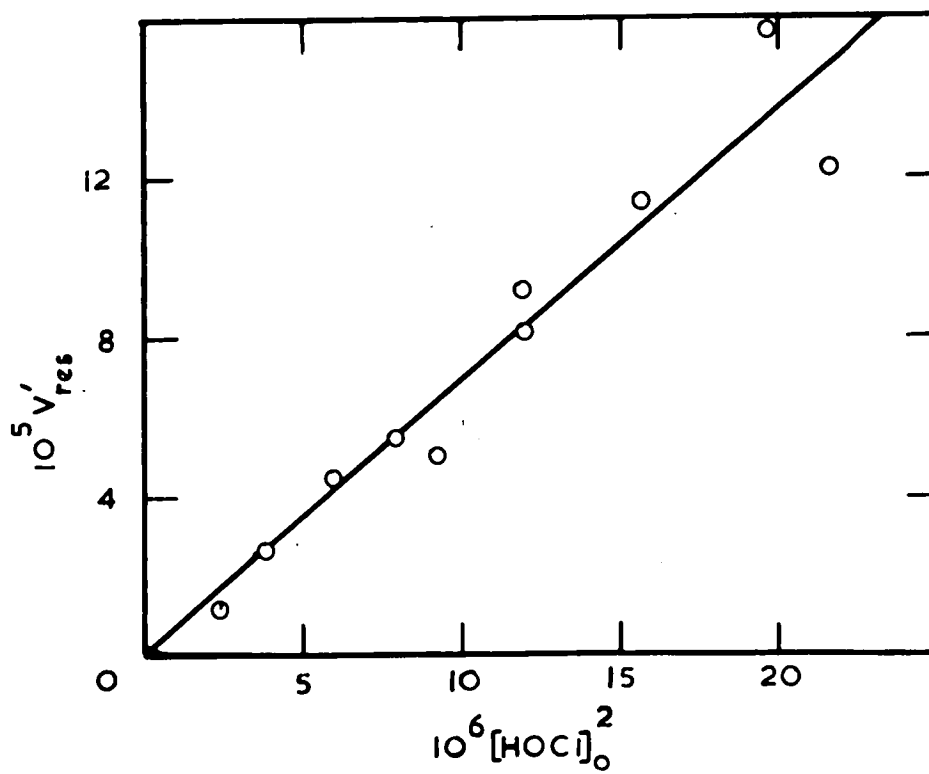


Figure 7

$$k' / (\text{HOCl})_0 = 14.96 + 4.00 \times 10^3 (\text{HOCl})_0 \dots\dots\dots \text{Eqn. (2:15)}$$

$$\text{i.e.} \quad k' = 14.96 (\text{HOCl})_0 + 4.00 \times 10^3 (\text{HOCl})_0^2 \dots \text{Eqn. (2:16)}$$

Substituting equations (2:14) and (2:16) in (2:12) we get the complete velocity equation,

$$\begin{aligned} V_0 = & 14.96 (\text{HOCl})_0 (\text{RCOOH})_0 + 4.00 \times 10^3 (\text{HOCl})_0^2 (\text{RCOOH})_0 \\ & + 6.9 (\text{HOCl})_0^2 \dots\dots\dots \text{Eqn. (2:17)} \end{aligned}$$

Since the direct attack of hypochlorous acid to an ethenoid centre involves both crotonic acid and its ion, the first term in equation (2:17) should be modified to include both $(\text{RCOOH})_0$ and $(\text{RCOO}^-)_0$.

The conversion of $(\text{RCOOH})_0$ in the second term is not necessary for reasons which will be advanced in Section 2.4. Thus the equation reduces to

$$\begin{aligned} V_0 = & 7.1 (\text{HOCl})_0 \{ (\text{RCOOH})_0 + (\text{RCOO}^-)_0 \} + 4.0 \times 10^3 (\text{HOCl})_0^2 (\text{RCOOH})_0 \\ & + 6.9 (\text{HOCl})_0^2 \dots\dots\dots \text{Eqn. (2:18)} \end{aligned}$$

Expressing this in a form analogous to equation (2:11), we have,

$$\begin{aligned} V_0 = & k_2^{\text{I}} (\text{HOCl}) \{ (\text{RCOOH}) + (\text{RCOO}^-) \} + k_3^{\text{II}} (\text{HOCl})^2 (\text{RCOOH}) \\ & + k_2^{\text{II}} (\text{HOCl})^2 \dots\dots\dots \text{Eqn. (2:19)} \end{aligned}$$

$$\begin{aligned} \text{where} \quad k_2^{\text{I}} &= 7.1 \text{ lit. Mol.}^{-1} \text{ min.}^{-1} \\ k_3^{\text{II}} &= 4.0 \times 10^3 \text{ lit.}^2 \text{ mol.}^{-2} \text{ min.}^{-1} \\ k_2^{\text{II}} &= 6.9 \text{ lit. mol.}^{-1} \text{ min.}^{-1} \end{aligned}$$

$$\text{and} \quad R = \text{CH}_3 \cdot \text{CH} = \text{CH}.$$

A comparison of the initial velocities calculated using equation (2:18) with the observed velocities (See Table VI) showed

the agreement summarised by the following analysis;

34 per cent of the calculated velocities have \leq 1 per cent error

78 per cent of the calculated velocities have \leq 3 per cent error

96 per cent of the calculated velocities have \leq 5 per cent error

The average error, neglecting the sign of the deviation from the observed velocity, was 2.2 per cent, while the average error taking into account the sign of the deviation was -0.4 per cent.

These figures demonstrate the fact that equation (2:18) represents the initial course of the reaction. To confirm that the general kinetic equation (2:19) is equally valid for the initial and intermediate stages of the reaction, we adopt the principle employed at 25° whereby the time for a certain percentage decrease in the hypochlorous acid concentration as calculated from the integration of equation (2:19) is compared with that obtained from the experimental data. This comparison is shown in Table VIII.

TABLE VIII

Run No.	$t_{1/10}$ (min.)		$t_{1/5}$ (min.)	
	obs.	calc.	obs.	calc.
D'3	1.1 ₃	1.1 ₈	2.4 ₃	2.5 ₇
F'4	0.7 ₉	0.8 ₃	1.6 ₇	1.8 ₅
H'3	0.9 ₂	0.9 ₅	1.9 ₇	2.1 ₆
H'5	0.6 ₂	0.6 ₃	1.3 ₀	1.4 ₂

The agreement is ~~now~~ satisfactory. We conclude therefore, that the same general rate equations (2:11) and (2:19) hold at both 25° and 35° and specific rate constants for the terms of these equations have been evaluated. The significance of these constants and

their temperature dependence will be discussed in Section 2.4.

2.3. Effect of pH variation on reaction velocity for crotonic acid at 25° and 35°.

The effect of pH on the rate of addition of hypochlorous acid to olefins has been noted previously. Israel, Martin and Soper (21) investigating the rate of addition of hypochlorous acid to allyl alcohol, found that in the presence of a borate buffer of pH 10, in which hypochlorous acid is 99.8 per cent ionised, very little reaction occurred, indicating that the reaction involved un-ionised hypochlorous acid and not the hypochlorite ion. In the rate equation developed by these workers, Eqn.(2:2), k_2^I and k_2^{II} were found to alter with pH according to Table IX.

TABLE IX.

pH	3.8	4.0	4.5
k_2^I	1.29	1.42	1.98
k_2^{II}	10.21	9.56	7.88

More recently, Shilov et al. (18) have found that the rate of addition of hypochlorous acid to trimethylallyl ammonium perchlorate varied with pH. They found that an increase in the pH with either alkali or buffer slowed down the reaction, stopping it altogether at pH 8.1.

In kinetic equations of the type so far established for crotonic acid, it is difficult to forecast the overall effect of a pH change. A pH change that increases the magnitude of one term in the equation may cause another term to decrease while the overall

result involves the sum of all the terms.

To investigate the effect of a variation in pH on the rate of the reaction between hypochlorous acid and crotonic acid, mixed crotonic acid-crotonate buffers were prepared according to Table II, Section 2.1. The results obtained are listed in Tables X and XI and presented graphically in Figures 9 and 10 for data at 25° and 35° respectively.

TABLE X

Temperature = 25 ± 0.01°

Run	(HOCl) ₀	(RCOOH) ₀ + (RCOO ⁻) ₀	(RCOOH) ₀	V ₀	pH
No.	x 10 ³	x 10 ³	x 10 ³	x 10 ⁵	t=0
A1	3.14	2.00	1.50	7.5	4.21
A2	3.13	2.00	1.33	8.2	4.39
A3	3.14	2.00	1.00	9.6	4.69
A4	3.13	2.00	0.67	10.2	4.99
A5	3.13	2.00	0.50	10.7	5.17
B1	3.11	4.00	3.00	12.5	4.21
B2	3.11	4.00	2.67	13.5	4.39
B3	3.10	4.00	2.00	14.4	4.69
B4	3.10	4.00	1.33	15.2	4.99
B5	3.11	4.00	1.00	15.7	5.17
C1	3.05	6.00	4.50	17.0	4.21
C2	3.05	6.00	4.00	18.2	4.39
C3	3.04	6.00	3.00	18.7	4.69
C4	3.04	6.00	2.00	18.7	4.99
C5	3.05	6.00	1.50	19.4	5.17
D1	3.08	8.00	6.00	21.5	4.21
D2	3.07	8.00	5.33	21.7	4.39
D3	3.07	8.00	4.00	23.2	4.69
D4	3.07	8.00	2.67	23.5	4.99
D5	3.07	8.00	2.00	23.7	5.17
E1	3.10	8.00	6.00	22.3	4.21
E2	3.11	8.00	5.33	24.3	4.39
E3	3.09	8.00	4.00	24.0	4.69
E4	3.09	8.00	2.67	24.1	4.99
E5	3.09	8.00	2.00	23.8	5.17

TABLE X (contd.)

Run	$(\text{HOCl})_0$	$(\text{RCOOH})_0 + (\text{RCOO}^-)_0$	$(\text{RCOOH})_0$	V_0	pH
No.	$\times 10^3$	$\times 10^3$	$\times 10^3$	$\times 10^5$	t=0
F1	3.24	8.00	6.00	21.4	4.21
F2	3.24	8.00	5.33	22.8	4.39
F3	3.24	8.00	4.00	24.5	4.69
F4	3.22	8.00	2.67	24.9	4.99
F5	3.22	8.00	2.00	25.0	5.17
G1	3.07	10.00	7.50	27.0	4.21
G2	3.07	10.00	6.67	28.0	4.39
G3	3.06	10.00	5.00	28.2	4.69
G4	3.06	10.00	3.33	27.8	4.99
G5	3.07	10.00	2.50	27.6	5.17
H1	2.98	10.00	7.50	21.7	4.21
H2	2.97	10.00	6.67	23.6	4.39
H3	2.97	10.00	5.00	25.5	4.69
H4	2.96	10.00	3.33	25.0	4.99
H5	2.96	10.00	2.50	25.0	5.17

TABLE XI

Temperature = $35 \pm 0.01^\circ$.

Run	$(\text{HOCl})_0$	$(\text{RCOOH})_0 + (\text{RCOO}^-)_0$	$(\text{RCOOH})_0$	V_0	pH
No.	$\times 10^3$	$\times 10^3$	$\times 10^3$	$\times 10^5$	t=0
A'1	2.43	4.00	3.00	13.9	4.21
A'2	2.43	4.00	2.67	14.9	4.39
A'3	2.43	4.00	2.00	15.7	4.69
A'4	2.43	4.00	1.33	16.6	4.99
A'5	2.43	4.00	1.00	17.0	5.17
B'1	2.42	8.00	6.00	25.3	4.21
B'2	2.40	8.00	5.33	25.9	4.39
B'3	2.40	8.00	4.00	26.6	4.69
B'4	2.40	8.00	2.67	26.4	4.99
B'5	2.40	8.00	2.00	26.0	5.17

The results of this section are more of a qualitative than a quantitative interest and a discussion of Figures 9 and 10 will be

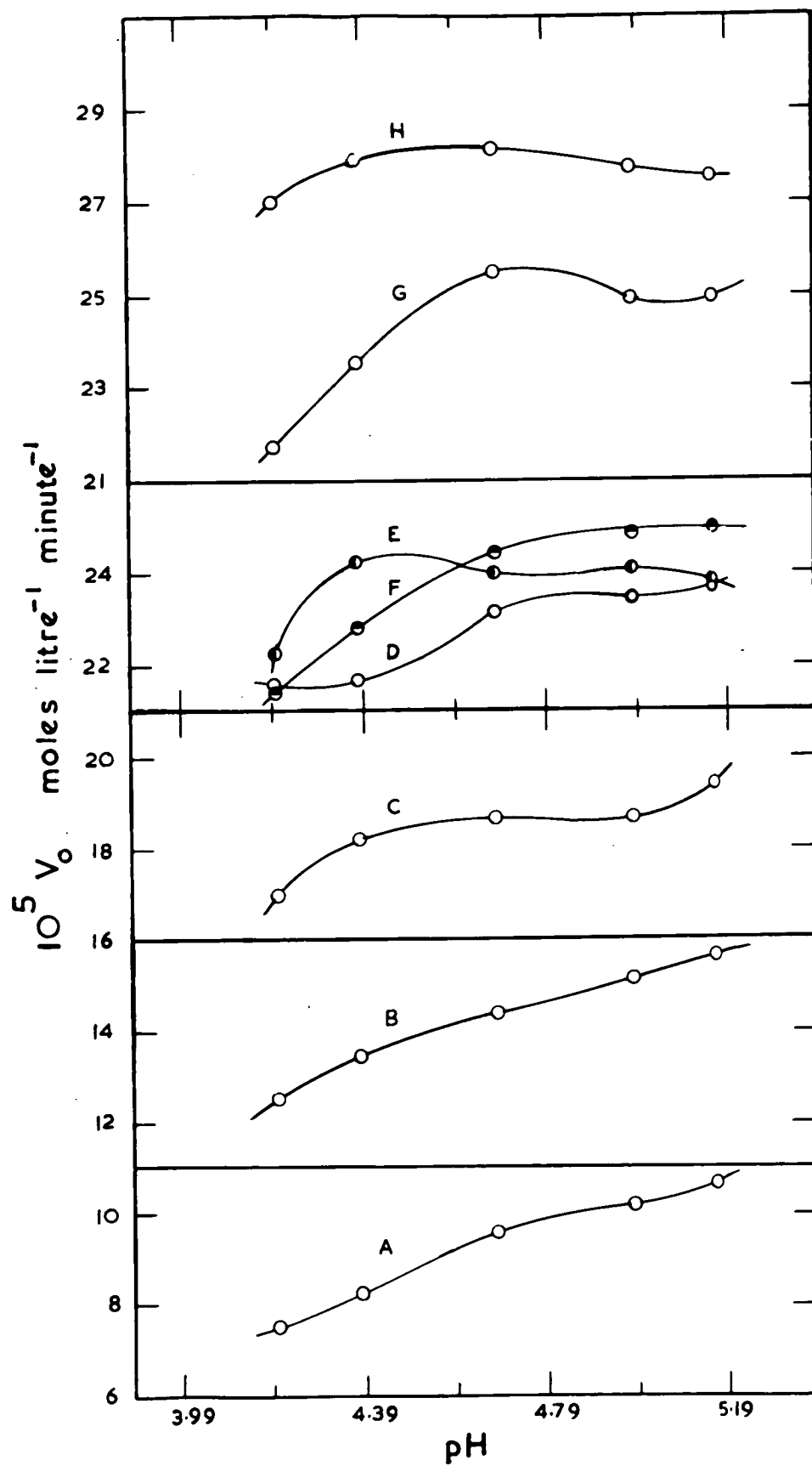


Figure 9

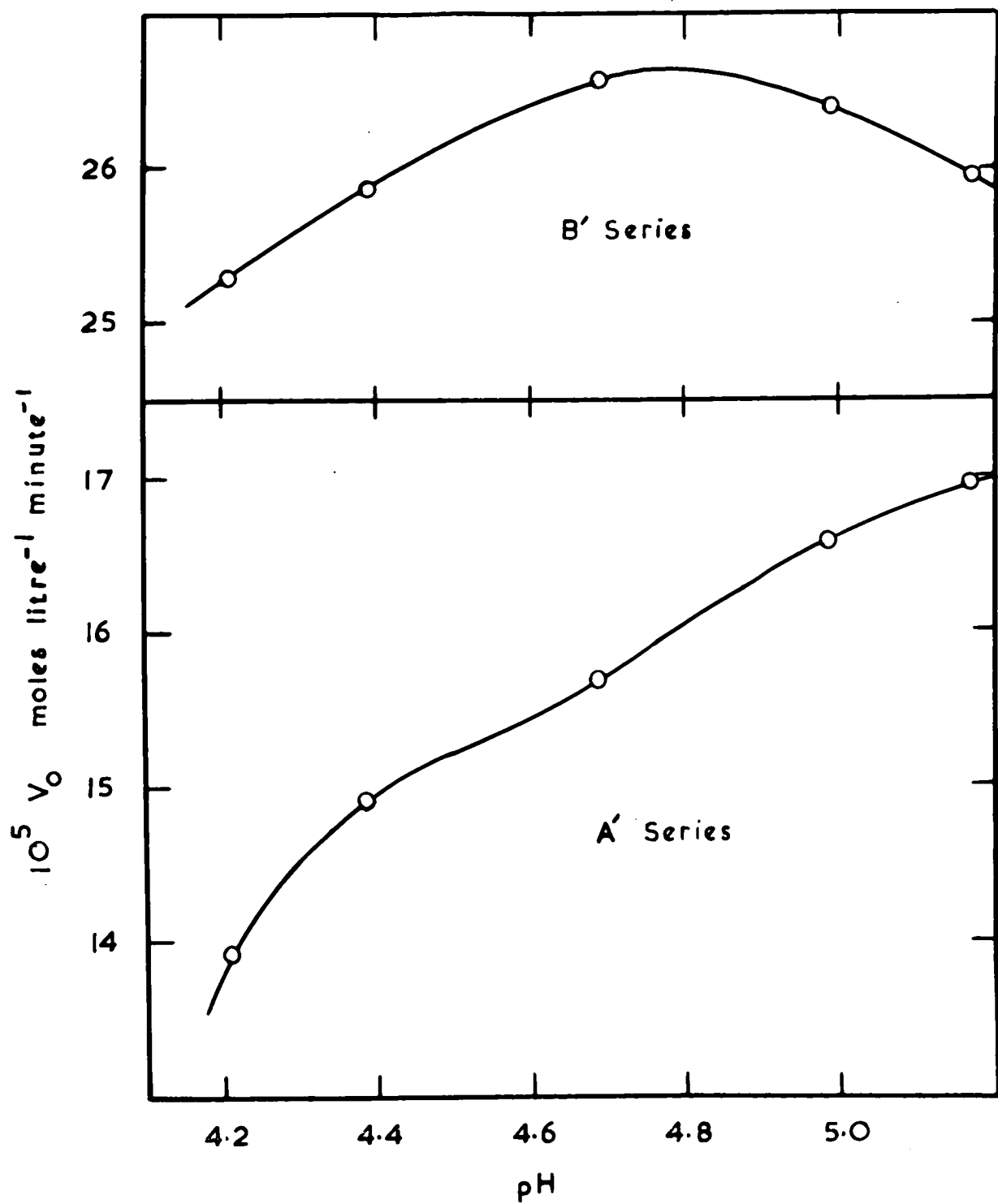


Figure 10

followed by an explanation of the behaviour of the initial reaction velocity with pH based on general considerations and previously recorded data.

In Figure 9, the initial hypochlorous acid concentration has been kept almost constant while the total concentration of olefin was varied from 0.002 - 0.010 molar. The total olefin concentration had a marked effect on the nature of this variation of velocity with pH. For low concentrations of crotonic acid plus crotonate, the velocity increased steadily with pH throughout the range investigated (e.g. A, B, C Series). At higher concentrations of olefin, (e.g. D, E, F Series), the increase in the velocity with pH was not as marked in the higher pH range 4.69-5.17, while in the G and H Series, the velocity reached its maximum value at a pH between 4.6 and 4.7.

In order to explain these results it is important to examine the effect of a pH change in relation to equation (2:11) i.e.

$$V = k_2^I(\text{HOCl}) \{(\text{RCOOH}) + (\text{RCOO}^-)\} + k_2^{II}(\text{HOCl})^2 + k_3^{II}(\text{HOCl})^2(\text{RCOOH}) \quad \text{Eqn. (2:11)}$$

Since the graphs in Figure 9 were plotted for constant $(\text{HOCl})_0$, we can modify Eqn. (2:11) accordingly, whence,

$$V = k_a \{(\text{RCOOH}) + (\text{RCOO}^-)\} + k_b + k_c (\text{RCOOH}) \quad \dots\dots\dots \text{Eqn. (2:20)}$$

The variation of (2:20) with pH is thus given by :

$$\begin{aligned} \partial V / \partial \text{pH} = \{(\text{RCOOH}) + (\text{RCOO}^-)\} \partial k_a / \partial \text{pH} + \partial k_b / \partial \text{pH} + (\text{RCOOH}) \cdot \partial k_c / \partial \text{pH} \\ + k_c \cdot \partial (\text{RCOOH}) / \partial \text{pH} \quad \dots\dots\dots \text{Eqn. (2:21)} \end{aligned}$$

since for any one series in Figure 9, the value of $(\text{RCOOH})_0 + (\text{RCOO}^-)_0$ is constant.

Let us examine the terms of the R.H.S. of (2:21) in more detail.

The reasons advanced by Israel et al. (21) for the variation of the rate constants in their velocity equation (2:2) and shown in Table IX should be applicable to equation (2:20) for crotonic acid. Thus

$$\partial k_a / \partial \text{pH} > 0 \quad \text{and} \quad \partial k_b / \partial \text{pH} < 0$$

Shilov et al. observed that the rate constant in Eqn.(2:1) decreased with increasing pH and extending this finding to k_c we see that

$$\partial k_c / \partial \text{pH} < 0$$

Thus since the terms on the R.H.S. of (2:21) are not all positive, it would be possible for $\partial V / \partial \text{pH}$ to change from positive, through zero to negative with changes in the total olefin concentration. The partial derivatives of the first three terms in (2:21) with respect to total olefin concentration are constants (or zero).

The last term, however, is the controlling factor and an examination of Table X shows that the variation of $\partial(\text{RCOOH}) / \partial \text{pH}$ with total olefin concentration is not constant but increases markedly with total olefin concentration. Now $\partial(\text{RCOOH}) / \partial \text{pH}$ is already negative and hence for large concentrations of crotonic acid plus sodium crotonate, this term becomes larger in magnitude (still retaining its negative sign) with the result that the other constant positive terms are exceeded to such an extent that $\partial V / \partial \text{pH}$ decreases through zero to eventually become negative.

It is possible to predict where this reversal of sign will take place; it will be near the pK_a value for crotonic acid (4.69)

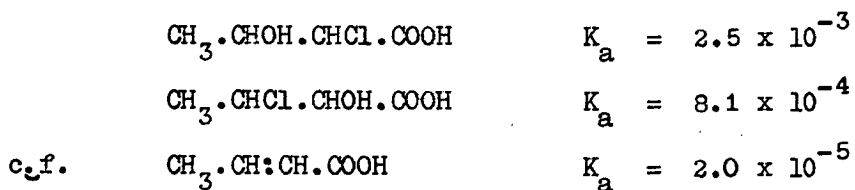
since it is here that the change $\partial(\text{RCOOH})/\partial\text{pH}$ is a maximum. This is illustrated by the G and H Series of Figure 9.

A smaller scale investigation was carried out at 35° and the results are given in Table XI. Since the general equation (2:19) derived for the reaction at 35° was similar to equation (2:11) derived for the reaction at 25° , the explanation given above should hold for a change in pH at 35° . This view is supported by Figure 10 in which the velocity is plotted against the pH for variable total olefin concentration and constant initial hypochlorous acid concentration.

2.4. DISCUSSION.

In Section 2.2 it was stated that the pH in the reacting solution during the reaction differed from the theoretical value of the crotonic acid-crotonate buffer. This depression of the pH may be attributed to one or more of the following factors:

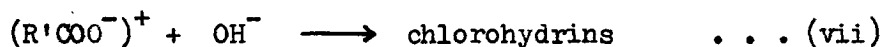
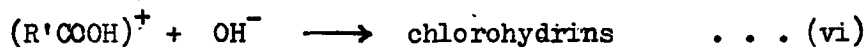
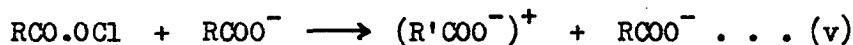
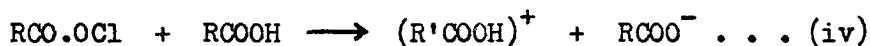
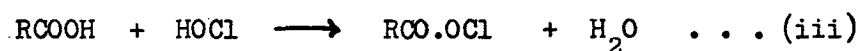
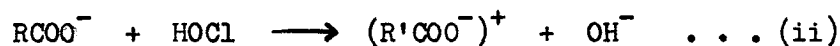
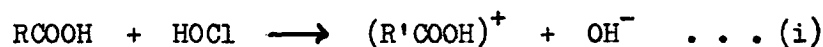
- (i) The pH of the hypochlorous acid added to the reaction flask was always less than 4.73.
- (ii) The preferential addition of hypochlorous acid to the organic anion that is known to occur will disturb the ratio of crotonate to crotonic acid in the solution with the resultant decrease in the pH.
- (iii) The most important factor probably arises from the presence of the α -chloro- β -hydroxy and the β -chloro- α -hydroxy butanoic acids and their salts formed during the reaction. These chlorohydrins are known to be stronger acids than crotonic acid Shilov (13) reported the following values of the dissociation constants at 25°.



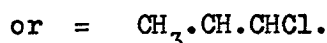
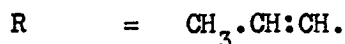
It was found that the pH measured after three minutes of reaction was substantially the same as the value recorded after five minutes; evidently the chloro-hydroxy acids formed were buffered by their salts at this lower pH.

We now consider the significance of the specific rate constants and the terms of the general equations (2:11) and (2:19).

The term, $k_2^I (\text{HOCl}) \{(\text{RCOOH}) + (\text{RCOO}^-)\}$ represents the rate of addition of hypochlorous acid to both un-ionised crotonic acid and to crotonate ion, as well as including a term for the rate of formation of crotonyl hypochlorite, R.CO.OCl , from crotonic acid and hypochlorous acid. Consider the following bimolecular reactions:



where



Reactions (i) and (ii) represent the formation of the carbonium ion intermediate by the direct bimolecular attack of hypochlorous acid at the ethenoid centre. Stereochemical and kinetic evidence points to these reactions as rate-determining. If they were not, the rate of electrophilic attack should be uninfluenced by the presence of electron-repelling (+I) substituents. Reaction (iii) represents the formation of the highly reactive crotonyl hypochlorite

while reactions (iv) and (v) represent the attack of this unstable reagent on crotonic acid and its ion.

With the addition of hypochlorous acid to allyl alcohol in the presence of an acetic acid-acetate buffer, Israel (22) found that the formation of the acetyl hypochlorite was a rate-determining step while similar work by Reeve (24) using ethyl crotonate, indicated that the addition of acetyl hypochlorite was rate determining. This was explained by the comparatively low reactivity of ethyl crotonate (in fact most esters) towards 'positive' chlorine reagents. Since crotonic acid and allyl alcohol have similar reactivities towards hypochlorous acid, the formation of crotonyl hypochlorite is likely to be a rate determining step. That this is so can be seen from the following argument.

Suppose reaction (iii) is an equilibrium reaction and that (iv) is now the rate determining reaction.

From (iii),

$$K_{\text{RCOOCl}} = \frac{(\text{RCOOCl})}{(\text{RCOOH})(\text{HOCl})}$$

From (iv),

$$V_{\text{RCOOCl}} = k_{\text{RCOOCl}} \cdot (\text{RCOOCl})(\text{RCOOH})$$

i.e. the velocity of the addition of the acyl hypochlorite to crotonic acid is

$$V_{\text{RCOOCl}} = k_{\text{RCOOCl}} \cdot K_{\text{RCOOCl}} \cdot (\text{RCOOH})^2 \cdot (\text{HOCl})$$

i.e.

$$V_{\text{RCOOCl}} = k_3 (\text{HOCl})(\text{RCOOH})^2$$

An examination of Figures 3 and 6 shows that such a velocity term involving the square of the olefin concentration does not exist and hence our assumption that (iv) was rate determining was incorrect.

The reactivity of these acyl hypochlorites has been known for some time (39, 43). That the formation of these acyl hypochlorites is due to the ^{un} dissociated carboxylic acid and not to the carboxylate ion has been demonstrated recently by Shilov and Kupinskaya (19) who found that the catalytic effect of the carboxylic acid and hypochlorous acid mixtures disappeared at a pH about 7.5 where the amount of free hypochlorous acid was still high, but where the amount of free carboxylic acid became insignificant.

The intermediate carbonium ions are highly reactive because the open sextet on a carbon atom leads to instability. This transient species seeks rapid stabilisation by the addition of a suitable anion and reactions (vi) and (vii) are unlikely therefore to determine the rate of the addition. Hydroxyl ions liberated in reactions (i) and (ii) or from a water molecule may complete the formation of the chlorohydrin but a test of the reaction order with respect to the solvent is impossible as the concentration of the solvent molecules cannot be changed without also changing the nature of the medium in which the reaction occurs.

If we denote the rate constants for the slow reactions (i) - (iii) by $k_{(i)}$, $k_{(ii)}$, and $k_{(iii)}$ respectively, then the following velocity functions should occur in the rate equation:-

$$\begin{aligned} V_{(i)} &= k_{(i)}(\text{HOCl})(\text{RCOOH}) \\ V_{(ii)} &= k_{(ii)}(\text{HOCl})(\text{RCOO}^-) \\ V_{(iii)} &= k_{(iii)}(\text{HOCl})(\text{RCOOH}) \end{aligned}$$

In the development of the general kinetic equations (2:11) and (2:19)

the ratio $(\text{RCOO}^-)_0/\text{RCOOH}_0$ was kept constant and hence $V_{(i)}$, $V_{(ii)}$ and $V_{(iii)}$ can be combined to give the overall velocity,

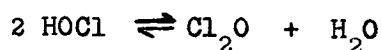
$$V = k_2^{\text{I}} (\text{HOCl}) \{ (\text{RCOOH}) + (\text{RCOO}^-) \}$$

which is the first term in these equations.

Summing up, we see that although the first term is simple in appearance, it is the result of a contribution from the rate of the direct attack of hypochlorous acid on both ^{un} dissociated crotonic acid and crotonate ion, and a contribution from the rate of formation of crotonyl hypochlorite from crotonic acid and hypochlorous acid.

The second term, $k_3^{\text{II}} (\text{HOCl})^2 (\text{RCOOH})$ may be interpreted as the formation of chlorine monoxide from hypochlorous acid under the catalytic influence of un-ionised crotonic acid, it being assumed that the crotonate ion is inactive in this respect. (c.f. Israel, (22)). The value of k_3^{II} found is of the same order as that found by Israel for the catalytic effect of un-ionised acetic acid. This result might have been expected since crotonic and acetic acids are approximately of the same strength, although this cannot be the only reason for the occurrence of this term in the rate equation. As we shall show later, this term does not appear in the corresponding rate equations for tiglic and β : β -dimethylacrylic acids even though these acids are of approximately the same strength as crotonic acid. Some alternative interpretation may therefore be required, but this cannot be given at this stage.

The third term, $k_2^{\text{II}} (\text{HOCl})^2$, probably represents the rate of formation of chlorine monoxide in solution according to the reaction,



That chlorine monoxide does exist to a small extent in aqueous solution has been demonstrated by Goldschmidt (44) and Secoy and Cady (45). The value of the equilibrium constant $K = (\text{Cl}_2\text{O})/(\text{HOCl})^2$, is 9.6×10^{-4} at 25° , (44).

Hypochlorous acid addition to both allyl alcohol and crotonic acid was carried out in aqueous solution at 25° and at a pH close to 4.73. For this reason, the rate constant k_2^{II} , should be expected to be independent of the olefin used provided that the reactivity of the olefin was not sufficient to alter the rate determining step of the reaction (c.f. ethyl crotonate (24)). However, the value of k_2^{II} for allyl alcohol and crotonic acid is 8.2 and 4.0 respectively, and a reason for this difference will be suggested when considering the nature of the second term in conjunction with work on other olefins.

The variations of the rate constants with temperature is summarised in Table XII.

TABLE XII

	k_2^{I}	k_3^{II}	k_2^{II}
25°	4.5_1	$2.0_6 \times 10^3$	4.0_1
35°	7.1_4	$4.0_6 \times 10^3$	6.8_9
$k_{35^\circ}/k_{25^\circ}$	1.58	1.94	1.72
ΔE Kg. Cals.	8.38	12.10	9.87

$k_{35^\circ}/k_{25^\circ}$ represents the ratio of the rate constants for 35° and 25° respectively, and ΔE is the activation energy calculated using the Arrhenius equation

$$k = A e^{-E/RT}$$

for each of these ratios.

It has been assumed that the probability factor of the non-exponential coefficient in this equation remains independent of the temperature. The absence of further rate constants prevents a test of this fact although Shilov and Kanyaev (12) found that the energy of activation for the addition of hypochlorous acid to crotonic acid in the 0-20° range was 7.57 Kg.Cals. It is not certain if the Arrhenius equation is applicable to the separate rate constants (46) although no real objection presents itself.

Further discussion of these results especially in regard to the significance of these activation energies and to the effects of methyl, carboxyl and carboxylate groups on the reactivity of the $\alpha\beta$ -double bond must be deferred until the results with other compounds have been presented.

PART 3.

THE REACTION BETWEEN HYPOCHLOROUS ACID AND TIGLIC ACID

at 25° and 35°.

3.1. Introduction.

The kinetics of the addition of hypochlorous acid to tiglic acid has not previously been investigated although the electrophilic addition of bromine, and the nucleophilic addition of bromine catalysed by hydrogen bromide in acetic acid solution, have been studied (2, 47, 48). The addition of bromine and chlorine in acetic acid solution at 25° to both tiglic and crotonic acids showed that tiglic acid reacted about six to ten times faster than crotonic acid.

The products of the reaction between hypochlorous acid and tiglic acid have been studied by Melikov (49) and by Bloomfield, Farmer and Hose (11) who were interested in the relative amounts of the chloro-hydroxy isomers formed in order to determine the orienting influence of the carboxyl group in a number of olefinic acids. They found that the addition of hypochlorous acid to both the free acid and its sodium salt was rapid (especially for the latter) and reported that tiglic acid gave 61-62 per cent of the β -chloro- α -hydroxy addition product while sodium tiglate gave 80 per cent of the sodium salt of β -chloro- α -hydroxy- α -methylbutanoic acid. Melikov (loc.cit.) stated that these chloro-hydroxy acids were soluble in water, diethyl ether and ethanol.

Purification and Properties of Tiglic Acid.

Tiglic acid is much less soluble in cold water than crotonic acid, being one to two per cent soluble, but is very soluble in hot water. Recrystallisation of B.D.H. tiglic acid (m.p. 59-61°) from water gave colourless prisms (m.p. 64.5°). A further recrystallisation

from water gave no change in this melting point. Literature figures report : $63.5 - 64^{\circ}$, Beilstein; 64° (48); 64.5° (50).

The addition of 0.1 N sodium hydroxide to 25 ml. of a 0.1 N tiglic acid solution at 18° was followed potentiometrically using a Leeds and Northrup pH meter, and the neutralisation curve was plotted. The value of the pH at the point of half neutralisation was 5.02 at 18° but, as the ionic strength at this point was about 0.05, the value of the pH at this point could not be accurately identified with the value of pK_a (51). The value of the dissociation constant at 25° from the literature is 0.957×10^{-5} corresponding to a pK_a value of 5.02 (52).

4.0044 gm. of twice-recrystallised tiglic acid was dissolved in about 500 ml. of water and enough 0.1 N sodium hydroxide added to make the ratio $(RCOO^{-})/(RCOOH) = 0.513$, the theoretical value for a resultant pH of 4.73, and the solution diluted accurately to one litre. In this stock solution,

$$\begin{aligned} (RCOOH) + (RCOO^{-}) &= 0.0400 \text{ moles litre}^{-1} \\ (RCOO^{-}) &= 0.0136 \text{ moles litre}^{-1} \end{aligned}$$

The measured pH of this solution at 18° was 4.70 using a potassium hydrogen phthalate buffer (4.00) as standard. The application of Pitzer's equation (see Mathematical Appendix F) for the variation of the dissociation constant with temperature gave a pK_a value of 5.01 at 35° and the ratio of the dissociation constants at 35° and 25° was 1.06. This change is negligible and hence the same tiglic acid-tiglate buffer solution was used at both these temperatures.

The stock solution kept well and no mould was evident after six months.

3.2. Experimental Results and Derivation of the Velocity Equation.

The experimental method used for the study of the addition of hypochlorous acid to tiglic acid at 25° and 35° was similar to that described in Part 1. The velocities were determined by the examination of the decay in the logarithm of the sodium thiosulphate titre with time. The hypochlorous acid solution used in this Part was prepared according to both the 'aqueous' and the 'non-aqueous' methods described in Section 2.1 and the results were independent of the method of preparation.

Eleven Series A - K were studied at $25 \pm 0.01^{\circ}$ and the results are listed in Table XIII. The pH values given in this Table are those measured five minutes after the reaction was started and the following units were adopted throughout:

Concentration : moles litre⁻¹
 Time : minutes
 Velocity ; moles litre⁻¹ minute⁻¹

TABLE XIII

Initial pH = 4.73			Temperature = $25^{\circ} \pm 0.01^{\circ}$		
Run	(HOCl) ₀	(RCOOH) ₀ + (RCOO ⁻) ₀	V ₀		pH
No.	x 10 ³	x 10 ³	x 10 ⁵		
			obs.	calc.	
A1	0.61	1.00	1.59	1.52	4.69
A2	0.61	2.00	2.82	2.75	4.66
A3	0.61	4.00	5.00	5.17	4.64
A4	0.60	6.00	7.55	7.61	4.64
A5	0.61	8.00	10.2	10.1	4.63

TABLE XIII (contd)

B1	0.91	1.00	2.51	2.46	4.62
B2	0.91	2.00	4.42	4.28	4.63
B3	0.90	4.00	8.03	7.93	4.63
B4	0.90	6.00	11.7	11.6	4.64
B5	0.90	8.00	15.7	15.3	4.64
C1	1.09	1.00	3.03	3.10	4.59
C2	1.09	2.00	5.13	5.31	4.58
C3	1.09	4.00	9.67	9.69	4.58
C4	1.09	6.00	13.9	14.1	4.58
C5	1.08	8.00	18.3	18.4	4.58
D1	1.31	1.00	3.88	3.94	4.52
D2	1.31	2.00	6.50	6.59	4.52
D3	1.31	4.00	11.8	11.8	4.53
D4	1.30	6.00	17.1	17.1	4.56
D5	1.30	8.00	22.3	22.4	4.56
E1	1.35	1.00	4.25	4.10	4.50
E2	1.34	2.00	6.57	6.77	4.52
E3	1.33	4.00	11.9	12.1	4.54
E4	1.33	6.00	17.1	17.4	4.55
E5	1.33	8.00	22.6	22.8	4.56
F1	1.57	1.00	4.88	5.02	4.40
F2	1.56	2.00	8.15	8.16	4.50
F3	1.56	4.00	14.5	14.4	4.53
F4	1.56	6.00	21.1	20.7	4.55
F5	1.56	8.00	28.0	27.0	4.56
G1	1.68	1.00	5.33	5.52	4.33
G2	1.68	2.00	8.45	8.39	4.42
G3	1.66	6.00	21.0	22.3	4.53
G4	1.66	8.00	28.5	29.0	4.54
H1	1.78	1.00	6.28	5.98	4.42
H2	1.77	2.00	9.45	9.54	4.45
H3	1.76	4.00	16.4	16.6	4.50
H4	1.76	6.00	23.2	23.7	4.52
H5	1.76	8.00	30.4	30.9	4.53
I1	1.89	1.00	6.18	6.49	4.32
I2	1.88	2.00	10.0	10.3	4.40
I3	1.88	4.00	17.3	17.8	4.45
I4	1.87	6.00	24.7	25.3	4.47
I5	1.87	8.00	32.5	32.9	4.48

TABLE XIII (contd.)

Run	$(\text{HOCl})_0$	$(\text{RCOOH})_0 + (\text{RCOO}^-)_0$	V_0		pH
No.	$\times 10^3$	$\times 10^3$	$\times 10^5$		
			obs.	calc.	
J1	1.96	1.00	6.99	6.85	4.23
J2	1.96	2.00	11.2	10.8	4.34
J3	1.95	4.00	18.8	18.6	4.44
J4	1.95	6.00	28.0	26.5	4.47
J5	1.94	8.00	35.0	34.3	4.52
K1	2.01	1.00	7.04	7.08	4.16
K2	2.00	2.00	11.1	11.1	4.31
K3	1.99	4.00	19.2	19.1	4.41
K4	1.99	6.00	27.3	27.1	4.46
K5	1.99	8.00	35.5	35.1	4.49

The plot of the initial velocity against the total initial concentration of tiglic acid and sodium tiglate is shown in Figure 11; the E, G, and J Series being omitted for clarity.

The equation of the line of best fit for each of the Series A - K shown in Figure 11 was calculated by the method of least squares and may be represented by the relation

$$V_0 = k \left\{ (\text{RCOOH})_0 + (\text{RCOO}^-)_0 \right\} + V_{\text{res}} \quad \text{..... Eqn. (3:1)}$$

where k is the gradient and V_{res} the residual velocity intercept for these lines. The values of k and V_{res} so obtained are listed in Table XIV, where the value quoted for $(\text{HOCl})_0$ is the mean value for the Series concerned. The general organic symbol, R , will be used throughout Part 3 to represent the radical, $\text{CH}_3\cdot\text{CH}:\text{C}(\text{CH}_3)$.

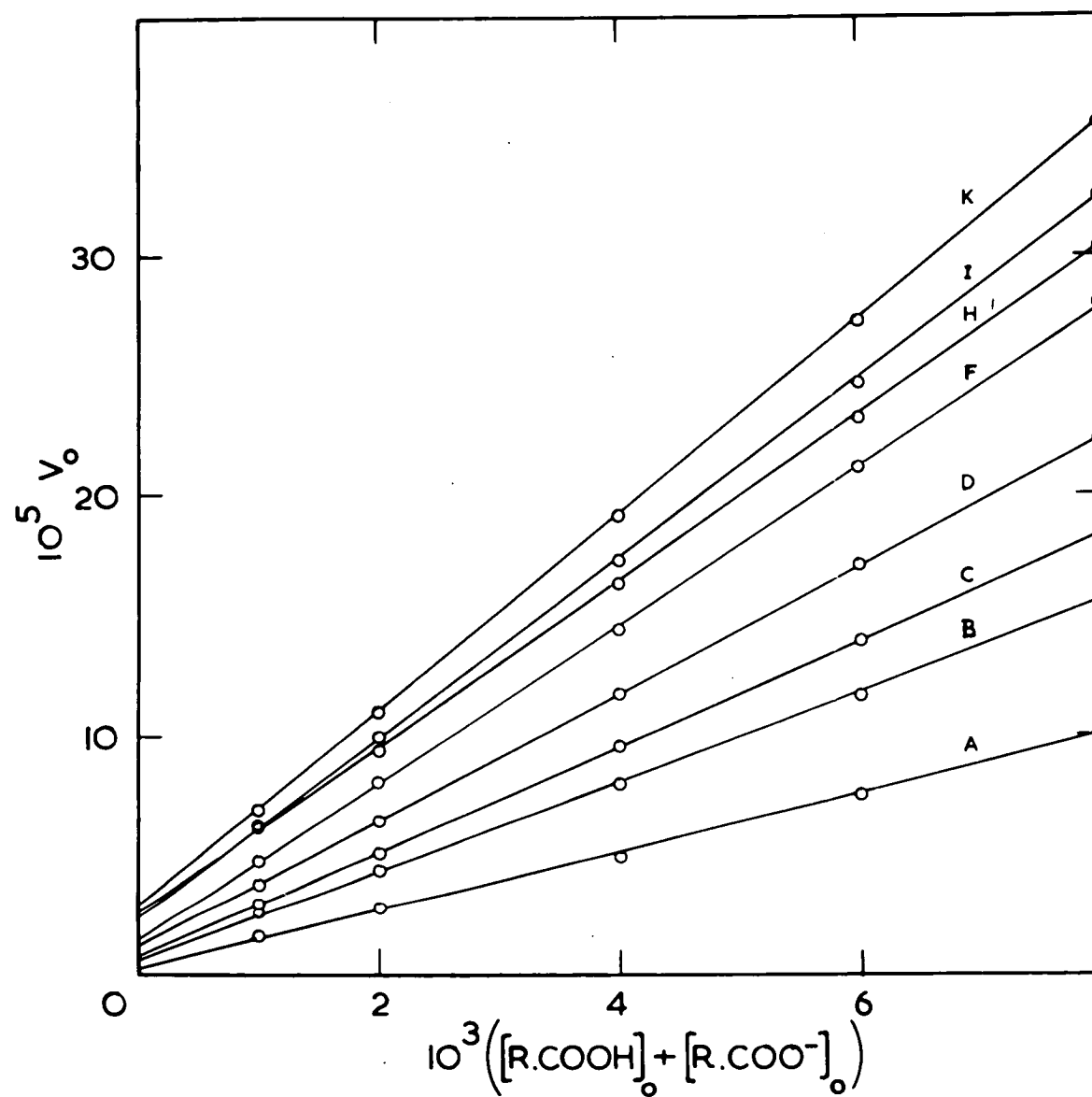


Figure 11

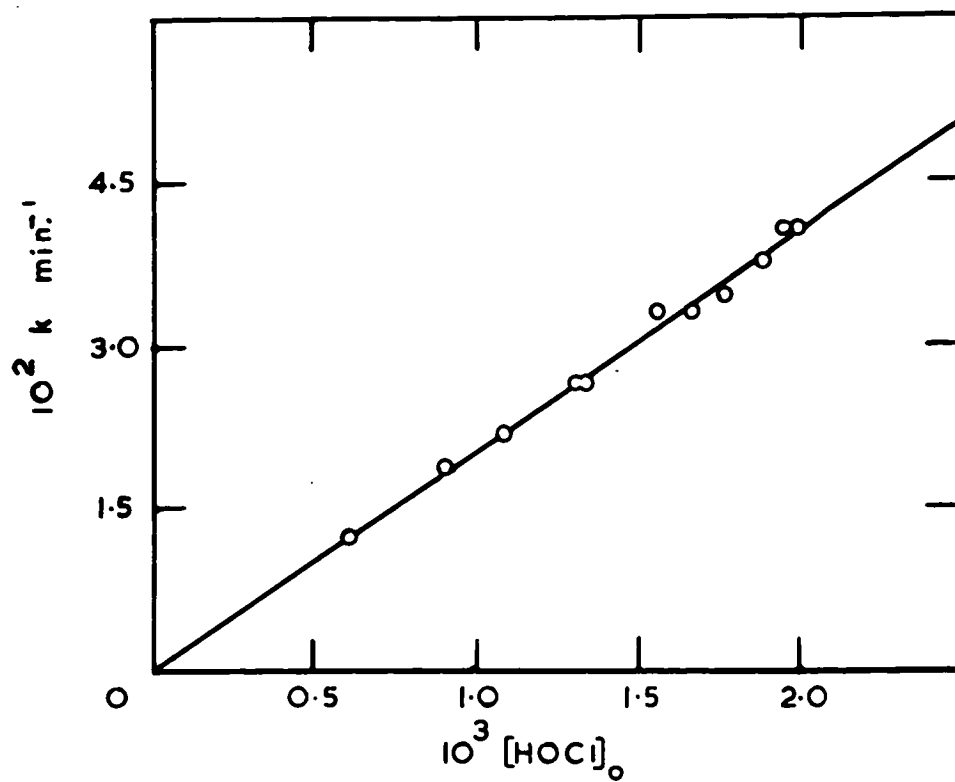


Figure 12

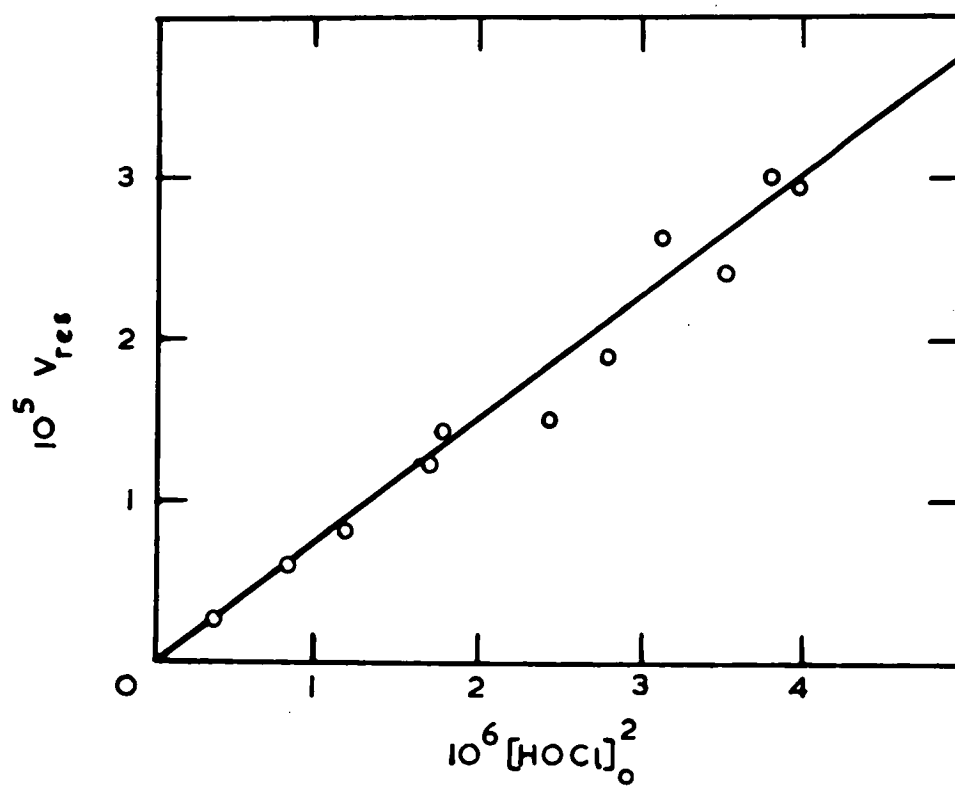


Figure 13

TABLE XIV

Series	$(\text{HOCl})_0$ $\times 10^3$ mol.lit. ⁻¹	k $\times 10^2$ min. ⁻¹	V_{res} $\times 10^5$ mol.lit. ⁻¹ min. ⁻¹
A	0.61	1.23	0.28
B	0.91	1.88	0.61
C	1.09	2.19	0.82
D	1.31	2.64	1.23
E	1.34	2.63	1.43
F	1.56	3.29	1.50
G	1.67	3.28	1.89
H	1.77	3.46	2.62
I	1.88	3.75	2.40
J	1.95	4.05	3.00
K	2.00	4.06	2.94

Examination of either Figure 11 or Table XIV shows that both the gradient and the ordinate intercept increase with increasing hypochlorous acid concentration. The plot of the gradient, k, against the initial hypochlorous acid concentration in Figure 12 shows a linear relationship of the form,

$$k = a (\text{HOCl})_0 + b \quad \text{..... Eqn.(3:2)}$$

where a and b are constants to be determined. Application of the method of least squares to the data of Table XIV determined the equation of the line of best fit to be

$$k = 20.24 (\text{HOCl})_0 - 0.007 \times 10^{-2} \quad \text{..... Eqn.(3:3)}$$

This residual term is negligible by comparison with values of k given in Table XIV, and equation (3:3) reduces to

$$k = k_2^I (\text{HOCl})_0 \quad \text{..... Eqn.(3:4)}$$

where $k_2^I = 20.2 \text{ lit.mol.}^{-1} \text{min.}^{-1}$

The variation of the residual velocity with the initial concentration of hypochlorous acid is shown graphically in Figure 13 in which the plot of V_{res} against the square of the initial hypochlorous acid concentration gives a straight line. The equation of the line of best fit was calculated by the method of least squares and found to be

$$V_{\text{res}} = 7.49 (\text{HOCl})_0^2 - 0.04 \times 10^{-5} \dots\dots\dots \text{Eqn. (3:5)}$$

Since the velocities range from $2 - 36 \times 10^{-5}$, this constant term can be neglected without serious error, and equation (3:5) becomes

$$V_{\text{res}} = k_2^{II} (\text{HOCl})_0^2 \dots\dots\dots \text{Eqn. (3:6)}$$

where $k_2^{II} = 7.5 \text{ lit.mol.}^{-1} \text{min.}^{-1}$

Combination of equations (3:4) and (3:6) with (3:1) gives the complete velocity equation:

$$V_0 = 20.2 (\text{HOCl})_0 \{ (\text{RCOOH})_0 + (\text{RCOO}^-)_0 \} + 7.5 (\text{HOCl})_0^2 \dots\dots\dots \text{Eqn. (3:7)}$$

Expressing this equation generally,

$$V = k_2^I (\text{HOCl}) \{ (\text{RCOOH}) + (\text{RCOO}^-) \} + k_2^{II} (\text{HOCl})^2 \dots\dots\dots \text{Eqn. (3:8)}$$

where $k_2^I = 20.2 \text{ lit.mol.}^{-1} \text{min.}^{-1}$

$k_2^{II} = 7.5 \text{ lit.mol.}^{-1} \text{min.}^{-1}$

and $R = \text{CH}_3.\text{CH}:\text{C}(\text{CH}_3).$

A comparison of the observed initial velocities with those calculated using equation (3:7), (see Table XIII) reveals that this velocity equation represents the initial course of the reaction with reasonable accuracy. An analysis of the deviations of the calculated

velocities from the observed velocities showed that:

30 per cent of the calculated velocities have \leq 1 per cent error

72 per cent of the calculated velocities have \leq 3 per cent error

93 per cent of the calculated velocities have \leq 5 per cent error

The average of the percentage errors, irrespective of the sign of the deviation was 2.1 per cent, while the average of these errors taking into account the sign of the error was -0.5 per cent.

The justification for writing the general equation (3:8) as a general form of equation (3:7) is that the initial reaction is in no way anomalous by comparison with the reaction after, say, two minutes. This generalisation is substantiated mathematically by a comparison of the time for a certain percentage decrease in the hypochlorous acid concentration obtained from the integration of the general equation (3:8) with the time for the same percentage decrease measured experimentally. This comparison is shown in Table XV for a number of runs taken at random and the equation used for the determination of the calculated times is given in Mathematical Appendix E.

TABLE XV

Run No.	$t_{1/10}$ (min.)		$t_{1/5}$ (min.)		$t_{1/4}$ (min.)	
	obs.	calc.	obs.	calc.	obs.	calc.
B5	0.6 ₀	0.6 ₂	1.2 ₈	1.3 ₄	1.6 ₅	1.7 ₄
D4	0.8 ₁	0.8 ₁	1.7 ₀	1.7 ₅	2.1 ₈	2.2 ₇
F3	1.1 ₃	1.1 ₇	2.4 ₃	2.5 ₄	3.1 ₈	3.3 ₁
K3	1.1 ₀	1.1 ₅	2.3 ₆	2.4 ₈	3.1 ₀	3.2 ₆

As the reaction between the tiglic acid and hypochlorous acid was followed for only 3.75 minutes at both 25° and 35°, runs for which the time for a decrease of 25 per cent in the concentration of hypochlorous acid was greater than 3.75 minutes could not be used in this Table. The agreement shown in this Table shows that the general equation is satisfactory for this reaction.

In view of this satisfactory development of a velocity equation, an investigation of the kinetics and mechanism of the addition at 35° was carried out and the results of this work are now presented.

As mentioned in Section 3.1, the same 0.04 molar tiglic acid-tiglate buffer that was used at 25° was used at 35°. Hypochlorous acid for the higher temperature reaction was prepared by the 'aqueous' method described in Section 2.1.

Figure 14 shows the plot of the initial velocity against the total olefin concentration for constant hypochlorous acid concentration while a list of the experimental results for the nine Series A' - I' is given in Table XVI.

TABLE XVI

Initial pH = 4.73

Temperature $35 \pm 0.01^\circ$

Run No.	$(\text{HOCl})_0$ $\times 10^3$	$(\text{RCOOH})_0 + (\text{RCOO}^-)_0$ $\times 10^3$	V_0 $\times 10^5$		pH
			obs.	calc.	
A'1	1.02	1.00	4.68	4.70	4.32
A'2	1.02	2.00	8.60	8.28	4.42
A'3	1.01	4.00	15.8	15.2	4.43
A'4	1.01	6.00	22.6	22.2	4.41
A'5	1.01	8.00	30.5	29.2	4.47
B'1	1.27	1.00	6.61	6.21	4.28
B'2	1.26	2.00	10.7	10.5	4.36
B'3	1.25	4.00	19.6	19.1	4.40
B'4	1.23	6.00	27.0	27.3	4.42
B'5	1.24	8.00	37.7	36.3	4.43
C'1	1.26	1.00	6.68	6.2	4.25
C'2	1.25	2.00	10.6	10.5	4.32
C'3	1.25	4.00	20.7	19.2	4.36
C'4	1.24	6.00	28.8	27.7	4.40
C'5	1.24	8.00	37.8	36.2	4.39
D'1	1.51	1.00	7.81	7.80	4.20
D'2	1.50	2.00	12.7	12.9	4.25
D'3	1.49	4.00	23.5	23.3	4.34
D'4	1.48	6.00	33.6	33.3	4.38
D'5	1.48	8.00	45.0	43.7	4.40
E'1	1.87	1.00	10.8	10.4	4.06
E'2	1.85	2.00	16.6	16.7	4.19
E'3	1.84	4.00	29.6	29.4	4.25
E'4	1.83	6.00	42.5	42.1	4.36
E'5	1.82	8.00	55.8	54.5	4.37
F'1	2.00	1.00	10.9	11.5	3.90
F'2	2.00	2.00	18.4	18.4	4.14
F'3	1.98	4.00	31.5	31.9	4.23
F'4	1.97	6.00	44.6	45.6	4.30
F'5	1.97	8.00	59.0	59.3	4.33
G'1	2.21	1.00	13.0	13.2	3.80
G'2	2.21	2.00	21.1	20.9	4.02
G'3	2.17	4.00	33.9	35.5	4.20
G'4	2.18	6.00	51.8	50.9	4.27
G'5	2.15	8.00	65.9	65.3	4.30

TABLE XVI (contd.)

Run	$(\text{HOCl})_0$	$(\text{RCOOH})_0 + (\text{RCOO}^-)_0$	V_0		pH
No.	$\times 10^3$	$\times 10^3$	$\times 10^5$		
			obs.	calc.	
H'1	2.50	1.00	15.7	15.8	3.70
H'2	2.50	2.00	24.7	24.4	3.90
H'3	2.46	4.00	39.5	41.1	4.09
H'4	2.45	6.00	56.8	58.0	4.17
H'5	2.45	8.00	75.7	75.0	4.20
I'1	2.81	1.00	18.6	18.6	3.50
I'2	2.79	2.00	26.1	28.1	3.77
I'3	2.77	4.00	45.4	47.2	4.00
I'4	2.73	6.00	62.1	65.5	4.12
I'5	2.73	8.00	82.3	84.4	4.17

The B' Series was omitted from Figure 14 for clarity but the equation of the line of best fit for each of the Series A' - I' was calculated by the method of least squares and may be represented by the equation:

$$V_0 = k' \{ (\text{RCOOH})_0 + (\text{RCOO}^-)_0 \} + V'_{\text{res}} \dots \dots \dots \text{Eqn. (3:9)}$$

where k' is the gradient and V'_{res} the residual velocity intercept for these lines. These constants are given in Table XVII and the initial hypochlorous acid concentration listed is the mean value for the Series concerned.

TABLE XVII

Series	$(\text{HOCl})_0$	k'	V'_{res}
	$\times 10^3$	$\times 10^2$	$\times 10^5$
	mol. lit. ⁻¹	min. ⁻¹	mol. lit. ⁻¹ min. ⁻¹
A'	1.01	3.64	1.15
B'	1.25	4.36	1.98
C'	1.25	4.51	1.92
D'	1.49	5.30	2.27
E'	1.85	6.45	3.96
F'	1.99	6.79	4.37
G'	2.18	7.58	5.31
H'	2.47	8.46	6.97
I'	2.77	9.11	8.64

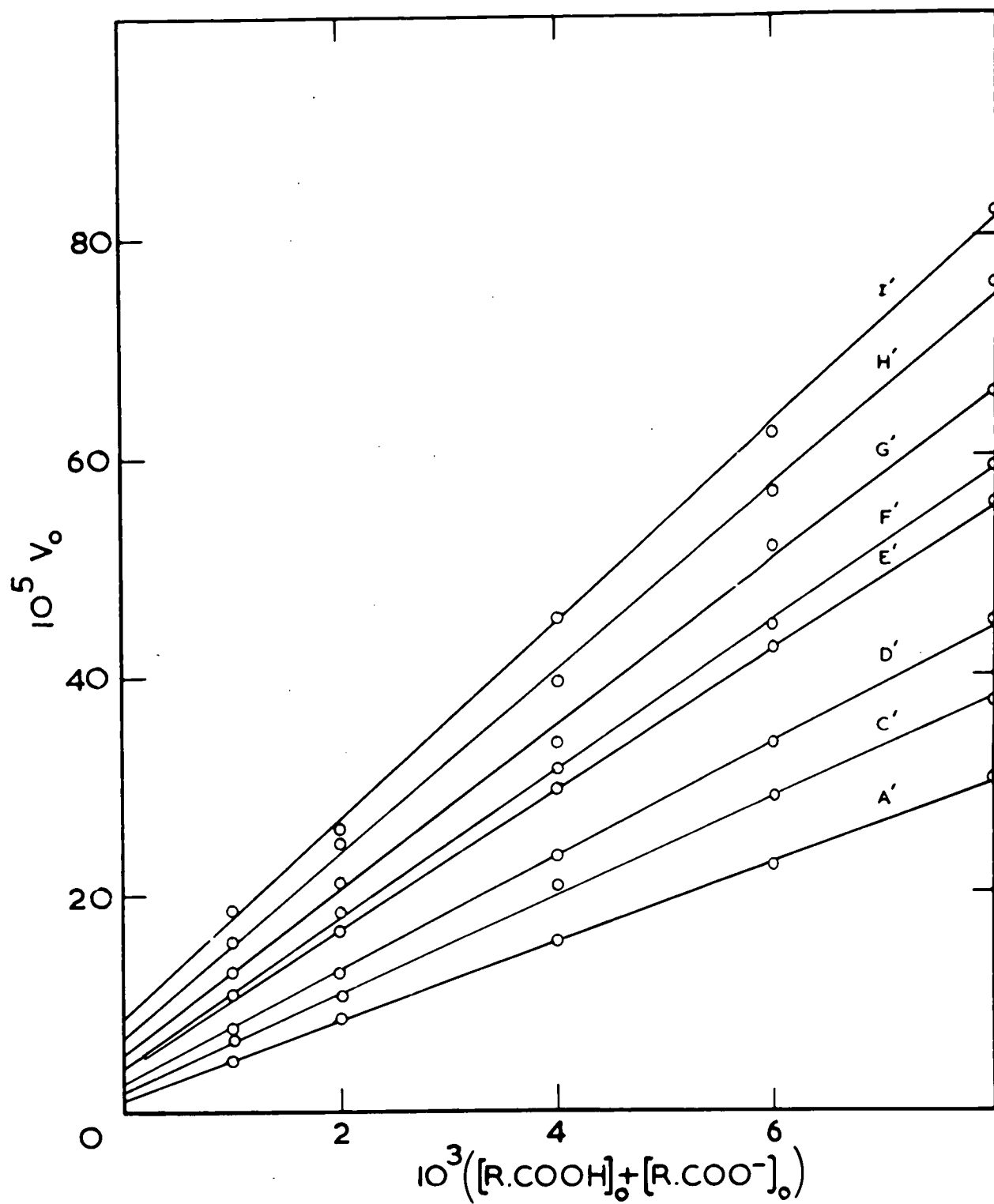


Figure 14

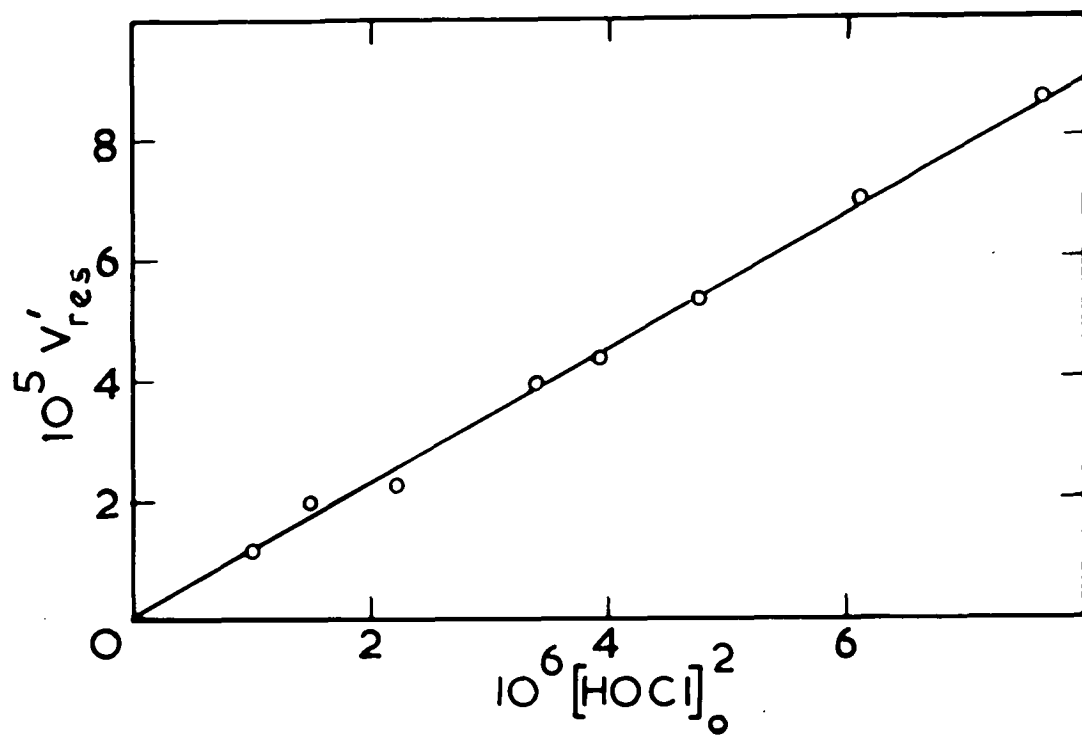


Figure 16

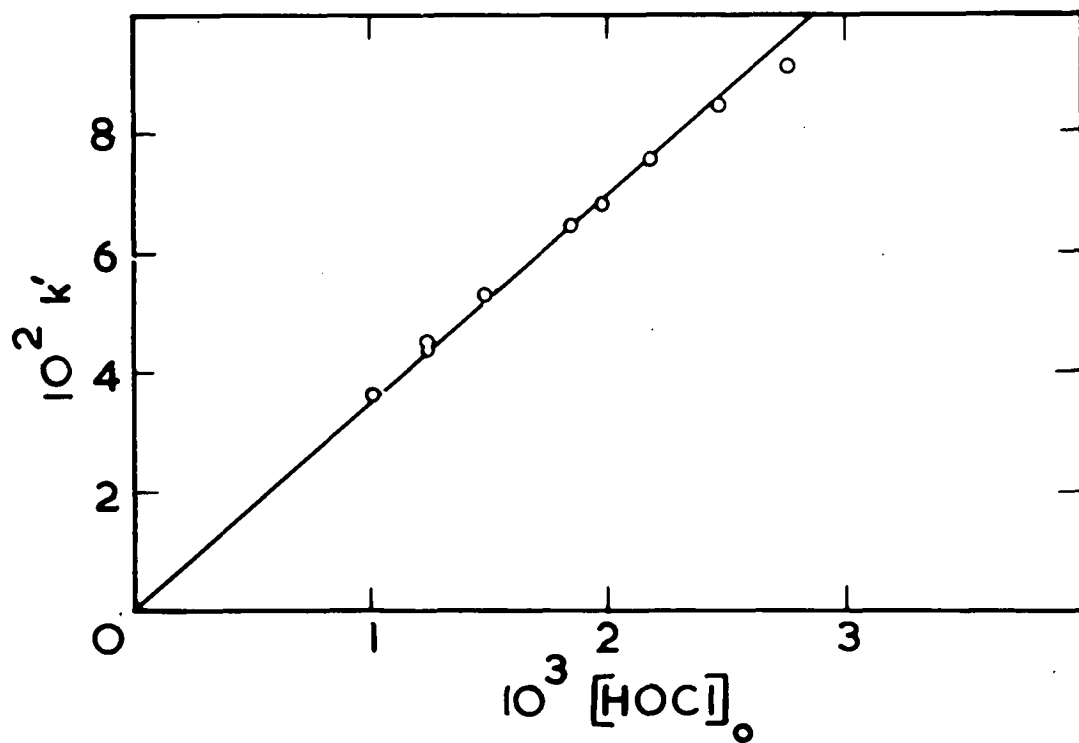


Figure 15

The variation of k' with the initial hypochlorous acid concentration is shown graphically in Figure 15 and is seen to be similar to Figure 12 representing the variation at 25° . The value of $k'/(HOCl)_0$ for the nine Series is given below and a slight decrease with increasing hypochlorous acid concentration is noticed.

<u>Series</u>	$k'/(HOCl)_0$	<u>Series</u>	$k'/(HOCl)_0$
A'	35.98	F'	34.22
B'	35.00	G'	34.71
C'	36.12	H'	34.20
D'	35.56	I'	32.94
E'	34.98	<u>Mean</u> :	<u>34.86</u>

For this reason the method of least squares was not used to determine the equation of this graph and the line shown in Figure 15 was obtained from the arithmetic mean of the above data. The equation to this line is

$$k' = 34.86 (HOCl)_0 \dots\dots\dots \text{Eqn. (3:10)}$$

$$\text{i.e. } k' = k_2^I (HOCl)_0 \dots\dots\dots \text{Eqn. (3:11)}$$

$$\text{where } k_2^I = 34.9 \text{ lit.mol.}^{-1} \text{ min.}^{-1}$$

The variation of the residual velocity, V'_{res} of equation (3:9) with the initial hypochlorous acid concentration is shown in Figure 16. The method of least squares was used to determine the equation to the line of best fit as

$$V'_{\text{res}} = 11.20 (HOCl)_0^2 + 0.053 \times 10^{-5} \dots\dots \text{Eqn. (3:12)}$$

The constant term of this equation can be neglected without serious error by a comparison with the observed velocities of Table XVI and we obtain the relation

$$V'_{\text{res}} = k_2^{II} (HOCl)_0^2 \dots\dots\dots \text{Eqn. (3:13)}$$

where $k_2^{II} = 11.2 \text{ lit.mol.}^{-1} \text{ min.}^{-1}$

Combination of equations (3:11) and (3:13) with (3:9) gives the complete velocity equation :

$$V_o = k_2^I (\text{HOCl})_o \left\{ (\text{RCOOH})_o + (\text{RCOO}^-)_o \right\} + k_2^{II} (\text{HOCl})_o^2 \dots\dots\dots \text{Eqn. (3:14)}$$

Assuming that this equation holds for all velocities, we obtained the general rate equation

$$V = k_2^I (\text{HOCl}) \left\{ (\text{RCOOH}) + (\text{RCOO}^-) \right\} + k_2^{II} (\text{HOCl})^2 \dots\dots\dots \text{Eqn. (3:15)}$$

where $k_2^I = 34.9 \text{ lit.mol.}^{-1} \text{ min.}^{-1}$

$k_2^{II} = 11.2 \text{ lit.mol.}^{-1} \text{ min.}^{-1}$

and $R = \text{CH}_3.\text{CH}:\text{C}(\text{CH}_3).$

Equation (3:14) was used to evaluate the calculated initial velocities given in Table XVI and comparison with the observed initial velocities showed that :

29 per cent of the calculated velocities have ≤ 1 per cent error

62 per cent of the calculated velocities have ≤ 3 per cent error

89 per cent of the calculated velocities have ≤ 5 per cent error

The average of the percentage errors, disregarding the sign of the deviation was 2.6 per cent, while if the sign of the error was included, the average error was 0.6 per cent.

The integration of the ~~general~~ ^{general} velocity equation (3:15) is given in the Mathematical Appendix E and a comparison of the times for a certain percentage decrease in the hypochlorous acid concentration obtained from the observed data and from this integrated equation is shown in Table XVIII. The runs listed here were chosen at random, and the satisfactory agreement found

in this Table shows that the generalisation of equation (3:14) is valid.

TABLE XVIII

Run No.	$t_{1/10}$ (min.)		$t_{1/5}$ (min.)		$t_{1/3}$ (min.)	
	obs.	calc.	obs.	calc.	obs.	calc.
A'4	0.4 ₈	0.4 ₉	1.0 ₀	1.0 ₃	1.8 ₁	2.1 ₃
C'3	0.6 ₄	0.7 ₀	1.3 ₅	1.5 ₁	2.5 ₄	2.8 ₃
F'5	0.3 ₅	0.3 ₆	0.7 ₅	0.7 ₆	1.3 ₆	1.4 ₂
H'2	1.0 ₇	1.1 ₄	2.4 ₇	2.6 ₂	-	-

A comparison of equation (3:15) with equation (3:2) shows that the reaction between tiglic acid buffered by sodium tiglate and hypochlorous acid conforms to the same general equation at 25° and 35°. The significance of the specific rate constants of these equations and their variation with temperature will be discussed in the following section.

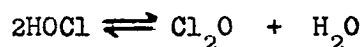
3.3. Discussion.

The values of the pH measured after the reaction had proceeded for five minutes and recorded in Tables XIII and XVI are seen to decrease with increasing hypochlorous acid concentration. The fact that hypochlorous acid adds very rapidly to sodium tiglate (11), thereby altering the constitution of the buffer, and that the pH decreases with increasing hypochlorous acid concentration, both suggest that the reasons given for this pH decrease in the case of crotonic acid apply equally to tiglic acid. Although no values of the dissociation constants of the chloro-hydroxy- α -methylbutanoic acids could be found in the literature, these acids should be stronger than tiglic acid.

The first term in the general velocity equation, viz., $k_2^I (\text{HOCl}) \{(\text{RCOOH}) + (\text{RCOO}^-)\}$, represents, as in the case of crotonic acid, contributions from a number of simultaneous reactions concerned with the direct attack of hypochlorous acid on either undissociated tiglic acid or tiglate ion and with the possible rate-determining formation of 2-methyl-crotonyl hypochlorite. A further discussion on these reactions is not necessary as the explanations given earlier for crotonic acid should also apply to tiglic acid.

The second and final term in the tiglic acid rate equation, $k_2^{II} (\text{HOCl})^2$, probably represents the rate of formation of chlorine monoxide from hypochlorous acid. Tiglic acid (or tiglate ion) will then react with this chlorine monoxide as fast as it is formed to give the carbonium complex, the stabilisation of which is completed by a suitable anion. Chlorine monoxide has been

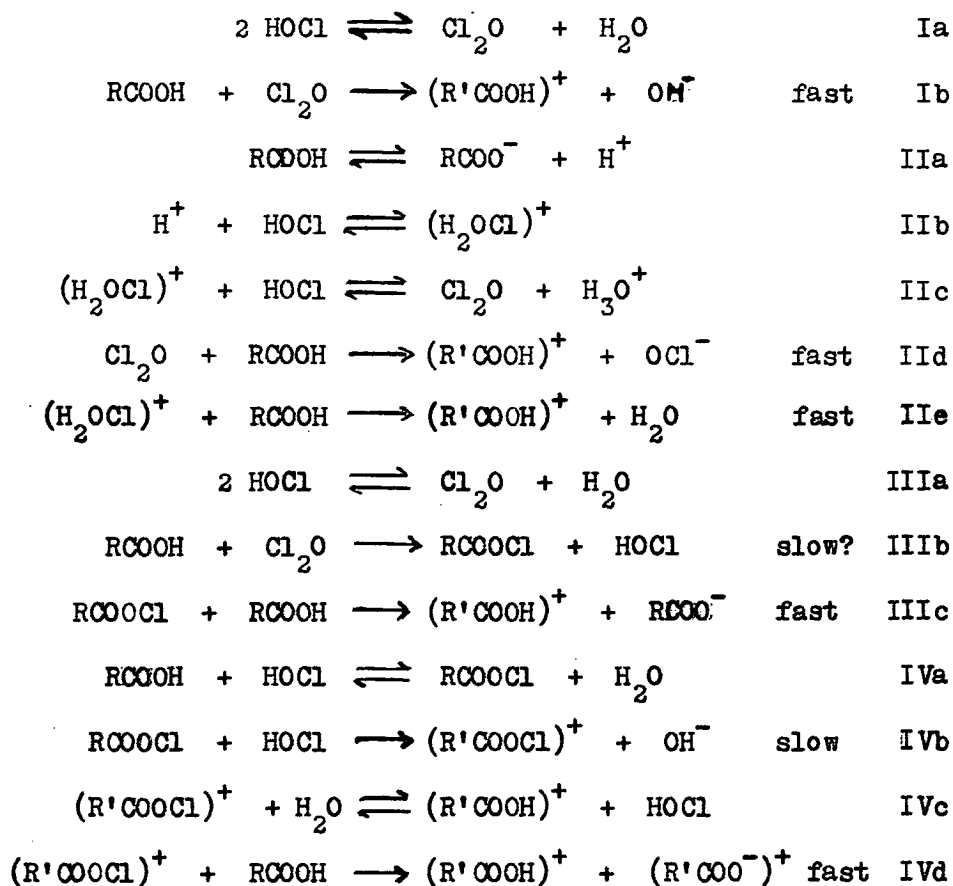
shown to be about 10^6 times more effective than hypochlorous acid as a source of 'positive' chlorine (21, 24) and it is unlikely, therefore, that this addition of chlorine monoxide would be rate determining. The value of k_2^{II} for tiglic acid was greater than the value for crotonic acid although the nature of the term would suggest that the rate constant should be independent of the olefin. A similarity between the value of k_2^{II} for the allyl alcohol reaction (8.2) and tiglic acid (7.5) was noted, but more recent work on allyl alcohol using lower concentrations of hypochlorous acid indicated that k_2^{II} decreased as low as 3.5 (53). A comparison of the activation energy of the process



calculated from the variation of k_2^{II} with temperature in Tables XII and XIX viz., 9.9 and 7.3 Kcal. per mole showed a definite variation. However, it would be unwise to attribute this difference to any one cause where concomitant reactions are involved especially in view of the fact that k_2^{II} at a particular temperature varied from one olefin to another.

No term involving the product $(\text{HOCl})^2(\text{RCOOH})$ was found for the tiglic acid reaction as distinct from the addition to crotonic acid. Previously this term had been explained as the acid-catalysed formation of chlorine monoxide from hypochlorous acid. As mentioned earlier, it is strange that such a term does not occur for tiglic acid whose strength is approximately the same as that of crotonic acid. Other reactions could take place to account for this term, but these reactions must be capable of explaining its occurrence in the case of the allyl alcohol and

crotonic acid reactions and its non-inclusion in the velocity equations for the more reactive tiglic and β : β -dimethylacrylic acids. The following sets of composite reactions are suggested and later analysed:



where RCOOH = olefinic acid or acetic acid

and $\text{R}' = \text{R} + \text{Cl}^+$ in the case of the olefinic acids.

These sets I - IV could account for the term $(\text{RCOOH})(\text{HOCl})^2$ under special circumstances, but to explain the observed velocity equations the rate determining step must be influenced by the reactivity of the olefin. Let us consider these sets in more detail:

Set I : Step Ib would need to be rate determining in the case of the addition of chlorine monoxide to allyl alcohol and crotonic acids, and step Ia would need to be rate determining in the case of tiglic and β : β -dimethylacrylic acids. Although a rate determining step of the type Ib did occur with the very unreactive esters, (24) such a step would be most unlikely to determine the kinetics for these more reactive olefins.

Set II : To account for the term $(\text{RCOOH})(\text{HOCl})^2$, step IIc would need to be rate determining while steps IIa and IIb should be, and are in fact, equilibrium reactions. However, for acids of approximately the same strength, steps IIa, IIb and IIc would be independent of the olefinic acid. Furthermore, the decomposition of the hydrated chlorine cation is most likely to take place rapidly by step IIe rather than by step IIc, as these chloro-ions are known to be very reactive towards olefins (54, 55, 56). The amount of this chloro-ion, $(\text{H}_2\text{OCl})^+$, formed in equation IIb would, in any case, be very small and may be calculated approximately using the relations:

$$(\text{H}_2\text{OCl})^+(\text{Cl}^-)/(\text{Cl}_2) = 10^{-30} \quad (57)$$

$$\text{and } (\text{HOCl})(\text{H}^+)(\text{Cl}^-)/(\text{Cl}_2) = 4.5 \times 10^{-4} \quad (58)$$

$$\text{whence } (\text{H}_2\text{OCl})^+(\text{H}^+)(\text{HOCl}) = 2.2 \times 10^{-27}$$

Set III : This set could be a possible solution to the problem provided the formation of acyl hypochlorites by step IIIb is slower in the case of acetic acid and crotonic acid than the formation

of chlorine monoxide by step IIIa, and faster than this forward reaction in the case of tiglic and β : β -dimethylacrylic acids.

In these latter cases the chlorine monoxide is used up as fast as it is formed and step IIIa becomes rate determining.

Set IV : This set involves the formation of the acyl hypochlorites by the reaction of hypochlorous acid with the ~~carboxyl~~ carboxyl group and further attack of hypochlorous acid on the double bond on this acyl hypochlorite to give the reactive complex, $(R'COOCl)^+$.

If step IVb is slow, then the velocity equation will contain the term $(RCOOH)(HOCl)^2$. This set would not account for the reactions involving acetic acid in the external buffer.

It seems as though Sets I and III are the only ones likely to provide a solution to the problem, but our knowledge of the relative rates of the equations of Sets III and IV is limited by the small amount of information available about these acyl hypochlorites. It is known, however, that they are unstable compounds and extremely active donors of 'positive' chlorine. (54)

The variation of the specific rate constants with temperature for the addition of hypochlorous acid to tiglic acid is given in Table XIX. The ratio of the rate constants is also given.

TABLE XIX

	k_2^I	k_2^{II}
25°	20.2 ₄	7.4 ₉
35°	34.8 ₆	11.2 ₀
k_{35}/k_{25}	1.72	1.50
ΔE Kg.Cals.	9.89	7.33

In this calculation of the activation energy, ΔE , it has been necessarily assumed that there was no change in the non-exponential portion of the Arrhenius equation in the temperature interval from 25° to 35°. The significance of the activation energy for the direct addition of hypochlorous acid to tiglic acid and the change in k_2^I from crotonic to tiglic acid will be discussed in Section 6.1.

PART IV

THE REACTION BETWEEN 3:3-DIMETHYLACRYLIC ACID

and

HYPOCHLOROUS ACID AT 25° and 35°.

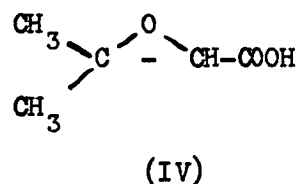
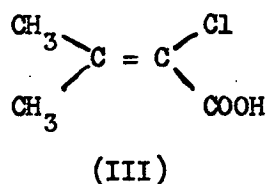
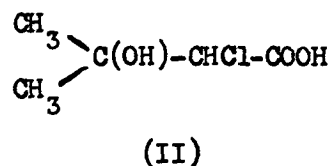
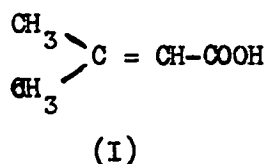
4.1. Introduction.

The kinetics and mechanisms of the addition of hypochlorous acid to β : β -dimethylacrylic acid have not previously been studied although the kinetics of both the electrophilic and the nucleophilic additions of halogens have been investigated by several workers (47, 2, 4). It was found that β : β -dimethylacrylic acid united with bromine in acetic acid solution by a rapid termolecular reaction which was only slightly catalysed by hydrogen bromide presumably because the inductive effect of the two geminal methyl groups favoured the electrophilic addition. The ratios of the velocity constants for the addition of bromine or chlorine in acetic acid solution to β : β -dimethylacrylic acid and crotonic acid varied from 20 to 80. It is to be expected that the addition of hypochlorous acid will be faster to β : β -dimethylacrylic acid than to crotonic acid.

Information concerning the products of the reaction between hypochlorous acid and β : β -dimethylacrylic acid given in the literature proved contradictory and it was thought that a study of the kinetics of the reaction might assist in determining the course of the addition reaction.

Prentice (59) found that hypochlorous acid and β : β -dimethylacrylic acid (I) gave a single homogeneous addition product, a chlorohydroxy-isovaleric acid in 82 per cent yield. This acid gave on dehydration α -chloro- β : β -dimethylacrylic acid (III) and treatment of the reaction product with alcoholic potassium hydroxide gave β : β -dimethylglycidic acid (IV). The chlorohydrin must have had the constitution (II). Even after

repeated work on this addition, Prentice could find no trace of a chlorohydrin other than the α -chloro- β -hydroxy acid, nor did he locate any neutral α -chloro compounds that were reported later by Bloomfield.



α -chloro- β -hydroxy-isovaleric acid, (II), crystallised in colourless, indistinct plates and was soluble in water, ethanol, chloroform and diethyl ether.

However, experimental work on the products of this reaction by Bloomfield et al. (11) proved that the reaction was more complex than similar reactions with crotonic and tiglic acids. The addition was fast and extraction of the reaction mixture yielded the following products:

<u>Neutral Portion</u>	<u>Acid Portion</u>
(i) $(\text{CH}_3)_2\text{C}=\text{CHCl}$	(i) Unreacted β : β -dimethyl-acrylic acid
(ii) $\text{C}_4\text{H}_8\text{OCl}_2$, probably an adduct of (i) and hypochlorous acid.	(ii) $(\text{CH}_3)_2\text{C}(\text{OH})-\text{CHCl}-\text{COOH}$
(iii) $(\text{C}_4\text{H}_7\text{Cl})_2$, probably a dimer of (i)	(iii) $(\text{CH}_3)_2\text{C}(\text{Cl})-\text{CHOH}-\text{COOH}$

Bloomfield et alia found that the α -chloro- β -hydroxy compound

was formed most easily and made up to 68 per cent of the total chlorohydrin which escaped decarboxylation. It was identified by the ease with which it was dehydrated by sulphuric acid to give α -chloro- β : β -dimethylacrylic acid. A small amount of the β -chloro- α -hydroxy compound was found contaminated with the α -chloro- β -hydroxy acid and could not be crystallised.

Acids of the type $R.CHOH.CHCl.COOH$ and $R.CHCl.CHOH.COOH$ tend to suffer decarboxylation during their conversion into unsaturated chloro-acids. Because of this, Bloomfield et.al., in estimating quantitatively the opposite modes of hypochlorous acid addition as 80 per cent, α -chloro- β -hydroxy and 20 per cent β -chloro- α -hydroxy, regarded all the neutral compounds formed in the reaction as secondary derivatives of α -chloro- β -hydroxy isovaleric acid (II).

Troell (60) found that β -chloro- α -hydroxy-isovaleric acid (m.p. 81°) was soluble in, but easily decomposed by water, especially under alkaline conditions, and this decomposition was not a simple bimolecular reaction.

Preparation and Properties of β : β -dimethylacrylic acid.

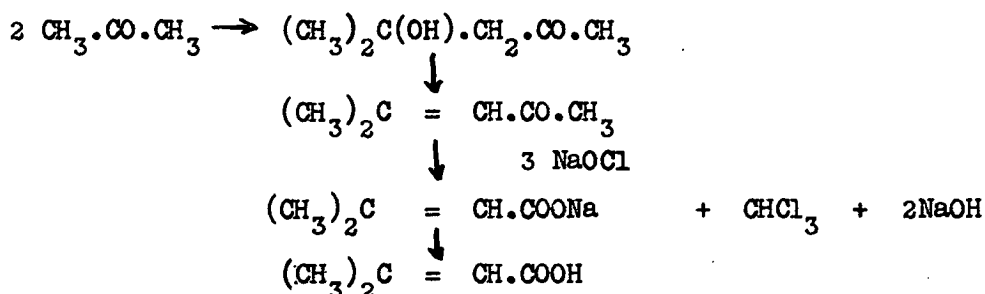
Several preparations were attempted before a satisfactory yield was obtained.

(i) Acetone was refluxed with malonic acid in pyridine solution containing a trace of piperidine for 42 hours, but only a trace of unsaturated acid was obtained.

(ii) A Reformatsky reaction between acetone and ethyl

bromoacetate in the presence of zinc dust was attempted but only a small yield of the ethyl ester of the olefinic acid was obtained.

(iii) The preparation that yielded about 30 per cent β : β -dimethylacrylic acid was the oxidation of mesityl oxide with sodium hypochlorite according to the method of Barbier and Léser (61,62). Neither mesityl oxide nor sodium hypochlorite were available and had to be prepared for use in this reaction. The following steps were carried out:



1.5 litres of acetone were refluxed in a Soxhlet apparatus containing barium hydroxide in the extraction thimble for 135 hours. This aldol condensation yielded 1.2 litres of crude diacetone alcohol (63). 1 litre of crude diacetone alcohol containing 0.2 gm. resublimed iodine was fractionally distilled and after 16 hours, 550 gm. of mesityl oxide (b.p. 126° - 130°) was obtained.

A solution of sodium hypochlorite was prepared by adding sodium hydroxide and sodium carbonate to a solution of commercial bleaching powder in hot water and filtering (64). The filtrate was added to a solution of mesityl oxide in dioxan and after cooling for half an hour, the reaction mixture was allowed to reflux steadily; after two hours a sample was taken and showed that all the sodium hypochlorite had been expended. The acidic product was liberated and extracted with ether

Distillation under reduced pressure gave 26 gm. of crude β : β -dimethylacrylic acid (b.p. 95° - 105° /12-15 mm. ; literature figures 90° /10 mm., 105° /15 mm.). This acid was recrystallised from petroleum ether (80° - 100° fraction), m.p. 67.5° - 68.5° , and a further recrystallisation from this solvent gave a colourless crystalline acid, m.p. 68.5° - 69° . Literature figures : 67.8° - 68.3° (65). 69° (34, 62).

β : β -dimethylacrylic acid was soluble in water to about the same extent as tiglic acid i.e. 1-2 per cent. Neutralisation of a 0.1 N. solution with sodium hydroxide at 16° gave a pH value of 5.05 at the half neutralisation point, and the neutralisation curve indicated a good buffering capacity at a pH of 4.73. The dissociation constant for β : β -dimethylacrylic acid at 25° is 0.759×10^{-5} (34, 66) corresponding to a pK_a value of 5.12. Application of Pitzer's equation (see Mathematical Appendix F) to this value showed that pK_a dropped to 5.10 at 35° i.e. the dissociation constant increased by 4 per cent to 0.791×10^{-5} . It was decided that a similar buffer would be used at 35° as was used at 25° .

4.0044 gm. of twice recrystallised β : β -dimethylacrylic acid was dissolved in about 600 ml. of water and sufficient sodium hydroxide was added so that in the final solution

$$\begin{aligned} (RCOOH) + (RCOO^{-}) &= 0.0400 \text{ moles litre}^{-1} \\ (RCOO^{-}) &= 0.0116 \text{ moles litre}^{-1} \\ R &= (CH_3)_2C:CH. \end{aligned}$$

corresponding to a calculated pH at 25° of 4.73. The measured value at 22° was 4.70.

It has been reported that β : β -dimethylacrylic acid undergoes acid-catalysed hydration to β -hydroxy-isovaleric acid in concentrated solution at temperatures about 90° and this is accompanied by simultaneous decarboxylation. However, the rate of decarboxylation of β : β -dimethylacrylic acid in pure water is negligible especially in weak solution at room temperatures. (11, 67)

The hypochlorous acid solution used at 25° was prepared as required by the 'non-aqueous' method of Section 2.1, while at 35° a freshly prepared 0.17 molar stock solution was made by the 'aqueous' method and stored in the refrigerator without decomposition.

3.2. Experimental Results and Derivation of the Velocity Equation.

Using the experimental method described in Part I, fifteen Series A - O were studied at $25 \pm 0.01^{\circ}$ and the results are shown in Table XIX. The pH values listed in this Table were those measured about five minutes after the reaction was started. The same stock 0.04 molar β : β -dimethylacrylic acid plus sodium β : β -dimethylacrylate solution was used for twelve of the Series but Series D, K, and O were carried out using similar buffer solution to the one above except that it was prepared at a different time and had a measured pH of 4.74 at 19° .

The following units were used in this Table:

Concentration	:	moles litre ⁻¹
Velocity	:	moles litre ⁻¹ minute ⁻¹
Time	:	minutes
and R	=	(CH ₃) ₂ C:CH.

TABLE XIX

Initial pH = 4.73

Temperature = $25 \pm 0.01^\circ$

Run	$(\text{HOCl})_0$	$(\text{RCOOH})_0 + (\text{RCOO}^-)_0$	V_0^{obs}	pH
No.	$\times 10^3$	$\times 10^3$	$\times 10^5$	
A1	0.81	1.00	3.17	4.70
A2	0.81	2.00	5.23	4.67
A3	0.81	4.00	10.1	4.65
A4	0.80	6.00	14.3	4.65
A5	0.79	8.00	18.7	4.65
B1	0.85	1.00	4.08	4.68
B2	0.85	2.00	6.44	4.67
B3	0.84	4.00	11.6	4.66
B4	0.83	6.00	16.2	4.66
B5	0.83	8.00	21.1	4.65
C1	0.90	1.00	4.38	4.68
C2	0.90	2.00	6.91	4.66
C3	0.90	4.00	12.2	4.66
C4	0.89	6.00	17.3	4.67
C5	0.89	8.00	22.5	4.67
D1	1.09	1.00	4.13	4.67
D2	1.08	2.00	7.28	4.68
D3	1.08	4.00	13.5	4.68
D4	1.07	6.00	19.2	4.68
D5	1.07	8.00	26.3	4.68
E1	1.17	1.00	5.06	4.60
E2	1.16	2.00	8.11	4.61
E3	1.15	4.00	15.0	4.60
E4	1.15	6.00	21.6	4.59
E5	1.15	8.00	28.7	4.60
F1	1.47	1.00	6.32	4.61
F2	1.46	2.00	10.1	4.61
F3	1.46	4.00	18.5	4.62
F4	1.44	6.00	26.4	4.63
F5	1.44	8.00	35.1	4.63
G1	1.53	1.00	7.11	4.64
G2	1.52	2.00	11.1	4.64
G3	1.51	4.00	19.3	4.62
G4	1.50	6.00	27.8	4.61
G5	1.49	8.00	35.7	4.62

TABLE XIX (contd.)

Run	$(\text{HOCl})^{\circ}$ $\times 10^3$	$(\text{RCOOH})^{\circ} + (\text{RCOO}^-)^{\circ}$ $\times 10^3$	$\text{V}^{\circ}_{\text{obs}}$ $\times 10^5$	pH
H1	1.66	1.00	8.01	4.60
H2	1.66	2.00	12.6	4.60
H3	1.65	4.00	22.6	4.60
H4	1.64	6.00	31.7	4.62
H5	1.64	8.00	41.6	4.62
I1	1.67	1.00	7.90	4.57
I2	1.67	2.00	13.0	4.58
I3	1.65	4.00	21.8	4.62
I4	1.65	6.00	31.3	4.62
I5	1.64	8.00	40.3	4.62
J1	1.96	1.00	9.08	4.51
J2	1.95	2.00	14.2	4.56
J3	1.92	4.00	23.5	4.60
J4	1.92	6.00	35.1	4.63
J5	1.91	8.00	45.8	4.63
K1	1.97	1.00 #	8.93	4.50
K2	1.96	2.00	14.7	4.55
K3	1.95	4.00	26.0	4.56
K4	1.95	6.00	37.5	4.57
K5	1.95	8.00	49.2	4.60
L1	2.03	1.00	9.28	4.55
L2	2.00	2.00	14.1	4.55
L3	2.00	4.00	25.5	4.57
L4	2.00	6.00	37.5	4.57
L5	2.00	8.00	48.7	4.59
M1	2.12	1.00	11.2	4.55
M2	2.10	2.00	16.3	4.54
M3	2.10	4.00	29.0	4.59
M4	2.09	6.00	41.1	4.60
M5	2.08	8.00	52.7	4.60
N1	2.50	1.00	12.3	4.46
N2	2.48	2.00	18.5	4.50
N3	2.48	4.00	32.4	4.55
N4	2.45	6.00	45.5	4.55
N5	2.45	8.00	61.3	4.57
O1	2.55	2.00 #	18.0	4.51
O2	2.55	4.00	32.6	4.54
O3	2.54	6.00	47.2	4.55
O4	2.53	8.00	61.8	4.57

A different stock buffer preparation was used for these Series.

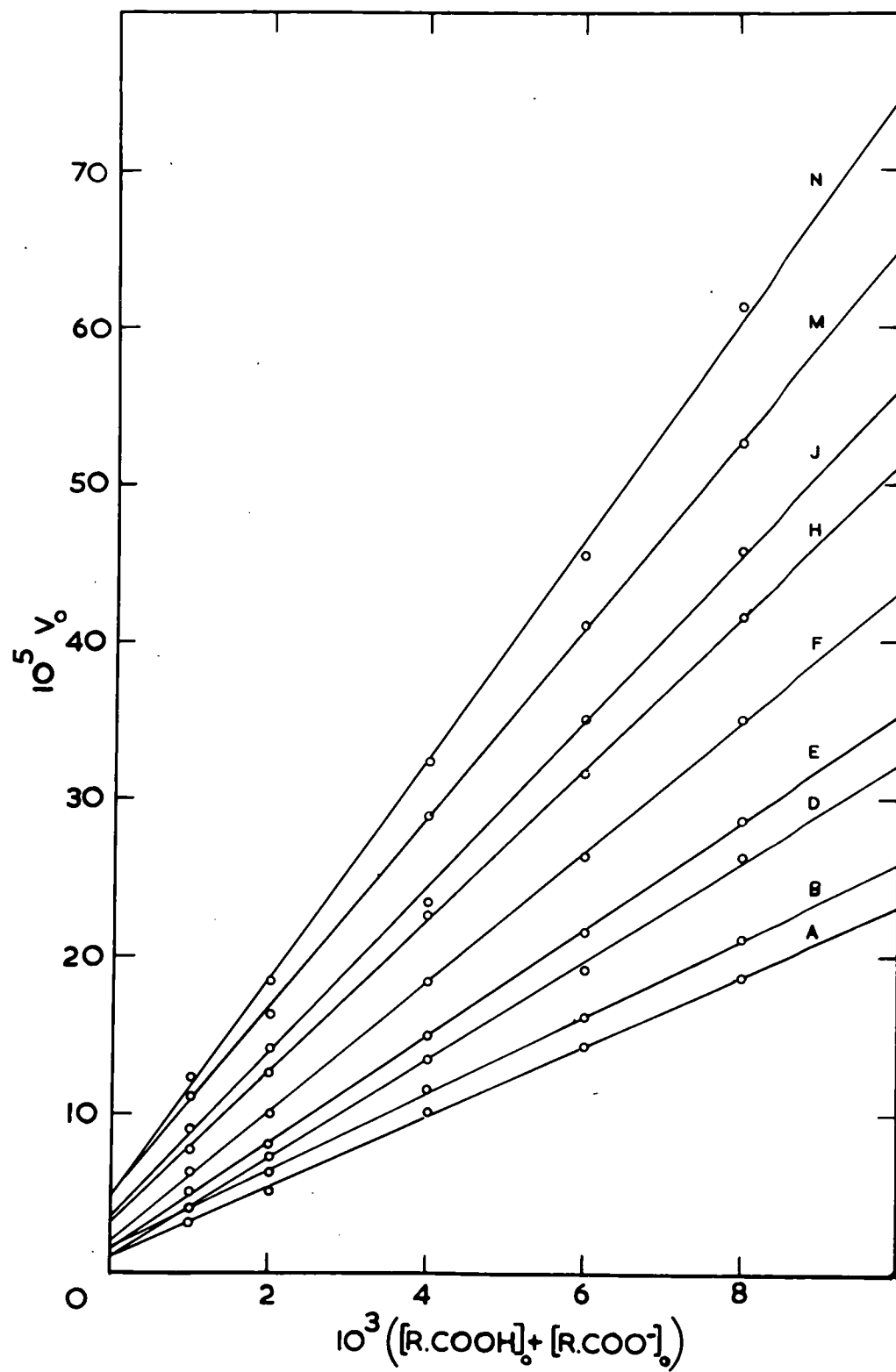


Figure 17

The variation of the initial velocity with the total initial olefin concentration at constant initial concentration of hypochlorous acid is shown in Figure 17 where nine of the fifteen series were plotted. These graphs conform to the equation,

$$V_o = k \{ (RCOOH)_o + (RCOO^-)_o \} + V_{res} \dots\dots\dots \text{Eqn. (4.1)}$$

The six remaining series C, G, I, K, and O were omitted from this Figure for purposes of clarity. The gradient, k , and the intercept, V_{res} , for all these series were evaluated by the method of least squares and the results are given in Table XX. In accordance with earlier work, the value of the hypochlorous acid concentration listed in this Table is the mean of the initial values for the runs of the series concerned.

TABLE XX

Series	$(HOCl)_o$ $\times 10^3$	$k \text{ (min}^{-1}\text{)}$ $\times 10^2$	V_{res} $\times 10^5$
A	0.80	2.22	1.01
B	0.84	2.43	1.57
C	0.90	2.59	1.78
D	1.08	3.13	0.95
E	1.16	3.38	1.50
F	1.45	4.11	2.02
G	1.51	4.11	2.97
H	1.65	4.79	3.17
I	1.66	4.60	3.52
J	1.94	5.25	3.48
K	1.96	5.74	3.17
L	2.01	5.69	3.11
M	2.10	6.00	4.85
N	2.47	6.97	4.75
O	2.54	7.30	3.42

Both k and V_{res} increased with increasing hypochlorous acid concentration and the variation of k with $(HOCl)_o$ is shown graphically in Figure 18. Application of the method of least

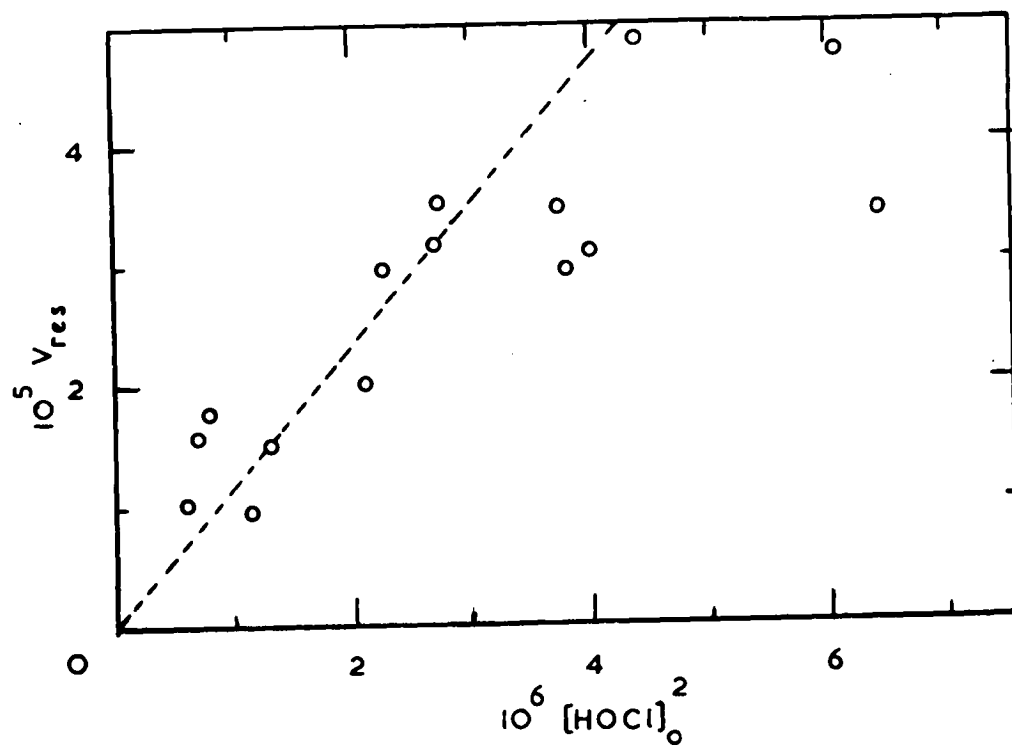


Figure 19

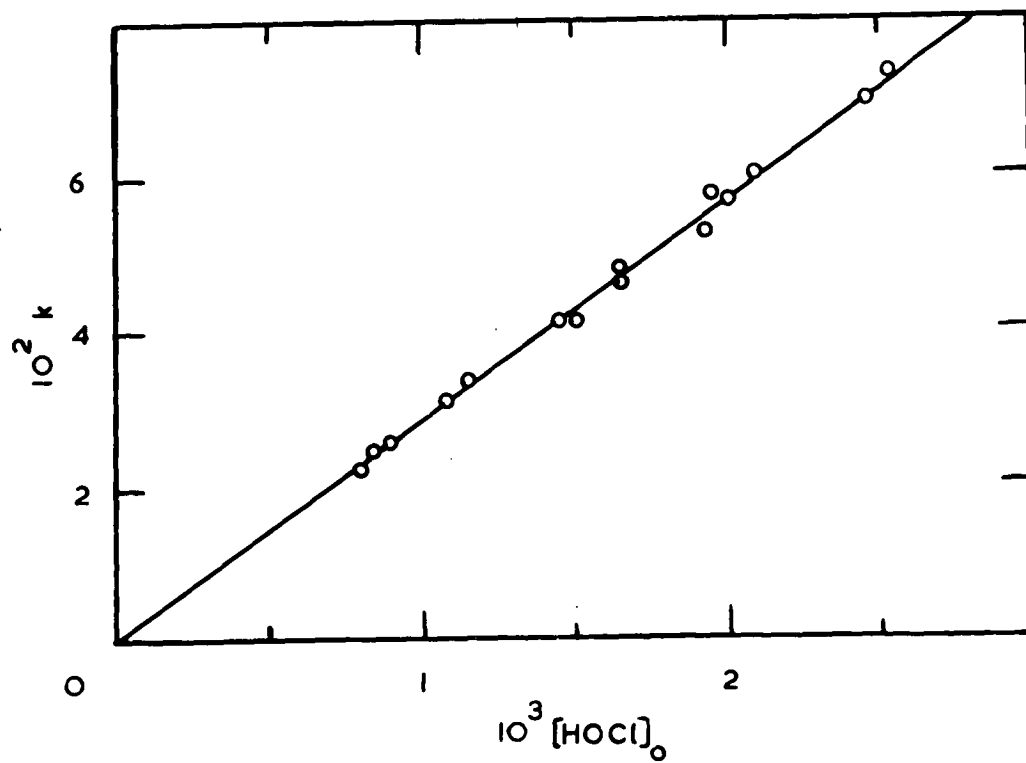


Figure 18

squares to this graph gave the equation to the line of best fit as

$$k = 28.30 (\text{HOCl})_0 + 0.017 \times 10^{-2} \dots\dots\dots \text{Eqn. (4.2)}$$

This constant residuum can be neglected without serious error to k , and hence to the initial velocity, and Eqn. (4.2) reduces to

$$k = k_2^I (\text{HOCl})_0 \dots\dots\dots \text{Eqn. (4.3)}$$

where $k_2^I = 28.3 \text{ lit.mol.}^{-1} \text{ min.}^{-1}$

Figure 18 shows that Eqn. (4.3) holds with reasonable accuracy and there is no indication of a third order term involving the square of the hypochlorous acid concentration and the olefin concentration. The reaction between hypochlorous acid and β : β -dimethylacrylic acid is similar to the tiglic acid reaction in this respect.

We now consider the variation of the residual velocity V_{res} , with the hypochlorous acid concentration. Table XX shows that while there is an increase in the residual velocity with increasing hypochlorous acid concentration, examination of Figure 19 shows that the nature of this increase is rather indefinite. By analogy with the results obtained for tiglic and crotonic acids, V_{res} was plotted against $(\text{HOCl})_0^2$ in Figure 19 and, in view of the ^{scatter, the} arithmetical mean of $V_{\text{res}}/(\text{HOCl})_0^2$ was calculated and is shown in this Figure by the dotted line. All attempts to correlate these variable values of $V_{\text{res}}/(\text{HOCl})_0^2$ and the general properties of the reactant solutions failed although this function seemed to decrease with increasing hypochlorous acid concentration.

The equation to this mean line of Figure 19 is :

$$V_{\text{res}} = 11.72 (\text{HOCl})_0^2 \dots\dots\dots \text{Eqn. (4:4)}$$

$$\text{i.e. } V_{\text{res}} = k_2^{\text{II}} (\text{HOCl})_0^2 \dots\dots\dots \text{Eqn. (4:5)}$$

The value of k_2^{II} calculated in this way is probably too high as both the B and C Series have very large values of $V_{\text{res}}/(\text{HOCl})_0^2$ and their exclusion reduced the average to 10.11.

Combination of equations (4:3) and (4:5) with (4:1) gives the approximate velocity equation,

$$V_0 = 28.3 (\text{HOCl})_0 \{ (\text{RCOOH})_0 + (\text{RCOO}^-)_0 \} + 11.7 (\text{HOCl})_0^2 \dots\dots\dots \text{Eqn. (4:6)}$$

or generalising,

$$V = k_2^{\text{I}} (\text{HOCl}) \{ (\text{RCOOH}) + (\text{RCOO}^-) \} + k_2^{\text{II}} (\text{HOCl})^2 \dots\dots\dots \text{Eqn. (4:7)}$$

$$\text{where } k_2^{\text{I}} = 28.3 \text{ lit.mol.}^{-1} \text{min.}^{-1}$$

$$k_2^{\text{II}} = 11.7 \text{ lit.mol.}^{-1} \text{min.}^{-1}$$

$$\text{and } R = (\text{CH}_3)_2\text{C:CH.}$$

Because of the approximations made in the development of this equation, evaluation of the calculated initial velocities would not be justified. Similarly, integration of equation (4:7) so that the time for a certain percentage decrease in the initial hypochlorous acid concentration could be calculated, was not warranted. For purposes of comparison with the results for tiglic acid at 25° (Table XV), the observed times for 10, 20 and 33-1/3 per cent decrease for four runs are listed in Table XXI.

TABLE XXI

Run	$t_{1/10}$ (min.)	$t_{1/5}$ (min.)	$t_{1/3}$ (min.)
No.	obs.	obs.	obs.
B2	1.40	2.95	-
D3	0.85	1.78	3.28
G5	0.43	0.92	1.58
N4	0.57	1.18	2.19

The reaction between hypochlorous acid and β : β -dimethyl-acrylic acid and its ion at 35⁰ was carried out for the ten series A - J the results of which are summarised in Table XXII. The pH values listed in this Table were measured four minutes after the reaction was started. The initial hypochlorous acid concentration and the initial velocities listed in this Table were both obtained from the log titre vs. time graphs. These graphs departed more from linearity for β : β -dimethylacrylic acid at 35⁰ than in the case of the previous olefinic acids and extrapolation was correspondingly more difficult. An examination of the reciprocal titre vs. time graphs showed that they could not be used to give reliable results as the curvature was too great for the extreme olefin concentrations.

Table XXII

Initial pH = 4.73

Temperature = $35 \pm 0.01^\circ$

Run	$(\text{HOCl})_0$	$(\text{RCOOH})_0 + (\text{RCOO}^-)_0$	V_0^{obs}	pH
No.	$\times 10^3$	$\times 10^3$	$\times 10^5$	
A'1	0.89	1.00	6.37	4.57
A'2	0.88	2.00	10.7	4.55
A'3	0.88	4.00	20.4	4.55
A'4	0.87	6.00	29.6	4.56
A'5	0.87	8.00	39.9	4.54
B'1	1.01	1.00	7.36	4.57
B'2	1.00	2.00	12.0	4.57
B'3	0.99	4.00	22.7	4.58
B'4	1.00	6.00	34.3	4.59
B'5	1.00	8.00	45.8	4.58
C'1	1.14	1.00	7.73	-
C'2	1.13	2.00	13.8	-
C'3	1.13	4.00	26.3	-
C'4	1.11	6.00	37.5	-
C'5	1.10	8.00	49.5	-
D'1	1.26	1.00	8.60	4.62
D'2	1.24	2.00	15.3	4.59
D'3	1.24	4.00	29.0	4.62
D'4	1.23	6.00	42.0	4.63
D'5	1.23	8.00	56.8	4.64
E'1	1.52	1.00	10.7	4.49
E'2	1.52	2.00	19.2	4.53
E'3	1.51	4.00	35.0	4.56
E'4	1.49	6.00	50.6	4.57
E'5	1.47	8.00	64.7	4.58
F'1	1.77	1.00	12.8	4.40
F'2	1.76	2.00	22.3	4.47
F'3	1.75	4.00	40.6	4.49
F'4	1.71	6.00	55.8	4.50
F'5	1.72	8.00	76.8	4.53
G'1	2.00	1.00	14.9	4.34
G'2	1.98	2.00	24.8	4.44
G'3	1.95	4.00	43.0	4.47
G'4	1.94	6.00	63.4	4.50
G'5	1.93	8.00	83.1	4.51

Table XXII (Contd.)

Run No. —	(HOCl) ₀ x 10 ³	(RCOOH) ₀ + (RCOO ⁻) ₀ x 10 ³	v ₀ ^{obs.} x 10 ⁵	pH
H'1	2.29	1.00	17.4	4.25
H'2	2.27	2.00	28.4	4.36
H'3	2.24	4.00	50.0	4.40
H'4	2.22	6.00	72.9	4.45
H'5	2.21	8.00	97.0	4.48
I'1	2.50	1.00	19.6	4.13
I'2	2.48	2.00	31.2	4.27
I'3	2.45	4.00	55.9	4.36
I'4	2.40	6.00	77.1	4.40
I'5	2.40	8.00	105.4	4.45
J'1	2.80	1.00	22.0	3.80
J'2	2.78	2.00	35.8	4.16
J'3	2.75	4.00	61.5	4.26
J'4	2.73	6.00	89.3	4.34
J'5	2.71	8.00	117.2	4.39

The dependence of the initial velocity upon the total olefin concentration for constant hypochlorous acid concentration can be seen in Figure 20. The equations to these graphs are of the form,

$$v_0 = k' \{(\text{RCOOH})_0 + (\text{RCOO}^-)_0\} + v'_{\text{res}} \dots\dots\dots \text{Eqn. (4.8)}$$

The equation of the line of best ^{fit} to each of the graphs in Figure 20 was determined by the method of least squares and the values of the gradient and the ordinate intercepts so obtained are given in Table XXIII.

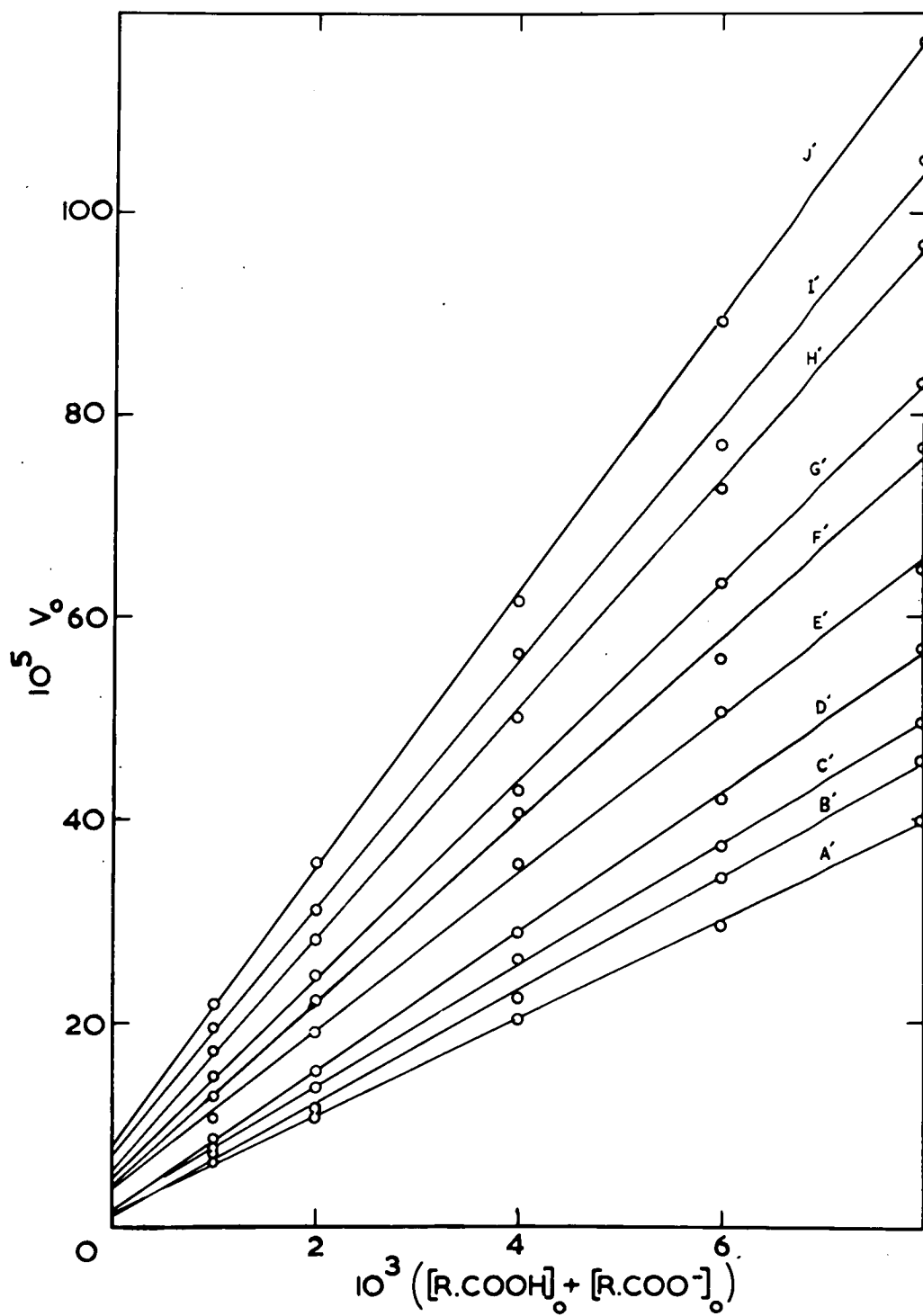


Figure 20

TABLE XXIII

Series	(HOCl) ₀ x 10 ³	k' (min. ⁻¹) x 10 ²	V' _{res} x 10 ⁵
A'	0.88	4.78	1.30
B'	1.00	5.53	1.19
C'	1.12	5.95	1.96
D'	1.24	6.85	1.58
E'	1.50	7.73	3.57
F'	1.74	8.97	4.01
G'	1.96	9.73	4.96
H'	2.25	11.33	5.52
I'	2.45	12.09	7.05
J'	2.75	13.66	8.14

The value of (HOCl)₀ quoted in this Table is the mean value for the series concerned.

The variation of k' with the initial hypochlorous acid concentration is shown in Figure 21. The equation of the line of best fit was calculated by the method of least squares but, unlike the equation for the addition reaction at 25⁰, this equation contained a residual term which was not negligible by comparison with k' viz.,

$$k' = 46.22 (\text{HOCl})_0 + 0.85 \times 10^{-2} \dots\dots \text{Eqn. (4.9)}$$

The continuous line in Figure 21 shows that this equation is obeyed closely. However, combination of equations (4.9) with (4.8) shows that the final velocity equation will contain a term, $0.85 \times 10^{-2} \{(\text{RCOOH})_0 + (\text{RCOO}^-)_0\}$. The significance of such a term is not understood.

The mean value of k'/(HOCl)₀ is shown dotted in Figure 21 and conforms to the relation:

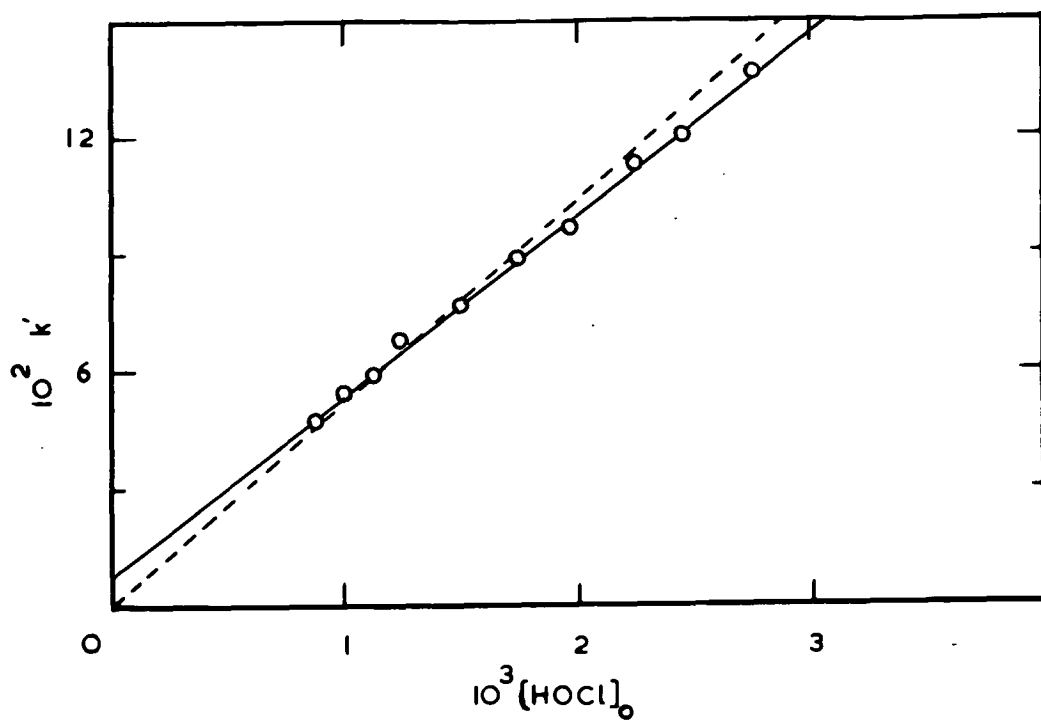


Figure 21

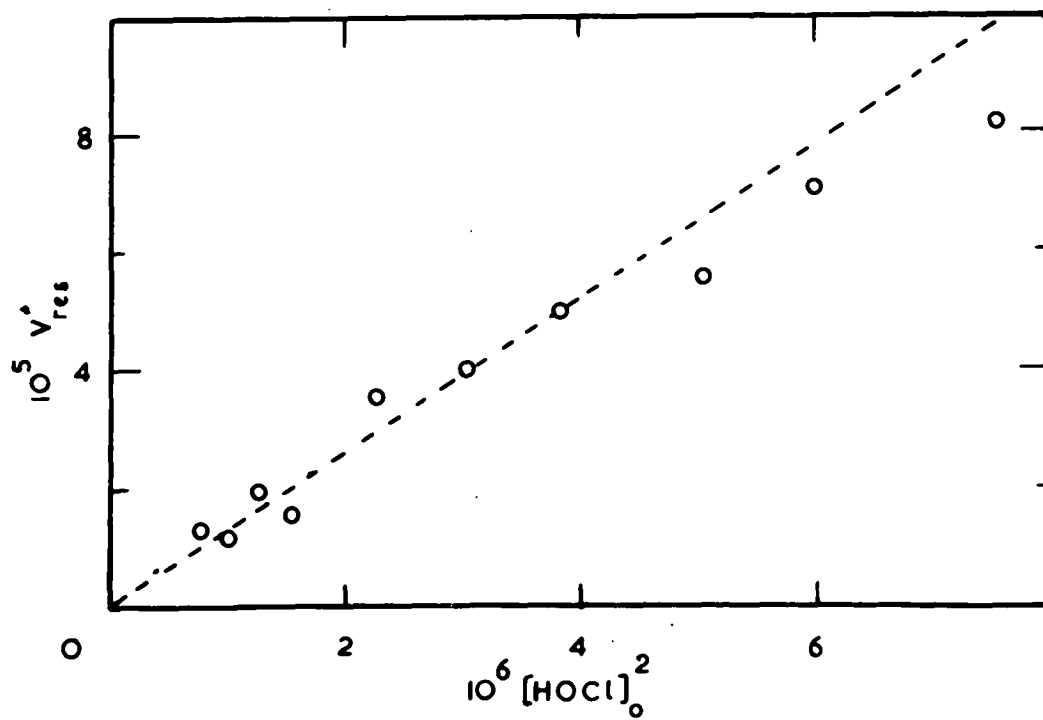


Figure 22

$$k' = 51.96(\text{HOCl})_0 \dots\dots\dots \text{Eqn. (4.10)}$$

$$\text{i.e. } k' = k_2^{\text{I}} (\text{HOCl})_0 \dots\dots\dots \text{Eqn. (4.11)}$$

Values of k_2^{I} for the A' - J' Series were within 5 per cent of this mean value but decreased with increasing hypochlorous acid concentration. Until some explanation is found for the uni-molecular term arising from Eqn.(4.9), Eqn.(4.11) will be used as an approximate representation of Figure 21.

The linear nature of the plot of k' vs $(\text{HOCl})_0$ indicates that there is no term of the type $(\text{RCOOH})(\text{HOCl})^2$ in the kinetic equation at 35° .

The variation of the residual velocity, V'_{res} , with the concentration of hypochlorous acid is shown in Figure 22 where V'_{res} is plotted against the square of the initial hypochlorous acid concentration. The dotted line in this Figure represents the mean value of $V'_{\text{res}}/(\text{HOCl})_0^2$ for the ten Series and the equation to this line is:

$$V'_{\text{res}} = 13.00 (\text{HOCl})_0^2 \dots\dots\dots \text{Eqn. (4.12)}$$

$$\text{i.e. } V'_{\text{res}} = k_2^{\text{II}} (\text{HOCl})_0^2 \dots\dots\dots \text{Eqn. (4.13)}$$

k_2^{II} decreases with increasing hypochlorous acid concentration and the deviations of the residual velocities from the mean line were considerable (cf. earlier work on this acid at 25°).

The errors in the measurement of the observed velocities would be greater (slightly) for β : β dimethylacrylic acid at 35° as the logarithm titre vs. time curves deviated more from linearity than similar graphs for the other olefinic acids.

All the deviations in Figures 21 and 22 could not, however, be attributed to these errors.

Combination of equations (4:10) and (4:12) with (4:8) gave the overall rate equation,

$$V_o = 51.96(\text{HOCl})_o \left\{ (\text{RCOOH})_o + (\text{RCOO}^-)_o \right\} + 13.00(\text{HOCl})_o^2 \dots\dots\dots \text{Eqn. (4:14)}$$

and this can be expressed in general form by the equation,

$$V = k_2^{\text{I}}(\text{HOCl}) \left\{ (\text{RCOOH}) + (\text{RCOO}^-) \right\} + k_2^{\text{II}}(\text{HOCl})^2 \dots\dots\dots \text{Eqn. (4:15)}$$

where $k_2^{\text{I}} = 52.00 \text{ lit.mol.}^{-1} \text{min.}^{-1}$

$$k_2^{\text{II}} = 13.0 \text{ lit,mol.}^{-1} \text{min.}^{-1}$$

$$\text{R} = (\text{CH}_3)_2\text{C:CH.}$$

It must be emphasised, however, that the derivation of this equation (4:14) involves several approximations that would limit its accuracy. For this reason neither the calculation of the initial velocities nor the integration of equation (4:15) were carried out. As at 25°, the time for a certain percentage decrease in the hypochlorous acid concentration was evaluated and the observed values for four runs are shown for purposes of comparison with tiglic acid in Table XXIV.

TABLE XXIV

Run No.	$t_{1/10}$ (min.)	$t_{1/5}$ (min.)	$t_{1/3}$ (min.)
B'2	1.43	2.43	-
D'3	0.46	0.96	1.73
F'4	0.33	1.05	1.88
H'3	0.47	1.00	1.83

In order to investigate the extent to which the reaction between hypochlorous acid and β : β -dimethylacrylic acid proceeded to completion at 35° , a Series of experiments were carried out for more than 24 hours in the presence of excess olefin. The pH of the resultant solution after this time was also measured and the results are summarised in Table XXV.

TABLE XXV

Initial pH = 4.73			Temperature = $35 \pm 0.01^{\circ}$		
Run	$(\text{HOCl})_0$	$(\text{RCOOH})_0 + (\text{RCOO}^-)_0$	$(\text{HOCl})_{\infty}$	Time	pH
No.	$\times 10^3$	$\times 10^3$	$\times 10^6$	in hours	
K'1	1.00	2.00	5.2	27	3.92
K'2	1.00	4.00	3.1	27	4.36
K'3	1.49	2.00	4.2	27	3.56
K'4	1.49	6.00	2.1	27	4.34
K'5	1.49	8.00	ca.0	27	4.42
K'6	1.99	4.00	2.1	27.5	3.80
K'7	1.99	6.00	1.0	27.5	4.19
K'8	2.49	8.00	9.4	27.5	4.22

After reaction for 27 hours the addition of hypochlorous acid had proceeded to the extent of at least 99.5 per cent. The pH of the solution after this time is considerably less than the initial value and, as expected, is greatest for those solutions containing the largest amounts of unreacted buffer.

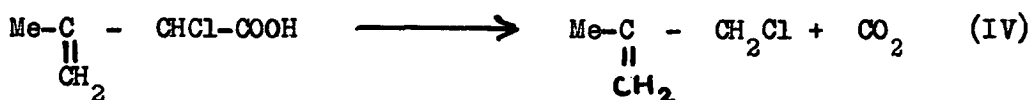
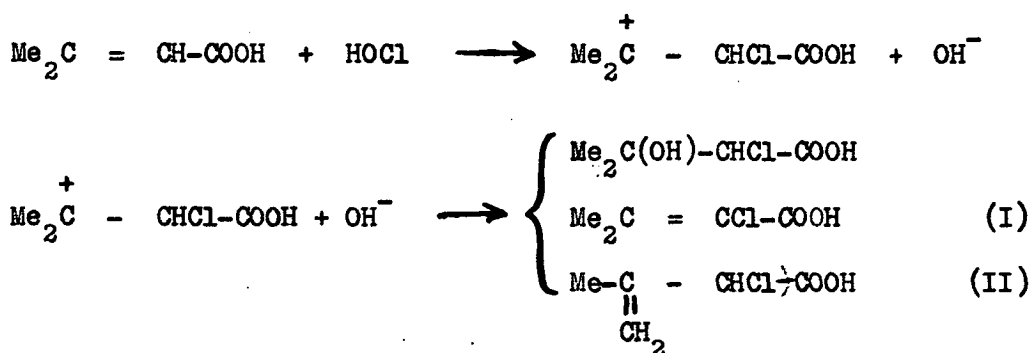
4.3. Discussion.

Investigation of Tables XIX and XXII shows that the pH was steady at values close to the initial pH for small initial concentrations of hypochlorous acid. High concentrations of hypochlorous acid, especially at 35°, lowered the pH after 4 minutes of reaction to values considerably lower than the optimum value. This behaviour is not unexpected in view of the results given in Table XXV where it is clear that the presence of hypochlorous acid is not the only factor leading to a decrease in the pH; the products of the reaction must also contribute to this decrease.

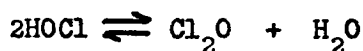
The general rate equations (4.7) and (4.15) obtained for the reaction between hypochlorous acid and β : β -dimethylacrylic acid are similar to the equations derived for the tiglic acid reaction. Any explanation of the significance of the rate constants would therefore be superfluous as the comments on these constants made in Section 3.3 should apply equally to this Section.

The accuracy of these rate constants needs comment; the value of k_2^I at 25° as seen in Figure 18 is closely represented by the line passing through the origin but the value of k_2^I at 35° and the values of k_2^{II} at 25° and 35° were determined by considering the arithmetical mean of $k'/(HOCl)_0$ and $V_{res}/(HOCl)_0^2$, respectively. This procedure is not to be generally recommended but was necessary here to eliminate either a concentration-independent term or a term involving the concentration of olefin alone. Both of these terms do not appear to have physical meanings.

The presence of products other than the simple chlorohydrins was found by Bloomfield et al. (11) and may provide an explanation of the abnormal deviations found with the rate equation for this olefinic acid. On the evidence of Bloomfield, the carbonium complex (or π -complex) formed by the initial attack of hypochlorous acid on the ethenoid centre could stabilize either by the formation of a chlorohydrin or suffer dehydration accompanied by decarboxylation yielding either, or both, of the isomers isocrotyl chloride (III) or methallyl chloride (IV) according to the reactions:



These reactive isocrotyl and methallyl chlorides should react with hypochlorous acid so that these resultant consecutive reactions possibly contribute to the discrepancies found in the derivation of this equation. All the olefins could also compete for chlorine monoxide formed in the equilibrium,



A comparison of the rate constants obtained for the reaction at 25° and 35° is shown in Table XXVI but in view of the approximations made above, these ratios and hence the activation energies must be treated with reserve.

TABLE XXVI

	k_2^I	k_2^{II}
25°	28.3 ₀	ca.11.7
35°	ca.52.0	ca.13.0
k_{35}/k_{25}	1.84	1.11
ΔE Kg.Cals	11.05	1.9

A comparison of the values of k_2^I obtained for $\beta\beta$ -dimethylacrylic acid with the values obtained for the other olefins investigated is given in Section 6.1

PART 5

THE ADDITION OF HYPOCHLOROUS ACID TO OTHER UNSATURATED
ACIDS AND ESTERS AT 25° IN BUFFERED SOLUTION.

5.1. Introduction.

In Parts 2, 3 and 4, we have been chiefly concerned with the effect of the position of a methyl group in relation to the double bond of an unsaturated acid on the rate of chlorohydrin formation. The compounds included in Part 5 were studied with a view to finding the effect of the carboethoxyl group and the effect of the location of the double bond in the acid on the rate of addition in buffered solution at 25°. Buffering was necessary as we have already seen that the pH had a marked effect on the rate of addition (see Section 2.3) and in the case of the three esters used in this Part, an external acetic acid-sodium acetate buffer of pH 4.74 was employed (cf. Israel (32); Reeve and Israel (24)).

Bloomfield et alia (11) found that $\alpha\beta$ -unsaturated esters yielded chlorohydrins much more easily than did the corresponding free acids. They found also that ethyl tiglate gave 50 per cent of each isomeric addition product indicating that the carboethoxyl group had no directive influence. There was, in fact, strong indication that the orienting influence of the carboxyl group was due entirely to the free charge on the organic anion, $R-CH=CR'-COO^-$, and was not directly connected with the carbonyl unsaturation or the direction of the dipoles present in the carboxyl and the carboethoxyl groups.

Reeve, in this Department, investigated the rate of addition of hypochlorous acid to ethyl crotonate (24) in the presence of an acetic acid-sodium acetate buffer of pH 4.74 at 25°

and derived the velocity equation,

$$V = k_2^I(\text{HOCl})(\text{EtR}) + k_3^{II}(\text{HOCl})^2(\text{EtR}) + k_3^{III}(\text{HOCl})(\text{HOAc})(\text{EtR}) \dots \text{Eqn. (5.1)}$$

where (EtR) is the concentration of ethyl crotonate.

$k_2^I(\text{HOCl})(\text{EtR})$ was interpreted as the rate of direct interaction of hypochlorous acid and ethyl crotonate,

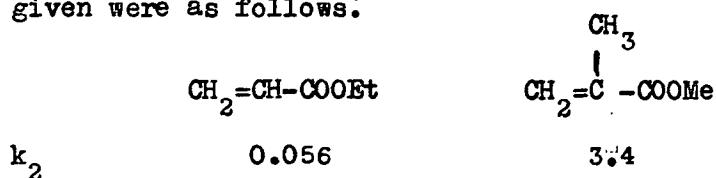
$k_3^{II}(\text{HOCl})^2(\text{EtR})$ as the rate of reaction of chlorine monoxide and the ester, and

$k_3^{III}(\text{HOCl})(\text{HOAc})(\text{EtR})$ as the rate of interaction of acetyl hypochlorite and the ester.

Unlike the reaction of hypochlorous acid with the unsaturated acids previously discussed, here the addition of the electrophilic reagent - hypochlorous acid, acetyl hypochlorite, and chlorine monoxide - and not its formation, was the rate determining step since all the terms in the velocity equation involved the concentration of ethyl crotonate.

Since the relative rates of addition of hypochlorous acid to crotonic and tiglic acids have been found, and the rate equation for ethyl crotonate established, the choice of ethyl tiglate for a kinetic investigation was an obvious one. Evans et alia (48) found that for the addition of chlorine in acetic acid solution at 25°, the rate constant, k_2 , increased 60-fold due to the presence of a methyl group in the α -position.

The values given were as follows:



They also stated that halogen addition to methyl and ethyl esters

of other unsaturated acids showed only slightly differing rates and for this reason the rate of chlorohydrin formation for methyl and ethyl acrylate was investigated, although not to any large extent.

In the past only compounds with $\alpha\beta$ -unsaturation have been used. In order to investigate kinetically the different rates of addition known to exist for the different positions of the double bond (10), the three pentenoic acids viz., 2-, 3-, and 4-pentenoic acids were chosen as suitable reactants. However, the tautomerism that existed between the 2- and 3-pentenoic acids led to some interesting conclusions culminating in a simple method being developed for the estimation of one tautomer relative to, and in the presence of the other.

5.2. Addition Reactions Involving Esters.

(a) Ethyl Tiglate:

B.D.H. tiglic acid (25 gm.) was dissolved in absolute alcohol (60 ml.) and concentrated sulphuric acid (1.8 ml.) added. This solution was refluxed for 18.5 hours and the ester extracted, dried with anhydrous magnesium sulphate and distilled under reduced pressure to give 19.3 gm. of crude ester (b.p. $70^{\circ}/35$ mm. (uncorr.)). This product was further dried with anhydrous sodium sulphate overnight and redistilled carefully to give a middle fraction b.p. $55^{\circ}/14$ mm. (cf. literature figures; $80.5-81.5^{\circ}/45$ mm., $55.5^{\circ}/11$ mm. from Heilbron).

An estimation of the solubility of ethyl tiglate in water at 18° showed that it would be about 0.3 per cent.

1.5632 gm. (0.0122 moles) were dissolved in distilled water and diluted to 1 litre, care being taken to wash the weighing bottle out with about 500 ml. of water during the transfer. This solution was well shaken and the pH after 12 hours was 5.49 showing that there was no appreciable hydrolysis. After three weeks the pH of this solution was 5.16 at 16°. A 0.01 molar solution was prepared later by dissolving 1.2817 gm of ethyl tiglate in 1 litre of solution. The pH of this solution after 48 hours was 5.16 and its strength was checked by saponification as follows: 15 ml. of 0.0258 N sodium hydroxide were added to 10 ml. of a 0.01 molar solution of ethyl tiglate and the mixture kept at 25° for 120 hours. The determination was carried out in duplicate and titration of the contents of each flask with 0.0180 N hydrochloric acid using a methyl red indicator gave titres of 16.00 and 16.20 ml. respectively. These corresponded to an ester solution of strength 0.0099 and 0.0096 molar which was slightly less than the amount weighed out. The end point was not sharp and an error of 0.1 ml. in the hydrochloric acid titre would account for this difference.

A stock acetic acid-sodium acetate buffer in which

$$(\text{HOAc}) = (\text{OAc}^-) = 0.02 \text{ moles litre}^{-1}$$

was prepared from A.R. acetic acid and A.R. sodium hydroxide solution. The pH of this solution measured at 18.5° was 4.72 compared with a calculated value of 4.74 (68).

The hypochlorous acid used in this investigation was a redistilled product from an 'aqueous' method preparation (see Section 2.1).

The experimental method used for these esters was described in Part 1. For ethyl crotonate, Reeve found that samples taken every half hour were sufficient as the reaction was very slow (the direct term for crotonic acid was 265 times the corresponding term for ethyl crotonate), but preliminary experiments with ethyl tiglate showed that although it was much slower than the free acid, samples taken every minute were found satisfactory and enabled the plot of the logarithm of the sodium thiosulphate titre to be extrapolated and the velocity data evaluated.

Experimental Results for Ethyl Tiglate.

Eleven Series A - K were studied at 25° and the results are shown in Table XXVII. The pH values recorded here were those measured between seven and eight minutes after the commencement of the reaction. The following units were adopted:

Concentration	:	moles litre ⁻¹
Velocity	:	moles litre ⁻¹ minute ⁻¹
Time	:	minutes

In the study of this reaction it was possible to vary the concentration of three reactants. To simplify the interpretation of the results, in each Series the initial concentration of two of the reactants were kept constant and the third reactant varied suitably.

TABLE XXVII

Run	(HOCl) _o	(EtR) _o	(HOAc) _o	V _o ^{obs}	pH
No.	x 10 ³	x 10 ³	x 10 ³	x 10 ⁵	
A1	2.02	0.61	2.00	0.91	4.66
A2	2.02	1.22	2.00	1.67	4.70
A3	2.01	1.83	2.00	2.23	4.66
A4	2.02	2.44	2.00	2.77	4.66
A5	2.02	3.05	2.00	3.37	4.65
B1	2.07	0.61	4.00	1.16	4.58
B2	2.07	1.22	4.00	2.23	4.56
B3	2.07	1.83	4.00	2.98	4.50
B4	2.07	2.44	4.00	3.86	4.55
B5	2.07	3.05	4.00	4.57	4.56
C1	2.04	0.61	6.00	1.32	4.69
C2	2.05	1.22	6.00	2.60	4.70
C3	2.03	1.83	6.00	3.29	4.65
C4	2.03	2.44	6.00	4.37	4.67
C5	2.04	3.05	6.00	5.38	4.70
D1	2.06	0.61	8.00	1.36	4.66
D2	2.06	1.22	8.00	2.75	4.64
D3	2.05	1.83	8.00	3.84	4.61
D4	2.05	2.44	8.00	5.07	4.63
D5	2.06	3.05	8.00	5.96	4.63
E1	2.06	1.83	1.00	2.24	4.63
E2	2.06	1.83	2.00	2.63	4.66
E3	2.06	1.83	3.00	2.93	4.62
E4	2.06	1.83	5.00	3.31	4.65
E5	2.05	1.83	6.00	3.58	4.65
F1	3.03	0.61	4.00	2.10	4.75
F2	3.02	1.22	4.00	4.07	4.70
F3	3.02	1.83	4.00	5.91	4.72
F4	3.02	2.44	4.00	7.57	4.73
F5	3.02	3.05	4.00	9.06	4.75
G1	2.99	0.61	6.00	2.04	4.75
G2	2.99	1.22	6.00	4.33	4.75
G3	2.99	1.83	6.00	6.15	4.74
G4	2.99	2.44	6.00	8.34	4.75
G5	2.99	3.05	6.00	9.72	4.75
H1	2.98	0.61	8.00	3.16	4.66
H2	2.98	1.22	8.00	5.15	4.69
H3	2.97	1.83	8.00	7.05	4.69
H4	2.96	2.44	8.00	8.63	4.67
H5	2.96	3.05	8.00	10.23	4.66

Table XXVII (contd.)

Run	(HOCl) _o	(EtR) _o	(HOAc) _o	V _o ^{obs.}	pH
No.	x 10 ³	x 10 ³	x 10 ³	x 10 ⁵	
I1	3.09	1.83	1.00	4.68	-
I2	3.07	1.83	2.00	5.09	-
I3	3.08	1.83	3.00	5.60	-
I4	3.08	1.83	4.00	6.25	-
I5	3.08	1.83	7.00	7.34	-
J1	4.03	0.50 *	6.00	3.18	4.67
J2	4.03	1.00	6.00	6.52	4.69
J3	4.03	1.50	6.00	8.58	4.67
J4	4.00	2.00	6.00	10.50	4.69
J5	4.00	2.50	6.00	12.86	4.70
K1	3.91	0.61	8.00	3.58	4.73
K2	3.89	1.22	8.00	6.63	4.75
K3	3.89	1.83	8.00	10.13	4.73
K4	3.89	2.44	8.00	12.73	4.72
K5	3.90	3.05	8.00	15.89	4.71

* A new stock solution of ester was used for this Series.

From this Table it can be seen that the concentration of hypochlorous acid had the most marked effect on the reaction rate while the effect of the acetic acid-acetate buffer was the least.

If an equation similar to that derived by Reeve and Israel (see equation 5:1) was applicable to ethyl tiglate, then the velocity should not only be a linear function of the ester concentration for constant initial hypochlorous acid and constant initial buffer concentrations, but also should be zero at zero ester concentration. Figure 23 shows the variation of velocity with ester concentration under these conditions, but although approximately linear plots were obtained, the lines did not pass through the origin.

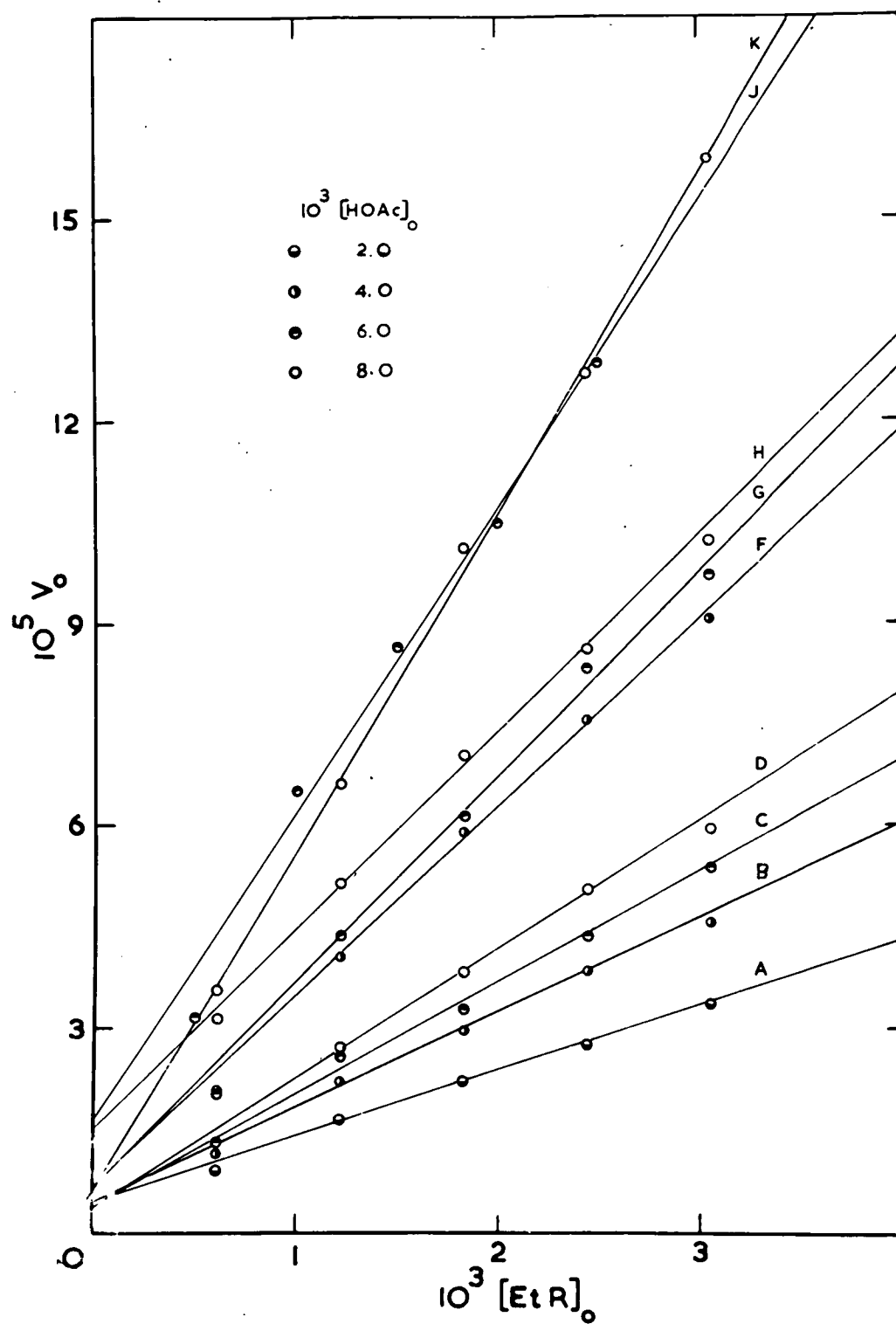


Figure 23

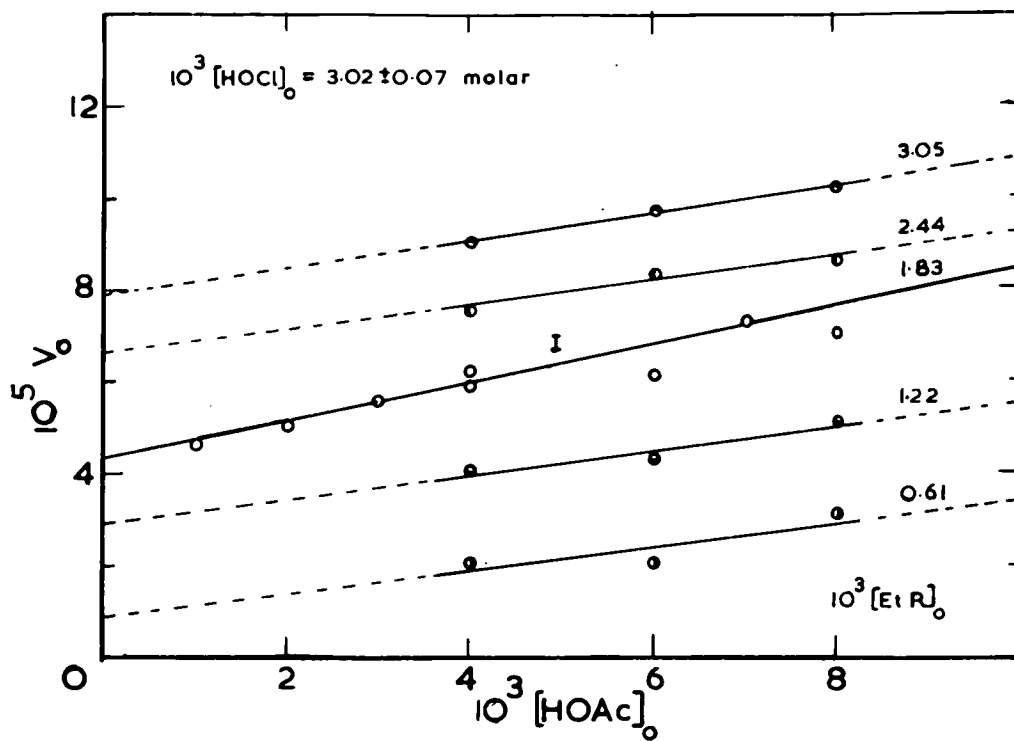


Figure 25

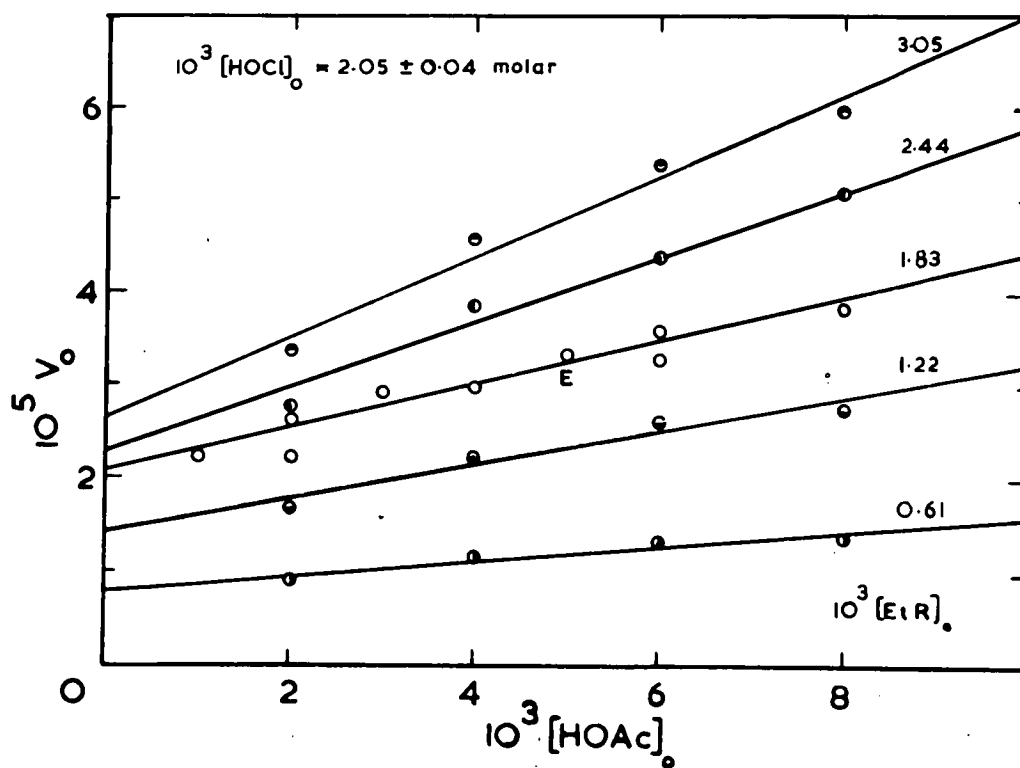


Figure 24

This was verified by the fact that the value of $V_0/(EtR)_0$ for constant initial hypochlorous acid and constant initial buffer concentrations decreased steadily with increasing ester concentration. The velocity equation must therefore contain at least one term independent of the ester concentration.

The E and I Series in which the concentration of hypochlorous acid and ethyl tiglate were both initially constant while the concentration of the acetic acid-acetate buffer was varied, were omitted from Figure 23 but are shown in Figures 24 and 25 respectively, where the initial velocity has been plotted against the initial concentration of acetic acid for constant initial hypochlorous acid and constant initial ester concentrations. The other four sets of points were plotted by suitably choosing data from Table XXVII assuming the initial hypochlorous acid concentrations were constant within the limits shown.

Figures 24 and 25 both show an approximately linear increase in velocity with increasing buffer concentration, but a comparison of these figures shows a steady increase in the slopes of the graphs with increasing ester concentration in Figure 24 while the slope is almost independent of the ester concentration in Figure 25. In this latter Figure, most of the graphs consist of only three points and it may be significant that the graph with the largest number of points (I Series) has a much greater slope than the other graphs.

In view of the poor reproducibility found using ethyl tiglate, the effect of light on the reaction was investigated

but found to be without effect in the early stages of the addition. A comparison of the results for a light and dark reaction is shown below:

	$(\text{HOCl})_0$ $\times 10^3$	$(\text{EtR})_0$ $\times 10^3$	$(\text{HOAc})_0$ $\times 10^3$	V_0 $\times 10^5$	pH at 6 mins.
Light	3.10	2.00	6.00	6.65	4.65
Dark	3.10	2.00	6.00	6.85	4.64

Titration with 0.00404 N sodium thiosulphate of a 10 ml. sample taken from the reaction flask after 17 hours at 25° , gave titres of 5.96 and 5.62 for the light and dark reactions respectively, although titres in the first six minutes differed by only 0.01 to 0.02 ml.

For the purpose of comparing the reactivity of ethyl tiglate with other olefins, it was desirable that an approximate rate equation should be developed. If the residual ~~term~~ velocity term was neglected, an equation similar to equation (5:1) was obtained by considering the mathematics of Figures 23, 24 and 25. The equation,

$$V_0 \approx 1.3 (\text{HOCl})_0 (\text{EtR})_0 + 2.2 \times 10^3 (\text{HOCl})_0^2 (\text{EtR})_0 + 6.6 \times 10^2 (\text{HOCl})_0 (\text{HOAc})_0 (\text{EtR})_0 \dots\dots\dots \text{Eqn. (5:2)}$$

was obtained but it should be emphasised that this equation was only approximate and errors of 25 per cent were possible. The only use of such an equation is to show, by comparing the rate constants of ethyl crotonate viz., 1.7×10^{-2} , 16.4, and 6.8 with the coefficients of the above equation in the order given, that ethyl tiglate is about 100 times more reactive than ethyl

crotonate towards hypochlorous acid at 25° in the presence of an acetic acid-acetate buffer of pH 4.72.

Further deductions from this equation would not be justified and additional work on ethyl tiglate was limited to attempts at increasing the reproducibility of results by using the other methods of following the addition process (see Part 1). These, as mentioned earlier, were of no use.

(b) Ethyl Acrylate:

Ethyl acrylate (Light and Co.) was dried with anhydrous magnesium sulphate for three days and distilled under reduced pressure using ice-cooled water in the condenser. A middle fraction, b.p. $46-47^{\circ}/100$ mm. (uncorr.), was collected and used for the preparation of a stock solution. A literature figure (69) for the boiling point was $44.5^{\circ}/100$ mm.

A test of the solubility in water of this ester showed that it was about 1 per cent at 19° . 0.04 moles were dissolved in distilled water, care being taken to remove all the ester from the weighing bottle by washing with about 600 ml. of water, and the solution diluted accurately to one litre. The pH of this stock solution after 2.5 hours was 5.98 at 17° . After 20 hours the pH was 5.90 and this figure indicated that hydrolysis was less than 0.0001 per cent.

The strength of this 0.04 molar ethyl acrylate solution was checked by saponification at 25° for 110 hours in a similar manner to that described for ethyl tiglate. Using the mean value of the hydrochloric acid titre, the strength of the ester

solution was calculated to be 0.0398 molar.

An acetic acid-sodium acetate buffer in which

$$(\text{HOAc}) = (\text{OAc}^-) = 0.02 \text{ moles litre}^{-1}$$

was prepared from A.R. acetic acid and an A.R. sodium hydroxide solution. The hypochlorous acid used in the three series of this investigation was prepared by an 'aqueous' method and diluted suitably.

Experimental Results:

Only three series were investigated for this ester as the reaction proved very slow even after increasing the concentrations of all the reactants to far beyond the range used for the olefinic acids described earlier. 10 ml. samples were taken from the reaction flask after 15, 45, 75, 150, and 210 minutes respectively and an examination of the titres showed that after 150 minutes, the hypochlorous acid concentration had decreased by only about 1 per cent in most of the runs. For example, in A3 the following data was obtained:

Time (min.)	0	15	45	75	150	210
Titre (ml.)	21.48	21.46	21.40	21.39(?)	21.30	21.21

These titres were for a 10 ml. sample taken from the reaction flask and titrating^{ed} with 0.00286 N sodium thiosulphate.

The experimental results are given in Table XXVIII but as the difference in the titres of successive samples was very small, the velocity results can only be regarded as approximate. The pH values listed in this Table are those measured 215 minutes

after the reaction had started, but this value seemed constant throughout the course of the reaction.

TABLE XXVIII

Run No.	(HOCl) ₀ x 10 ³	(EtR) ₀ x 10 ³	(HOAc) ₀ x 10 ³	V ₀ x 10 ⁷	pH
A1	3.07	6.00	4.00	2.2	4.70
A2	3.07	6.00	5.00	2.5	4.70
A3	3.07	8.00	4.00	1.6	4.70
A4	3.07	10.00	4.00	3.7	4.71
A5	3.83	7.50	3.75	2.3	4.70
B1	6.44	8.00	2.00	4.9	4.64
B2	6.44	8.00	3.00	4.5	4.64
B3	6.41	8.00	4.00	4.4	4.66
B4	6.41	8.00	5.00	4.5	4.64
B5	6.43	8.00	6.00	5.1	4.65
C1	10.32	20.00	4.00	18.8	4.61
C2	10.30	20.00	5.00	18.1	4.62
C3	10.28	20.00	6.00	17.8	4.60
C4	10.28	20.00	7.00	17.4	4.62
C5	10.30	16.00	9.00	13.8	4.63

where the concentrations are expressed in moles litre⁻¹, the velocity in moles lit.⁻¹ min.⁻¹, and R = CH₂=CH-COO.

The following points were noted from an examination of Table XXVIII:

(i) The rate of the addition reaction was practically independent of the acetic acid-sodium acetate buffer concentration. A small decrease in the velocity with increasing buffer concentration was noticed in runs B1-B3 and C1-C4.

(ii) A comparison of C4 and C5 showed that the initial velocity was proportional to the initial ester concentration.

(iii) Provided points (i) and (ii) are satisfied, a comparison of all three series indicated that the initial velocity was proportional to the initial hypochlorous acid concentration.

Summing up, it seems likely that the reaction between hypochlorous acid and ethyl acrylate at 25° conformed to the simple bimolecular reaction,

$$V_o = k_2(\text{HOCl})_o(\text{EtR})_o \dots\dots\dots \text{Eqn. (5.3)}$$

where k_2 decreases slightly with increasing buffer concentration.

The rate constant k_2 was calculated for the three series and the values obtained are shown in Table XXIX.

TABLE XXIX

Run No.	$k_2 \times 10^3$	Run No.	$k_2 \times 10^3$
A1	12	B4	9
A2	14	B5	10
A3	7		
A4	12	C1	9
A5	8	C2	9
		C3	9
B1	10	C4	8
B2	9	C5	8
B3	9		
<u>Mean value of k_2 = 9×10^{-3} lit.mol.⁻¹min.⁻¹</u>			

This value of k_2 , although only approximate, does serve as some measure of the rate of direct interaction of hypochlorous

acid with ethyl acrylate and a comparison of this value with the value of k_2^I obtained by Reeve et al. (24) viz., 0.017 lit.mol.⁻¹ min.⁻¹, for ethyl crotonate shows that the presence of a methyl substituent roughly doubles the contribution of the direct attack term.

In an aqueous acetic acid-sodium acetate medium, the stabilisation of the carbonium ion formed in the initial attack may occur by the addition of either a hydroxyl or an acetate ion. Stabilisation by the latter mechanism could account for the decrease in k_2 noticed for high concentrations of buffer. Reeve (24, 25) reported a decrease in the value of the rate constant k_3^{II} (see Equation 5:1) with increasing buffer concentration and he attributed this decrease to the smaller concentration of acetyl hypochlorite available as an active electrophilic reagent due to the possible formation of an α -chloro- β -acetoxy derivative. That these intermediate cations are capable of combinations with any available anion has been demonstrated by Francis (71).

(c) Methyl Acrylate:

Methyl acrylate (Light and Co.) was allowed to stand over anhydrous magnesium sulphate for two weeks. Examination of the literature showed that methyl acrylate was only slightly soluble in water and that it polymerised at its boiling point of 80.5°. It was necessary, therefore, to distil at a lower temperature under reduced pressure and by plotting the vapour pressure-temperature results available (70) in the usual Clausius-Clapeyron manner, 200 mm. Hg. was chosen as a suitable pressure

for distillation. Distillation in an all-glass apparatus using ice-cooled condenser water gave a middle fraction, b.p. 42.0 - 42.5°/186 mm. (uncorr.) and this compared favourably with the figure of 43.5°/186 mm. obtained from the above graph.

As estimation of the solubility of methyl acrylate in water showed that it was about 2.5 per cent and a 0.08 molar stock solution was prepared in a similar manner to that described for the ethyl ester. The pH of this solution after 15 hours was 5.75, indicating negligible hydrolysis.

The strength of the solution was checked by saponification at 25° for 100 hours and the mean of duplicate experiments returned the value of 0.079 molar.

The same stock buffer and hypochlorous acid solutions were used for this ester as for ethyl acrylate.

Experimental Results:

Only one run was carried out for this ester as the results showed that it was an even slower addition reaction than in the case of the ethyl ester and hence reproducible results would be difficult to obtain. The results of this run are shown in Table XXX.

TABLE XXX

Initial pH = 4.73		Temperature = 25 ± 0.01°.		
Run	(HOCl) ₀	(MeR) ₀	(HOAc) ₀	V ₀
No.	x 10 ³	x 10 ³	x 10 ³	x 10 ⁷
A1	10.11	20.00	5.00	4.9

where the units and symbols have the same values as reported in Table XXVIII.

A comparison of this run with C2 for ethyl acrylate shows that the ethyl ester is more reactive than the corresponding methyl ester. It was felt that a more detailed study of this ester would not be profitable.

5.3. Addition Reactions Involving Pentenoic Acids.

(a) 2- and 3-pentenoic acids:

Because of the 3-carbon tautomerism that exists between γ -substituted butenoic acids (72), and the cis-trans isomerism possible for each tautomer, the properties of the 2- and 3-pentenoic acids recorded in the literature are often confused.

2-pentenoic acid has been reported to melt at 7° (73), at 9.5-10.5° (74), and at 10° (75), 3-pentenoic acid has been reported to crystallise in flat needles at 1° (76). Recently Evans et alia (48) separated these isomers by the Sudborough and Thomas method of partial esterification (73). These latter authors found that the $\alpha\beta$ -double bond had a retarding effect on the rate of esterification and a comparison of the esterification rate constants showed that the 3-pentenoic acid was esterified at 15° by methanol nearly 50 times faster than 2-pentenoic acid (77). However, it has been reported (78) that the purification of these acids beyond a certain point had no appreciable effect on the velocity of interconversion and, provided any mineral impurity was eliminated, the change was definite and at a reproducible rate.

Before the preparation of 2-pentenoic acid was attempted,

the vapour pressure-temperature data given in Table XXXI was collected. The term 'graph' in the reference column means that these values have been obtained graphically from a plot of the vapour pressure-temperature data available.

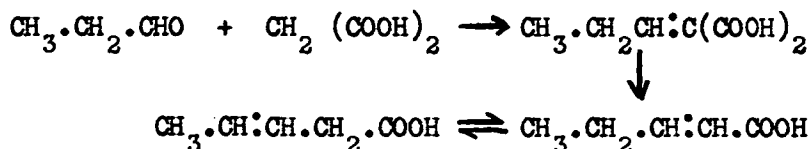
TABLE XXXI

	<u>Temperature °C</u>	<u>Vap.Press.mm.Hg.</u>	<u>Reference</u>
(i) 2-pentenoic acid	199-202	760	74
	105	19	79
	108	17	48
	108	17	80
	100-102	13.5	81
	99	10	80
	73	2.5	graph
	71	2	80
	62-66	1.5	75
	60	1	graph
(ii) 3-pentenoic acid	193	760	82
	192-193.5	760	73
	191-192	747	65
	98	19	79
	94-96	17	83
	94	16	80
	90	10	34
	45	1	graph

Preparation of 2-Pentenoic Acid.

Propionaldehyde (180 gm.), malonic acid (150), pyridine (150 ml.) and piperidine (0.7 ml.) were added in that order to a one litre flask fitted with a reflux condenser (cf. 79). Some heat was evolved together with a lot of frothing and loss of the volatile aldehyde was prevented by cooling the flask in an ice-bath. It was later transferred to the refrigerator for 50 hours at 5° after which it was allowed to stand at room temperature for 5.5 hours before refluxing gently for one hour.

Distillation was carried out up to 145° to remove as much of the volatile solvents as possible and to partially decarboxylate the condensation product.



The remaining viscous, sickly smelling liquid was extracted with 10 per cent sodium carbonate and washed with ether. The acid was then liberated with concentrated hydrochloric acid, extracted with ether and dried for 48 hours with anhydrous magnesium sulphate. This etheral extract was distilled at atmospheric pressure up to 45° and then under reduced pressure using a small Dufton column. The main portion of the middle fraction distilled at $75^{\circ}/2.5$ mm. but the range $71-77^{\circ}/2.5$ mm. was collected at this stage and amounted to 73 gm. (Yield : 51 per cent). The refractive index for this fraction was $n_D^{20} = 1.4476$ while the final fraction was $n_D^{20} = 1.4507$.

As the vapour pressure-temperature curves for two acids in Table XXXI diverge at low pressures, the crude pentenoic acid obtained above was redistilled in an all-glass apparatus and 15 ml. of a middle fraction b.p. $60-62.5^{\circ}/1$ mm.; $n_D^{20} = 1.4430$ was collected. This 15 ml. fraction was again distilled and a main fraction b.p. $60-61^{\circ}/1$ mm.; $n_D^{20} = 1.4460$ collected; cf. $n_D^{20} = 1.4513$ (84). Attempts to crystallize this product failed at temperatures as low as -15° .

This acid, presumably 2-pentenoic acid by a comparison with Table XXXI, was soluble to the extent of 2.5 per cent in

water at 20° and a 0.1 N solution was prepared by dissolving 5.0055 gm. in distilled water and diluting accurately to 500 ml. The pH of this solution was 2.93 at 21°. A neutralisation curve was plotted using a Leeds and Northrup pH meter standardised at 4.00 and the ionic strength at the point of half neutralisation was less than 0.01. The pH at this point was 4.60 whence $K_a = 2.51 \times 10^{-5}$ at 19°. The buffer capacity at pH 4.73 would be high according to this neutralisation curve.

The following values of the dissociation constants have been reported:

	$K_a \times 10^5$	pK_a	Reference
(i) <u>2-pentenoic acid</u>			
	2.02	4.69	(34)
	1.48	4.83	(85)
(ii) <u>3-pentenoic acid</u>			
	3.11	4.51	(34)
	3.35	4.48	(85)

Because of the variable figures for the dissociation constant, and the uncertainty as to the absolute constitution of the 2-penten^{ic} acid prepared above, a 0.04 molar stock buffer solution was prepared by adding 77.30 ml. of 0.414 N sodium hydroxide to 200 ml. of 0.1 N pentenoic acid solution to give a final pH of 4.73. This solution was diluted accurately to 500 ml. whence,

$$\begin{aligned} (\text{RCOOH}) + (\text{RCOO}^-) &= 0.0400 \text{ moles litre}^{-1} \\ (\text{RCOO}^-) &= 0.0226 \text{ moles litre}^{-1} \end{aligned}$$

where R = $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}:\text{CH}.$ or $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CH}_2.$ or both.

The hypochlorous acid used in this investigation was prepared by the 'aqueous' method.

Experimental Results and Discussion.

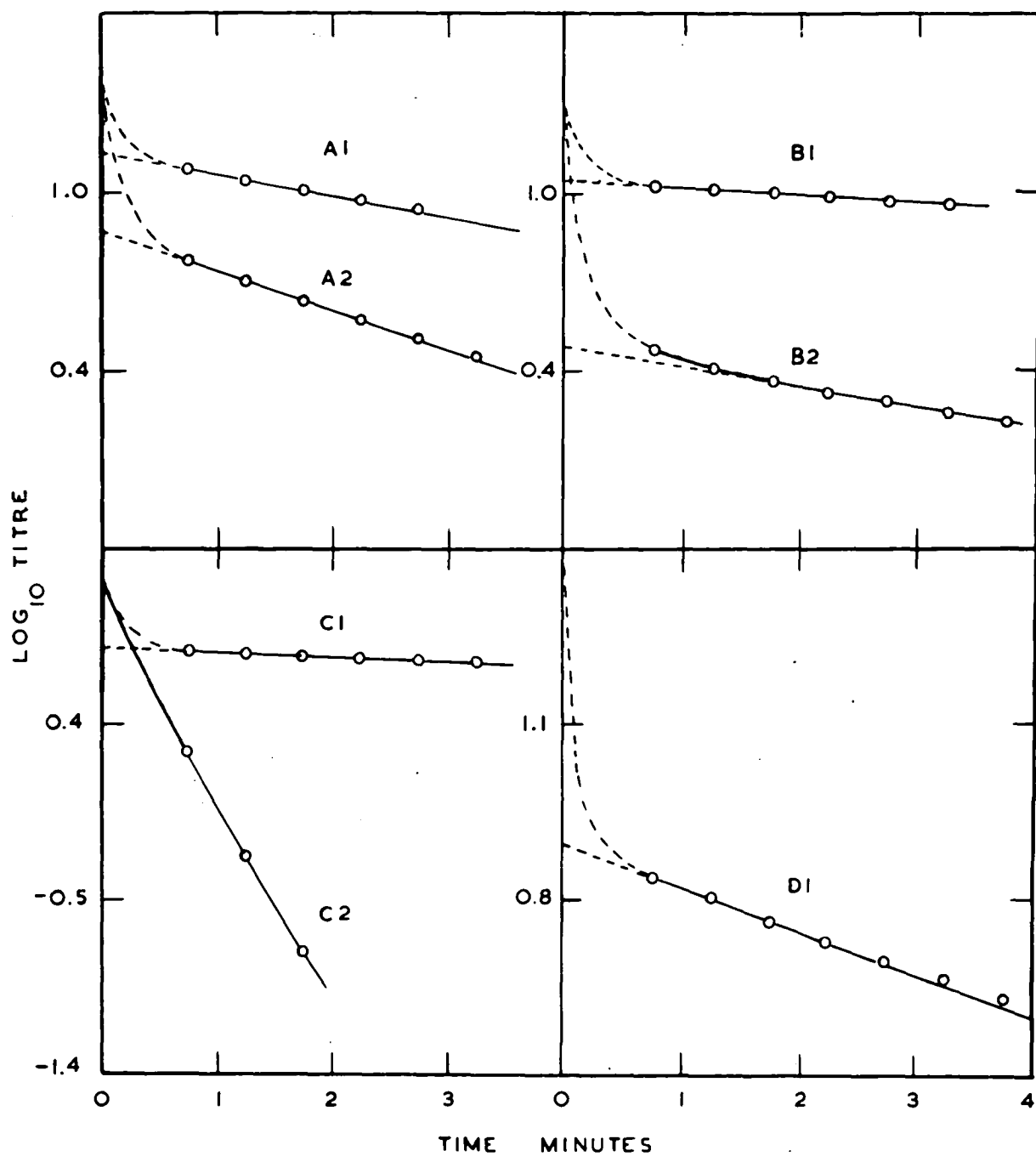
This investigation was divided into four Series A - D shown graphically in Figure 26 in which the logarithm of the sodium thiosulphate titre for a 10 ml. sample has been plotted against the time of reaction. The results obtained from these graphs together with the known initial conditions are given in Table XXXII.

TABLE XXXII

Initial pH = 4.73		Temperature = $25 \pm 0.01^\circ$			
Run	$(\text{HOCl})_0^{\text{Theor.}}$	$(\text{HOCl})_0^{\text{Extra}}$	$(\text{RCOOH})_0 + (\text{RCOO}^-)_0$	$V_0^{\text{obs.}}$	pH
No.	$\times 10^3$	$\times 10^3$	$\times 10^3$	$\times 10^5$	
A1	3.29	1.69	4.00	29.3 _a	4.60
A2	3.29	0.95	6.00	31.6	4.74
A3	3.29	<u>b</u>	10.00	<u>b</u>	4.82
B1	1.90	1.11	2.00	6.7	4.74
B2	1.90	0.30	4.00	4.8	4.83
C1	1.43	0.64	2.00	3.7	4.80
C2	1.43	1.43 <u>c</u>	4.00	386. <u>c</u>	4.84
D1	2.38	0.80	4.00	13.8	4.76

a : The observed velocities reported in this column are the values calculated from the straight lines shown extrapolated in Figure 26 and apply to 2-pentenoic acid.

b : In this case, extrapolation was impossible and hence neither the velocity nor the extrapolated hypochlorous acid concentration could be obtained as all the hypochlorous acid was consumed in

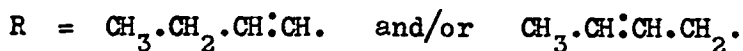


A Series $[\text{Na}_2\text{S}_2\text{O}_3] = 0.00245 \text{ N}$
 B, C & D " " = 0.00201 N

Figure 26

about one minute after the reaction was started.

c : This velocity, as explained later, applies to the addition of hypochlorous acid to 3-pentenoic acid.



$(\text{HOCl})_0^{\text{Th.}}$ is the value of the initial hypochlorous acid concentration as prepared for the reaction.

$(\text{HOCl})_0^{\text{Ex.}}$ is the value of the initial hypochlorous acid concentration obtained from the extrapolation of the curves in Figure 26.

As soon as the samples for A1 were titrated and the log titre vs. time graph plotted, it was realised that the initial hypochlorous acid concentration obtained by extrapolating the graph to zero time was only about half the expected value. A similar behaviour was observed in A2, while in A3, 99.5 per cent of the hypochlorous acid had reacted 0.75 minutes after the reaction had started and further samples from the flask failed to liberate any iodine from an acidified potassium iodide solution. For this reason, A3 is omitted from Figure 26.

It was concluded, therefore, that there must have been some 'impurity' present in the 2-pentenoic acid that reacted very quickly with the hypochlorous acid. Any hypochlorous acid remaining after this initial rapid addition would continue to react with 2-pentenoic acid in the normal way at a rate comparable with the other olefinic acids. This 'impurity' was presumably 3-pentenoic acid as it is well known that $\beta\gamma$ -olefinic acids react much faster with electrophilic reagents than their $\alpha\beta$ -analogues (10, 48, 79, 86, 87).

The B Series was of a similar pattern to the A Series and deserves no comment at this stage.

The C Series, however, warrants discussion. C1 was orthodox compared with the A and B Series but C2 was a very fast, but measurable, reaction. Evidently in this run, the amount of 3-pentenoic acid (assuming that this is the reactive agent) was greater than the initial hypochlorous concentration. Thus at no stage of the reaction would all this isomer be consumed and the log titre vs. time curve (Figure 26) would represent the rate of addition of hypochlorous acid to 3-pentenoic acid together with a comparatively small contribution from the rate of addition to 2-pentenoic acid.

D1 was similar to the runs of the A and B Series and was used to provide a different initial hypochlorous acid concentration for the purpose of calculating the percentage of 3-pentenoic acid in a mixture of these tautomers. (see later).

We have now discussed the runs separately, but no overall description of the reaction has been given. Any analysis of the results must be applied to the additions separately.

Consider the addition of hypochlorous acid to 2-pentenoic acid. The effective concentration of hypochlorous acid i.e. the concentration of hypochlorous acid remaining after portion of it had reacted with 3-pentenoic acid, the actual concentration of 2-pentenoic acid present in the reaction medium, and the velocity of this reaction are given in Table XXXIII.

TABLE XXXIII

Run	(HOCl) _o	(Pent.) _o	V _o	V _o /(HOCl) _o	V _o /(Pent.) _o
No.	x 10 ³	x 10 ³	x 10 ⁵	x 10 ²	x 10 ²
			obs. calc.		
C1	0.64	1.21	3.7 3.9	5.8	3.1
B1	1.11	1.21	6.7 6.7	5.0	5.5
B2	0.30	2.42	4.8 5.2	16.0	2.0
D1	0.80	2.42	13.8 13.9	17.3	5.7
A1	1.69	2.42	29.3 29.3	17.3	12.1
A2	0.95	3.62	31.6 32.0	33.3	9.0

where (Pent.)_o refers to the total initial concentration of 2-pentenoic acid and its ion in the solution.

The derivation of a velocity equation from such a small number of results necessitated a different treatment from the methods used previously. As seen in Table XXXIII, V_o/(HOCl)_o increased with increasing olefin concentration and was constant for constant values of the olefin concentration. This increase was found graphically to be non-linear and probably of the form,

$$V_o(\text{HOCl})_o = k_a \left\{ (\text{RCOOH})_o + (\text{RCOO}^-)_o \right\} + k_b \left\{ (\text{RCOOH})_o + (\text{RCOO}^-)_o \right\}^2 \dots\dots \text{Eqn. (5.4)}$$

where the concentrations of both reactants may vary.

A plot of V_o/ { (RCOOH)_o + (RCOO⁻)_o } against (HOCl)_o for constant olefin concentration showed that in the case of C1 and B1 on the one hand, and B2, A1 and D1 on the other, straight lines could be drawn through their co-ordinates and the origin. By analogy with these findings, a line was drawn through the co-ordinates

of A2 and the origin and the slopes of all three lines evaluated.

Let the equation to these lines be

$$V_o / \left\{ (\text{RCOOH})_o + (\text{RCOO}^-)_o \right\} = k (\text{HOCl})_o \dots\dots\dots \text{Eqn. (5:5)}$$

where $\left\{ (\text{RCOOH})_o + (\text{RCOO}^-)_o \right\}$ is constant for any one value of k .

Table XXXIV shows the values of the slopes obtained.

TABLE XXXIV

k (lit.mol. ⁻¹ min. ⁻¹)	$(\text{RCOOH})_o + (\text{RCOO}^-)_o$ $\times 10^3$
50	1.21
71	2.42
94	3.62

An examination of Table XXXIV gave the variation of k with olefin concentration as

$$k = 28 + 18 \times 10^3 \left\{ (\text{RCOOH})_o + (\text{RCOO}^-)_o \right\} \dots\dots\dots \text{Eqn. (5:6)}$$

Combining equations (5:5) and (5:6) we obtain

$$V_o = 28 (\text{HOCl})_o \left\{ (\text{RCOOH})_o + (\text{RCOO}^-)_o \right\} + 18 \times 10^3 (\text{HOCl})_o \left\{ (\text{RCOOH})_o + (\text{RCOO}^-)_o \right\}^2 \dots\dots\dots \text{Eqn. (5:7)}$$

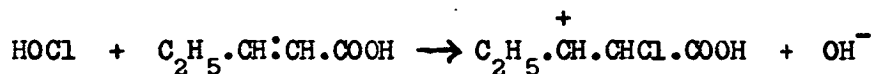
This equation is in agreement with equation (5:4) and the initial velocities calculated using equation (5:7) are in close agreement with the observed initial velocities as may be seen from Table XXXIII.

Equation (5:7) may be represented by the general kinetic equation,

$$V = k_2^I (\text{HOCl}) \left\{ (\text{RCOOH}) + (\text{RCOO}^-) \right\} + k_3^I (\text{HOCl}) \left\{ (\text{RCOOH}) + (\text{RCOO}^-) \right\}^2 \dots\dots\dots \text{Eqn. (5:8)}$$

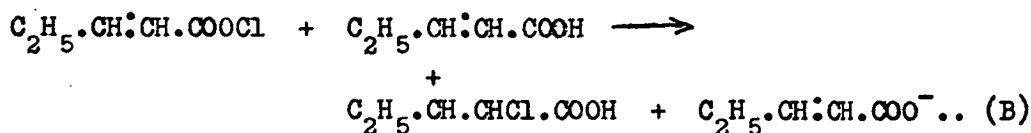
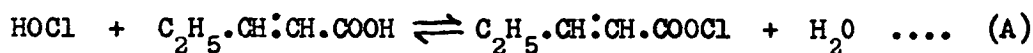
k_2^I is interpreted as the rate constant for the direct attack of

hypochlorous acid on the double bond according to the equation



The ion is expected to react similarly.

k_3^I may be interpreted as the rate constant for the addition of 2-pentenoyl hypochlorite to 2-pentenoic acid (or its ion), the stages of this process being represented by the equations



If equation (A) is an equilibrium with constant K,

$$K = (\text{C}_2\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COOCl})/(\text{HOCl})(\text{C}_2\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COOH})$$

and hence the velocity of the rate determining equation (B), is given by

$$\begin{aligned} V &= k'(\text{C}_2\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COOCl})(\text{C}_2\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COOH}) \\ &= k'K(\text{HOCl})(\text{C}_2\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COOH})^2 \end{aligned}$$

or since the pH is constant

$$(\text{C}_2\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COO}^-)/(\text{C}_2\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COOH}) \text{ is constant and}$$

$$V = k_3^I (\text{HOCl}) \{ (\text{RCOOH}) + (\text{RCOO}^-) \}^2$$

Neither the addition nor the formation of chlorine monoxide appears to be rate determining as there is no indication of a term involving $(\text{HOCl})^2$. However, it must be remembered that this derivation is based on a limited amount of kinetic data, and a too-detailed analysis of the results may not be justified.

We now consider the rate of addition of hypochlorous acid to 3-pentenoic acid. Run C2 has an effective hypochlorous acid concentration of 1.43×10^{-3} molar and a 3-pentenoic acid concentration of 1.58×10^{-3} molar. A comparison of the observed velocity of this reaction with the velocity for the corresponding 2-pentenoic acid reaction using these concentration figures in equation (5.7), showed that 3-pentenoic acid reacted 30 times faster than 2-pentenoic acid. However, this is the only comparison that can be made from the available data. Linstead (87) investigated the rate of addition of bromine to 1/60 molar solutions of these unsaturated acids at 25° and found that the $\beta\gamma$ -isomer reacted from 10 to 100 times faster than the $\alpha\beta$ -isomer.

One important point viz. the calculation of the percentage of 3-pentenoic acid present in a mixture of these isomers, remains to be considered. We have already seen that 3-pentenoic acid reacted 30 times faster than 2-pentenoic acid, and hence the difference between the theoretical and the extrapolated hypochlorous acid concentrations seen in Table XXXII and Figure 26 can be attributed without serious error, solely to its rapid addition to the more reactive isomer. Thus the ratio of this difference to the total initial olefin concentration should afford a measure of the 3-pentenoic acid content of the stock buffer solution. This ratio has been evaluated and is given in Table XXXV.

TABLE XXXV

Run No.	$\frac{(\text{HOCl})_0^{\text{Th.}} - (\text{HOCl})_0^{\text{Ex.}}}{(\text{RCOOH})_0 + (\text{RCOO}^-)_0} \times 100 \text{ per cent}$
A1	40.0
A2	39.0
A3	> 33
B1	39.5
B2	40.0
C1	39.5
C2	> 36
D1	39.5
<u>Mean value:</u>	39.6 per cent

The constancy of this percentage is independent of both the initial hypochlorous acid and the initial total olefin concentrations and shows that the stock solution of '2-pentenoic acid' was in fact a tautomeric mixture of the 2- and 3-pentenoic acids, the former to the extent of 60.4 per cent and the latter, 39.6 per cent. Evidently there had been sufficient time for the establishment of equilibrium in the stock solution as its composition was independent of the time at which it was used in the above investigation. This figure of 60.4 per cent is in close agreement with values of the equilibrium ratio reported by other workers. Goldberg and Linstead (79) carried out analyses of these equilibrated acids and found that 2-pentenoic acid comprised 75 per cent of the isomeric mixture. Later Linstead and Noble (78) reported that the 2- and 3-pentenoic acids had attained equilibrium after digestion with 25 per cent potassium hydroxide at 100° for eight hours.

2-pentenoic acid was present to the extent of 68 per cent in this solution. More recently, Ives and Kerlogue (75) found that 2-pentenoic acid existed as 62 percent of the equilibrium mixture of 2- and 3-pentenoic acids. They used the method of Linstead and Nobel^{le} with a modification to improve the recovery of the isomers, especially the more volatile 3-pentenoic acid.

Methods of Estimating Mixtures of Isomeric Unsaturated Acids.

Sudborough and Thomas (86) suggested that the markedly different rates of addition of bromine to $\alpha\beta$ - and $\beta\gamma$ -unsaturated acids could be used to determine the position of the double bond. The quantitative estimation of mixtures of isomeric unsaturated compounds was investigated by Linstead (87) using a bromine addition method. The principle of this method was that the composition of a mixture of $\alpha\beta$ - and $\beta\gamma$ -isomerides could be determined by comparing the velocity of addition of halogen to it with the velocity of addition to one of the pure substances. Later, Goldberg and Linstead (79) determined the iodine numbers of samples of concentration M/300 ten minutes after the reaction was started and used these values for estimating the percentage of the $\alpha\beta$ -unsaturated acid present.

These methods suffer from several disadvantages. They require pure isomers for calibration purposes and involve the use of halogens which, from the practical viewpoint, are more difficult to handle than hypochlorous acid.

The present kinetic study of the addition of hypochlorous

acid to the pentenoic acids suggests the following useful method of estimating an $\alpha\beta$ -unsaturated isomer in the presence of its $\alpha\beta\gamma$ -analogue. The following points should be noted in connection with this method:

(i) The concentrations of the two reactants, hypochlorous acid and the isomeric mixture, should be about 0.001 molar so that addition to the $\alpha\beta$ -isomer is not rapid enough to interfere with the simultaneous faster addition to the $\beta\gamma$ -isomer.

(ii) The initial hypochlorous acid concentration, $(\text{HOCl})_0^{\text{Th.}}$; must be determined and must exceed the concentration of the $\beta\gamma$ -isomer so that after the rapid addition there is sufficient hypochlorous acid remaining to continue reacting with the $\alpha\beta$ -isomer. It is suggested that in the absence of an approximate estimate of the concentration of the $\beta\gamma$ -isomer, the initial hypochlorous acid concentration should be equal to the combined total olefin concentration. If the approximate composition of the isomeric mixture is known, then greater accuracy can be achieved by making the hypochlorous acid concentration about ten per cent greater than the concentration of the reactive isomer.

(iii) These reactants are now mixed, and four samples taken at minute intervals delivered into acidified potassium iodide according to the method described in Part 1.

(iv) The plot of the logarithm of the sodium thiosulphate titre for each sample against the time of sampling is extrapolated to zero time; this gives the initial extrapolated hypochlorous acid concentration, $(\text{HOCl})_0^{\text{Ex.}}$. The difference between this

value and the theoretical initial hypochlorous acid concentration, will be equal to the amount of $\beta\gamma$ -isomer present. The ratio,

$$\frac{(\text{HOCl})_0^{\text{Th.}} - (\text{HOCl})_0^{\text{Ex.}}}{(\text{T.O.})_0} \times 100$$

where $(\text{T.O.})_0$ represents the total olefin concentration initially present, ^{of the} is equal to the percentage $\beta\gamma$ -isomer in the presence of the $\alpha\beta$ -isomer. The accuracy of the method has already been demonstrated in Table XXXV.

This method does not require a pure isomer and the results are both quick to obtain and simple to interpret. Linstead and May (88) used a similar method for the analysis of mixtures of isomeric acids which were inseparable to a pure form by an iodometric method using a convenient iodine-containing solution such as Wijs or Hanus solutions.

In an endeavour to check this figure of about 60 per cent for the amount of 2-pentenoic acid present in the stock solution, an independent method for its estimation was sought. It was thought that these acids may be separable polarographically as this means has been used for the determination of $\alpha\beta$ -unsaturated esters in the presence of $\beta\gamma$ -unsaturated isomers, (89). A comprehensive literature search did not reveal any polarographic determinations applied to the pentenoic acids although it was suggested (89, 90) that acids (or esters) containing a carboxyl (or carboethoxyl) group conjugated with a double bond were reducible.

If, as suspected 3-pentenoic acid was not reducible, then only one polarographic step would be obtained and a pure sample of 2-pentenoic acid would be necessary for the evaluation of the diffusion coefficient in the Ilkovic equation. If two steps were obtained, the ratios of the diffusion currents could be taken as the ratio of the concentrations by assuming ^{that} the diffusion coefficients for these acids were the same.

Three solutions were prepared each containing 0.1 molar potassium chloride as the supporting electrolyte. Table XXXVI summarises the results of this polarographic investigation using a Tinsley Type S10600 polarograph.

TABLE XXXVI

Temperature = 25°			$m^{2/3} t^{1/6} = 1.91 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$		
Sample No.	pH Theor.	pH Act.	Olefinic Acid Conc. $\times 10^3$	Mean Half-Wave Potential Volts	Mean Diffusion Current $\mu\text{A.}$
1 *	4.73	4.67	1.6	-1.77	2.0
2 *	4.73	4.65	4.0	-1.83	5.5
3	4.73	4.64	4.0	-1.88	5.8

* These samples contained 0.015 per cent gelatin as maximum suppressor but this was found to be unnecessary.

Only one step was found before the cathodic reduction potential of the sodium ions present was reached (-2.15 volts). Thus if separate steps do occur for these acids, and this is doubtful in view of earlier comments, their half wave potentials must be close enough to give superimposed waves i.e. within 0.2 volts.

In the absence of pure isomers, this polarographic investigation was not pursued further. It is possible, however, to report that an aqueous solution of 2- and 3-pentenoic acids buffered by their sodium salts to a pH of 4.73 exhibits a half-wave potential in the vicinity of -1.83 volts at 25° .

(b) 4 -Pentenoic Acid.

4-pentenoic acid (Light and Co.) was redistilled under reduced pressure and three fractions collected although there was very little difference in their boiling points. They were all in the range $46-48^{\circ}/1-2$ mm. and refractive index measurements of these samples were identical viz., $n_D^{17} = 1.4315$. Beilstein reported $n_D^{7.5} = 1.4341$, and boiling points $82-83^{\circ}/9.5$ mm. (91), and $90-92^{\circ}/16-17$ mm. were obtained from the literature. Extrapolation of these vapour pressure-temperature figures to low pressures gave the values, $41^{\circ}/1$ mm. and $53^{\circ}/2$ mm. . The solubility of this acid in water was found to be about 2 per cent at 17° .

A 0.1 molar stock solution of 4-pentenoic acid was prepared by dissolving 5.0055 gm. of the middle fraction of the above distillation in water and diluting accurately to 500 ml. . 10 ml. of this solution was titrated potentiometrically at 16° using a Leeds and Northrup pH meter with a 0.0349 N sodium hydroxide solution and the ionic strength at the point of 50 per cent neutralisation was arranged to be less than 0.01. The value of the pH at this point was 4.52 (c.f. $pK_a = 4.67$ (91)) while the equivalence point titre gave the strength of the stock solution as 0.0890 molar.

Another potentiometric titration was carried out after an interval of three weeks using a 25 ml. sample of the stock 4-pentenoic acid solution and titrating with 0.127 N sodium hydroxide. The strength of the stock solution on this occasion was found to be 0.0896 molar and in view of these independent estimations, the strength of this 4-pentenoic acid solution was taken to be 0.0893 molar.

The dissociation constant for 4-pentenoic acid at 25° has been variously stated as 2.12 (91), 2.10 (34), and 2.09×10^{-5} (85) with pK_a values of 4.67, 4.68, 4.68 respectively. Because of the difference between the value of pK_a from the literature and the value of 4.52 found above, the composition of the buffer solution to give a final pH of 4.73 was evaluated from the neutralisation curve. Two stock solutions were made up at different times and because of slight errors, these solutions had the composition shown below:

<u>Solution 1</u> :	$(RCOOH) + (RCOO^-)$	=	0.0398 mol.lit. ⁻¹
(A and B Series)	$(RCOO^-)$	=	0.0257 mol.lit. ⁻¹
	pH	=	4.80 at 19°
<u>Solution 2</u> :	$(RCOOH) + (RCOO^-)$	=	0.0411 mol.lit. ⁻¹
(C and D Series)	$(RCOO^-)$	=	0.0248 mol.lit. ⁻¹
	pH	=	4.80 at 17°

The hypochlorous acid solutions used in these reactions was prepared by the 'aqueous' method.

Experimental Results.

Five Series A - E were carried out for 4-pentenoic acid at 25° and the results are given in Table XXXVII. The pH values reported in this Table were measured five minutes after the reaction was started. The initial hypochlorous acid concentration and the velocity results were obtained from the extrapolation of the reciprocal of the sodium thiosulphate titre against time curves (See Mathematical Appendix A (ii)) as the log titre vs. time curves were considerably curved and hence difficult to extrapolate.

TABLE XXXVII

Initial pH = 4.80			Temperature = 25 ± 0.01°	
Run	(HOCl) ₀	(RCOOH) ₀ + (RCOO ⁻) ₀	V ₀	pH
No.	x 10 ³	x 10 ³	x 10 ⁵	
			obs. calc.	
A1	1.43	0.50	4.4	5.00
A2	1.43	1.00	7.1	5.06
A3	1.42	1.49	10.3	5.00
A4	1.42	1.99	13.3	5.00
A5	1.42	2.49	17.2	5.00
B1	1.95	0.80	9.3	5.00
B2	1.95	1.59	15.9	4.96
B3	1.95	2.39	24.1	4.96
B4	1.95	3.18	33.1	4.94
B5	1.95	3.98	40.5	4.93
C1	2.02	1.03	11.6	4.80
C2	2.02	2.05	21.4	4.83
C3	2.02	3.08	32.3	4.82
C4	2.02	4.11	45.9	4.80
D1	2.49	2.05	27.5	4.83
D2	2.50	4.11	58.4	4.83
D3 *	2.50	8.22	126.5	4.81
D4 *	2.50	10.28	169.5	4.82
E1	3.32	4.11	79.4	4.84

* Extrapolation was difficult in these runs as both 1/titre and log titre vs. time graphs were considerably curved.

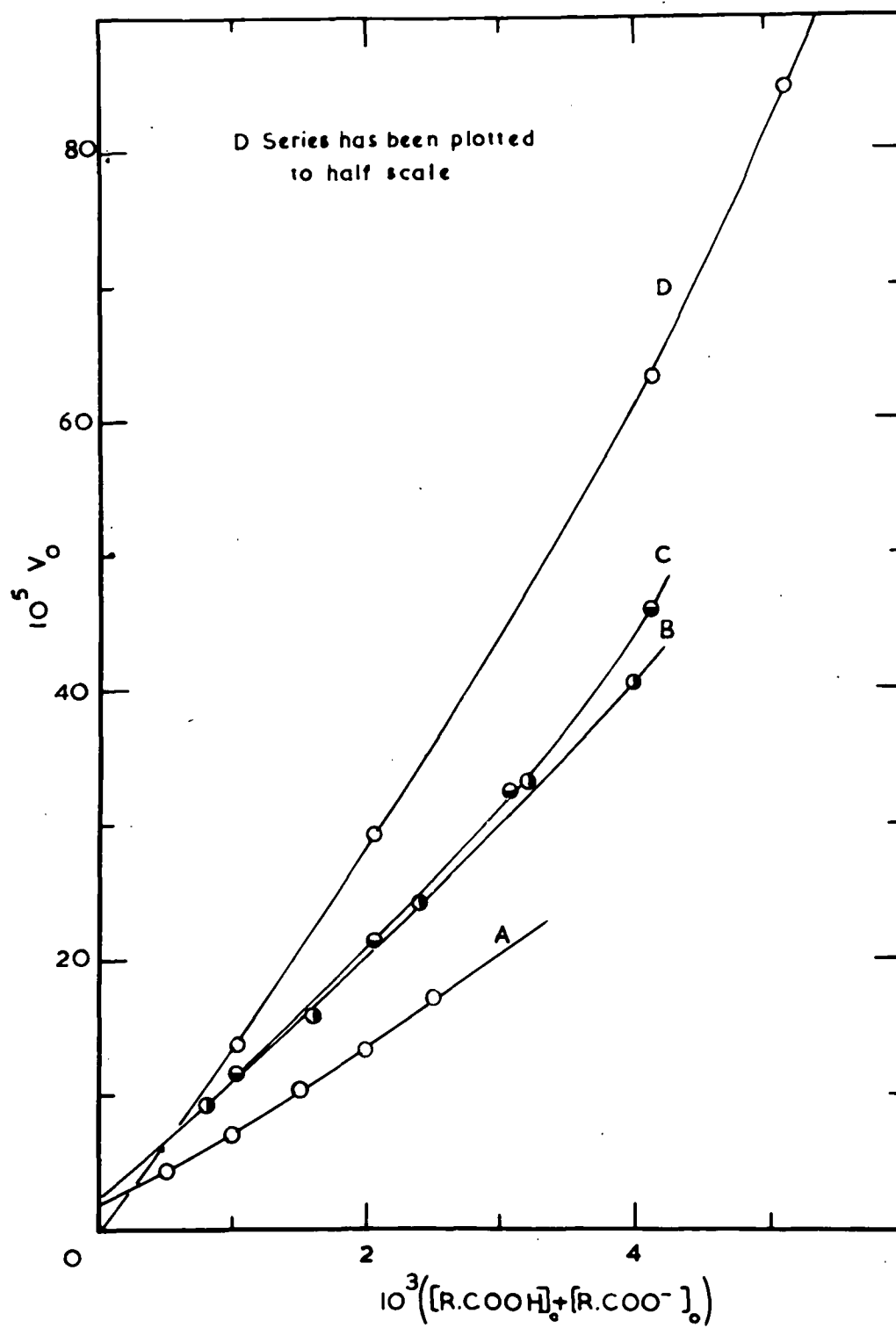


Figure 27

The initial velocity was plotted against the initial concentration of 4-pentenoic acid plus its sodium salt for each Series and resulted in slightly curved graphs extrapolation of which to zero olefin concentration gave residual velocities from $0 - 2 \times 10^{-5}$ mol.lit.⁻¹min.⁻¹. (See Figure 27). However, the curved nature of these graphs and the limited data available did not justify an application of the method of least squares to the velocity figures. This curvature mentioned above was examined by studying the variation of $V_o / \{(RCOOH)_o + (RCOO^-)_o\}$ with total olefin concentration for each Series. No systematic variation was observed and the mean value of this function for each Series is shown in Table XXXVIII.

TABLE XXXVIII

Series	$V_o / (T.O.)_o$ (mean) $\times 10^2$	$V_o / (HOCl)_o \cdot (T.O.)_o$ (mean)
A	7.27	50.8
B	10.44	53.6
C	10.73	53.6
D	14.90	59.6
E	19.30	58.3

where $(T.O.)_o$ has been used to represent the initial total olefin concentration i.e. 4-pentenoic acid plus its ion.

The variation of the mean of $V_o / (T.O.)_o$ with the initial hypochlorous acid concentration was not linear but a smooth curve could be drawn through these points and the origin (0,0). The values of $V_o / (T.O.)_o \cdot (HOCl)_o$ given in this Table above show this non-linearity, but so

that an estimate of the direct rate constant could be obtained for comparative purposes, the mean of these values was calculated as $55.2 \text{ lit. mol.}^{-1} \text{ min.}^{-1}$. Thus the rate of addition of hypochlorous acid to 4-pentenoic acid can be described approximately by the relation,

$$V_0 = 55.2(\text{HOCl})_0 \left\{ (\text{RCOOH})_0 + (\text{RCOO}^-)_0 \right\} \quad \dots\dots \text{Eqn. (5.9)}$$

The initial velocities calculated using equation (5.9) were within 10 per cent of the observed velocities but are omitted from Table XXXVII as their accuracy cannot be guaranteed.

Extension of this work on 4-pentenoic acid was not justified for the following reasons:

(i) The reaction was a particularly fast one and increasing the concentration ranges would have made extrapolation of the reciprocal titre vs. time curves even more difficult than for D3 and D4.

(ii) Decreasing the concentration of hypochlorous acid would render its estimation difficult.

(iii) The results already obtained did not conform to any regular pattern essential for the derivation of a velocity equation, but varied from Series to Series.

Despite the limited number of results available for this olefin, the following points appear to be established.

Except for the very reactive 3-pentenoic acid, 4-pentenoic acid reacted faster with hypochlorous acid than any of the previously studied olefins. Figure 27 indicated a term involving the

square of the olefin concentration (c.f. 2-pentenoic acid) and a small residual velocity term independent of the olefin concentration.

The pH measurements shown in Table XXXVII were nearly always greater than the initial pH (c.f. 2- and 3-pentenoic acids). This increase in pH could be due to the removal of hypochlorous acid and 4-pentenoic acid from the system and their replacement by the δ -chloro- γ -hydroxy or the γ -chloro- δ -hydroxy-n-valeric acids which, in view of the 'distant' substitution, should be acids of approximately the same strength as n-valeric acid and thus weaker than the original unsaturated acid.

No details of the products of this reaction could be found in the literature but in view of its similarity to 1-butene, the δ -chloro- γ -hydroxy compound would be expected in an almost quantitative yield.

PART 6

GENERAL DISCUSSION.

6.1. Influence of Substituents.

Before we can discuss the changes in the value of the rate constants in terms of the nature of the substituent groupings, it is necessary to show that factors which often influence the addition of halogens or hydrogen halides to olefinic compounds, such as surface catalysis, photochemical activation, induction periods and the presence of peroxides, were absent in the investigated addition reactions involving hypochlorous acid.

The reactions were shown to be homogeneous by adding powdered glass to a reaction flask and comparing the rate of reaction between hypochlorous acid and the olefin in this case with a duplicate experiment carried out in the absence of powdered glass. No variation in the rate of the reaction was observed.

Although addition reactions which are catalysed by light usually take place in the gaseous phase (or in a non-polar solvent) and involve the formation of free radicals, the influence of light on the addition of hypochlorous acid to olefins was investigated. Duplicate experiments one of which was carried out in the dark were compared, and no variation in the initial velocity was found. It was concluded, therefore, that photochemical activation played no part in the reaction.

Anantakrishnan and Venkataraman (2, 47) found induction periods ranging from one to one thousand minutes for the addition of bromine to olefinic acids. As distinct from these reactions, no induction periods were observed for any of the reactions

involving hypochlorous acid.

The presence of peroxides was considered by Kharasch (92) to be responsible for the many conflicting results recorded in the literature for the addition of hydrogen bromide to olefins. However, he has shown that $\alpha\beta$ -unsaturated acids were free from the complication of a peroxide effect. In addition it has been reported that hypochlorous acid adds normally whether a peroxide is present or not. In this respect hypochlorous acid is similar to hydrogen iodide, which also leads to a 'normal' product.

A summary of the rate constants for all the addition reactions at 25° is shown in Table XXXIX while the values of the rate constants at 35° are contained in Table XL.

As previously established,

k_2^I is the coefficient of $(\text{HOCl}) \{(\text{RCOOH}) + (\text{RCOO}^-)\}$
or $(\text{HOCl}) (\text{EtR})$

k_2^{II} is the coefficient of $(\text{HOCl})^2$

k_3^I is the coefficient of $(\text{HOCl}) \{(\text{RCOOH}) + (\text{RCOO}^-)\}^2$

k_3^{II} is the coefficient of $(\text{HOCl})^2(\text{RCOOH})$ or $(\text{HOCl})^2(\text{EtR})$

k_3^{III} is the coefficient of $(\text{HOAc})(\text{EtR})(\text{HOCl})$

all symbols have their usual meaning.

TABLE XXXIX

25°

Olefin	k_2^I	k_2^{II}	$k_3^I \times 10^{-3}$	$k_3^{II} \times 10^{-3}$	k_3^{III}
I. Crotonic acid	4.5	4.0	-	2.1	-
II. Tiglic acid	20.2	7.5	-	-	-
III. β : β -dimethyl- acrylic acid	28.3	11.7	-	-	-
IV. 2-pentenoic acid	28.	-	18	-	-
V. 3-pentenoic acid	840.	-	-	-	-
VI. 4-pentenoic acid	55.2	-	?	-	-
VII. Ethyl tiglate	1.3	-	-	2.2	660
VIII. Ethyl acrylate	0.009	-	-	-	-
IX. Methyl acrylate	< 0.009	-	-	-	-
X. Ethyl crotonate ^a	0.017	-	-	0.0164	6.8
XI. Allyl alcohol ^b	2.0	8.2	-	1.6	14.5 ^c

a : Investigated by Reeve (24)

b : Investigated by Israel (22)

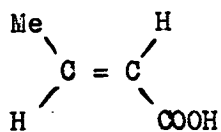
c : Rate constant, k_2^{III} , coefficient of (HOCl)(HOAc)

TABLE XL

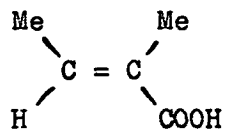
35°

Olefin	k_2^I	k_2^{II}	k_3^{II}
Crotonic acid	7.1	6.9	4.0×10^3
Tiglic acid	34.9	11.2	-
β : β -dimethylacrylic acid	52.0	13.0	-

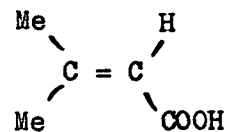
The effect of substituents in the olefin on the rate constant k_2^I at 25° is best seen diagrammatically. The values of the rate constants shown below, except in the case of ethyl crotonate (Reeve (24)) and allyl alcohol (Israel (22)), were obtained by the author.



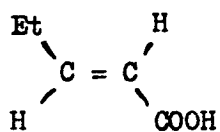
(I) 4.5



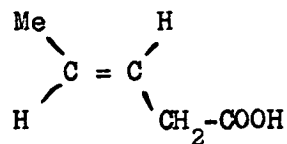
(II) 20.2



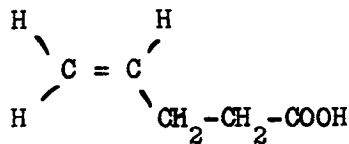
(III) 28.3



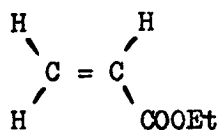
(IV) ca. 28



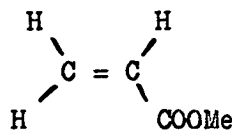
(V) ca. 840



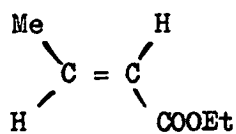
(VI) ca. 55.2



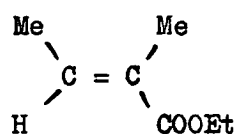
(VIII) ca. 0.009



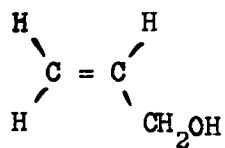
(IX) < 0.009



(X) 0.017



(VII) ca. 1.3



(XI) 2.0

Olefins are essentially nucleophilic reagents and if by suitable substitution the electron density at the double bond can be increased, the rate of attack by an electrophilic reagent, such as hypochlorous acid, will be considerably enhanced. However, changes in the reactivity of the parent olefin by substitution are not only caused by the availability of electrons at the point of attack; the presence of substituents can also influence the rate of addition by steric hindrance.

We will now examine the effect of substituents on the rate of chlorohydrin formation from the results shown above:

(i) Olefinic acids.

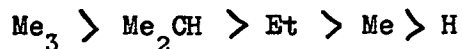
The rate constant, k_2^I , was derived for the direct attack of hypochlorous acid on both the undissociated olefinic acid and its ion, and it may be argued that a comparison of these values would not be justified in view of the superior reactivity of the ion towards electrophilic addition agents (93). However, the ratio $(RCOO^-)_0 / (RCOOH)_0$ for all these acids was of the same order since these acids were approximately of the same strength and the reactions were carried out in solutions of initially the same pH. For this reason the values of k_2^I given above should serve as a measure of the reactivity of the olefin towards hypochlorous acid.

The introduction of a methyl group into the α -position of crotonic acid considerably increased the velocity of the addition of hypochlorous acid even although the +I effects (1) of the two methyl groups opposed one another. This behaviour is similar to the effect observed by Ingold and Ingold (1) who

found that electrically and structurally symmetrical tetramethylethene reacted with bromine in methylene chloride solution faster than the asymmetrical dimethylethene. The tetramethylethene should have an increased value of the steric factor, P , insofar as the need for orientation of the reactant molecules would not be necessary to the extent required by an asymmetrical compound. Bloomfield (et al. 11) found that the isomeric chlorohydrins formed by the addition of hypochlorous acid to tiglic acid were present as 40 per cent α -chloro- β -hydroxy and 60 per cent β -chloro- α -hydroxy compounds, while Michael (35) found that the relative amounts of these chlorohydrins formed from crotonic acid were 74 and 26 per cent respectively. Thus orientation of the reactant molecules is less stringent in the case of tiglic acid and the steric factor, P , on this count should be greater for tiglic acid than crotonic acid. In addition, the electron-repelling methyl groups would increase the polarisability of the π -electrons.

The introduction of a methyl group into the β -position of crotonic acid considerably increases the +I activity ^{so} that the deactivating -I and -E effects of the carboxyl groups are overlaid. The release of strain associated with the steric hindrance of the geminal methyl groups in β : β -dimethylacrylic acid should facilitate the formation of the carbonium cation. It is interesting to notice the similarity between the rate constants for β : β -dimethylacrylic acid and 2-pentenoic acid (β -ethylacrylic acid). The +I effect of the ethyl group is greater than that of a methyl group and is comparable with that of the dimethyl group in accordance with the well-known order of

the electron-repelling groups,



The deactivating effect of the carboxyl group is evident when comparing the specific rate constants of the 3- and 4-pentenoic acids with the $\alpha\beta$ -unsaturated acids. In the former acids, the carboxyl group is separated by one or two methylene groups from the ethenoid link with the result that, these olefinic acids are much more reactive towards hypochlorous acid. The presence of a methyl group in the γ -position makes the 3-pentenoic acid an extremely reactive olefin.

(ii) Esters.

The most marked feature of the addition reactions for the esters in the presence of an acetic acid-sodium acetate buffer was the marked decrease in the reactivity compared with the corresponding acids. The methyl ester was slightly slower than the ethyl ester. This may be attributed to the fact that EtO is more +E than MeO and thus COOEt is less -E than COOMe. The ester group must possess a large deactivating influence as both ethyl and methyl acrylates react more slowly with hypochlorous acid than ethene (cf. Shilov et al. (14)).

The introduction of a methyl group in the β -position of ethyl acrylate nearly doubled the reactivity while the further substitution of a methyl into α -position to give ethyl tiglate increased the rate of reaction nearly 80-fold above ethyl crotonate. This large increase is probably the result of two

factors. In the first place, the complete absence of any orientation effect would increase the probability or steric factor of the Arrhenius equation. Bloomfield et al. (11) have shown that the addition of hypochlorous acid to ethyl tiglate yielded 50 per cent of each of the isomeric chlorohydrins indicating that the carboethoxyl group has no directional influence. While considering the various factors likely to influence the value of the probability factor, Hinshelwood (94) suggested that the correct orientation of the colliding molecules was necessary for the reaction to take place on collision. In the second place, the presence of two methyl groups would increase the nucleophilic activity of ethyl tiglate, by increasing the polarisability of the double bond. These facts would combine to make ethyl tiglate a much more reactive olefin than would be anticipated from either effect alone. Thus we see that the specific rate constants for the addition of hypochlorous acid to these ethenic compounds are in line with our established views relating to group influence.

6.2. Influence of Temperature.

An investigation of the influence of temperature on the rate of a complex reaction involves the determination of the velocity equation describing the reaction at at least two temperatures. Provided the velocity equations at these two temperatures are similar, temperature coefficients for the component steps can be calculated.

The complex nature of the reaction at 25° suggested an examination of the reaction at 35° to see whether the same general mechanism persisted at this elevated temperature and, if so, whether the increased values for the rate constants were due to changes in the energy of activation or to changes in the probability factor.

The effect of increasing the temperature from 25° to 35° on the rate of the addition of hypochlorous acid to crotonic acid, tiglic acid and β : β -dimethylacrylic acid was investigated and the activation energy and allied constants are combined in Table XLI.

TABLE XLI

	Crotonic Acid	Tiglic Acid	β : β -dimethylacrylic Acid
ΔE_1	8.30	9.89	ca. 11.05
ΔE_2	9.90	7.33	ca. 1.9
ΔE_3	12.10	-	-
PZ ^{obs.}	9.23×10^4	6.02×10^6	5.97×10^7
logPZ	4.962	6.779	7.776
Z ^{calc.}	2.08×10^{11}	2.02×10^{11}	2.02×10^{11}
P	4.4×10^{-7}	3.0×10^{-5}	2.9×10^{-4}

ΔE_1 is the activation energy in Kg.Cals. for the direct attack term and calculated from the ratio $(k_2^I)_{35^\circ}/(k_2^I)_{25^\circ}$

ΔE_2 is the activation energy in Kgs.Cals. calculated from the ratio, $(k_2^{II})_{35^\circ}/(k_2^{II})_{25^\circ}$.

ΔE_3 is the activation energy in Kg.Cals. calculated from the ratio,
 $(k_3^{II})_{35^0}/(k_3^{II})_{25^0}$.

In all three cases, the equation , $k = PZ e^{-E/RT}$ has been used assuming PZ to be temperature-independent in the 25^0-35^0 range. The value of $PZ^{obs.}$ given in Table XLI refers to the direct attack rate constant, k_2^I , and has been calculated using this value and the corresponding activation energy term ΔE_1 . It is expressed in $\text{lit.mol.}^{-1}\text{sec.}^{-1}$.

$Z^{calc.}$ is an approximate value of the collision number based on an estimated 5 \AA for the sum of the mean molecular radii of the reactant molecules. (It has been reported (2) that crotonic, tiglic and β : β -dimethylacrylic acids have mean molecular diameters of 6.8, 7.5 and 7.5 \AA respectively.)

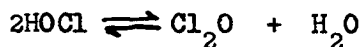
Table XLI shows that both the activating energy and the frequency factor, PZ, vary with olefinic acid. The variation in the activation energy, ΔE , is only small however, and the change in PZ completely outweighs this effect. These changes in both the activation energy and PZ would be expected for these compounds as the substituent methyl group is situated near the point of attack causing disturbances of both an electrical and geometrical character. It is seen that an increase in the activation energy is accompanied by an increase in PZ (or P since Z is approximately constant) and this increase is such that the plot of ΔE_1 against $\log PZ$ is roughly linear for these acids. A linear relation of this sort has been found for other reactions e.g. the effect of temperature on the bromination of substituted

acetophenones. A change in solvent or a change in the mechanism of the reaction is often suspected where the variation of the PZ term is of prime importance in a velocity equation. In this investigation, solvent conditions were unaltered but the absence of the term, $k_2^{II}(\text{HOCl})^2(\text{RCOOH})$ from the rate equations for tiglic and β : β -dimethylacrylic acids indicates a change in the mechanism of the reaction.

Chlorohydrin formation obviously falls into the class of 'slow' reactions and the small values of P are often associated with reactions involving complex molecules.

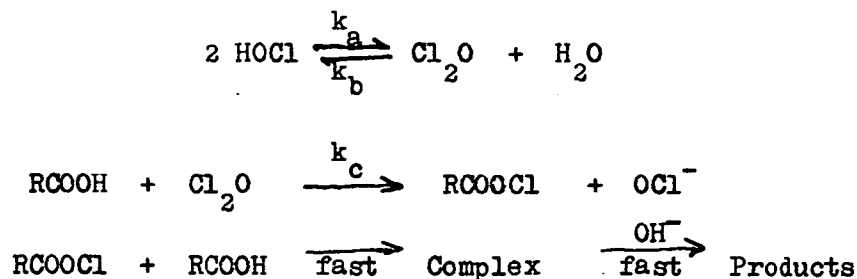
Anantakrishnan and Venkataraman (2) who investigated the rate of bromine addition catalysed by hydrogen bromide to crotonic, tiglic and β : β -dimethylacrylic acids found that the activation energies at 35.5° were 10.1, 6.4, and 4.4 Kg.Cals. respectively. From these values and values of the rate constants given in their paper, relative values of PZ were calculated as 5.4×10^5 , 6.8×10^3 and 1.0×10^3 respectively. Thus the presence of substituents altered both the activation energy and the frequency factor. Reactions of this type involving the catalytic effect of hydrogen bromide on bromine addition are often nucleophilic attacks initiated by HBr_3 (4) and this may explain the reversed order of the activation energies and probability factors found for the electrophilic reaction.

The variable nature of k_2^{II} and the activation energy of the process



with different olefins still persists.

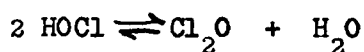
On the basis of consecutive reactions, it can be derived that for the reaction,



the overall velocity is

$$V = \frac{k_a k_c (\text{HOCl})^2 (\text{RCOOH})}{k_c (\text{RCOOH}) + k_b}$$

Depending on the relative values of k_b and k_c , this velocity term reduces to either $k'(\text{HOCl})^2(\text{RCOOH})$ or $k''(\text{HOCl})^2$ or some intermediate value which would make the determination of k_2^{II} difficult. It is suggested that the variable nature of k_2^{II} is due to it being the sum of two values; one a constant or fundamental value for the rate determining process,



and independent of the olefin, and the other a variable value arising from k'' , the value of which is, from the above derivation, dependent on the nature of the olefin. It will be remembered that k_2^{II} in the rate equations for the more reactive olefinic acids for which the term $k_3^{\text{II}}(\text{HOCl})^2(\text{RCOOH})$ was absent, was larger than in the velocity equation for crotonic acid, in accordance with the above suggestion.

Further work using other olefinic acids under similar conditions of solvent, concentration, etc. and possessing similar reactivity may help to provide an answer to this problem. α -methylacrylic acid is suggested.

The absence of the rate determining acid-catalysed formation of chlorine monoxide from hypochlorous acid from the mechanisms for the reaction of the olefinic acids other than crotonic acid, prevented any comparison of ΔE_3 , the activation energy for this process, being made. Any comparison of this value of ΔE_3 could only be made by using an olefinic acid similar in strength and reactivity to crotonic acid.

6.3. Conclusion.

The kinetics and mechanisms of the addition of hypochlorous acid to crotonic, tiglic and β : β -dimethylacrylic acids have been investigated at 25° and 35° in aqueous solutions of constant pH and velocity equations for these reactions have been developed. To a lesser extent, the addition of hypochlorous acid to a mixture of 2- and 3-pentenoic acids, 4-pentenoic acid and the esters, thethyl tiglate, and ethyl and methyl acrylate has been studied at 25° in solutions buffered by either the sodium salt of the olefinic acid or by the presence of an external acetic acid-acetate buffer of constant pH. The effect of pH on the rate of addition of hypochlorous acid to crotonic acid was investigated at 25° and 35° and reasons advanced for the behaviour exhibited. Arising

from the work on the pentenoic acids, a simple method was established for the relative estimation of 2-pentenoic acid in the presence of 3-pentenoic acid.

This study demonstrated one salient feature - the formation of chlorohydrins is a complex reaction involving not only hypochlorous acid but also, to varying extents, chlorine monoxide and the reactive acyl hypochlorites. The equations derived for the velocity of the addition reactions have indicated the presence of concomitant processes in the reacting phase. The number of these competing reactions and their relative contributions to the overall rate depended on the olefin, or more precisely, on the nature of the substituents attached to the double bond.

For unreactive olefins, we have seen that the interaction of the electrophilic reagent (hypochlorous acid, chlorine monoxide, etc.) with the olefin was the rate determining step. Consequently terms involving the product of hypochlorous acid, chlorine monoxide, and acyl hypochlorite concentrations each with the concentration of the olefin were present in the velocity equation. On the other hand, olefins possessing considerable nucleophilic activity reacted rapidly with such agents and the rate of the reaction in these cases was determined by the rate of formation of the electrophilic reagent from hypochlorous acid.

Therefore, unless the reactivity of the olefin can be accurately ascertained beforehand, no prediction of the constitution of the rate equation can be made.

Compared with the addition of halogen and/or hydrogen halide, the determination of rate constants for the addition of hypochlorous acid to the double bond presented considerable complexity and many reactions at various concentrations must be carried out to evaluate a rate constant at one temperature. This is, of course, a consequence of the two or more processes each with ^{its}~~their~~ own activation energy taking place between hypochlorous acid and the olefin. Under these circumstances, conventional methods for determining rate constants fail.

MATHEMATICAL APPENDIX.

MATHEMATICAL APPENDIX

The mathematical derivations and devices used in this thesis have been brought together in this appendix to prevent the interruption of chemical discussions and interpretations.

A. Determination of the Initial Velocity from Graphical Data.

Let a = initial concentration of hypochlorous acid,
 $a - x$ = concentration of hypochlorous acid at time t ,
 V = velocity of the reaction at time t
 $= dx/dt$.

(i) log titre data:

$$\text{Now} \quad \frac{d \ln(a-x)}{dt} = \frac{-1}{a-x} \frac{dx}{dt}$$

$$\begin{aligned} \text{i.e.} \quad dx/dt &= -2.303 (a-x) \frac{d \log(a-x)}{dt} \\ &= V \end{aligned}$$

Extrapolating the log titre vs. time data to zero time,

$$\begin{aligned} V_0 &= -2.303 \lim_{x \rightarrow 0} \left\{ (a-x) \frac{d \log(a-x)}{dt} \right\} \\ &= -2.303 a.g \end{aligned}$$

$$\text{i.e. Initial Velocity} = -2.303 \times (\text{HOCl})_0 \times \text{Gradient}$$

where g = Gradient is the gradient of the log titre vs. time curve at zero time.

(ii) 1/titre data:

$$\text{Now} \quad \frac{d \, 1/(a-x)}{dt} = 1/(a-x)^2 \cdot dx/dt$$

$$\begin{aligned} \text{i.e.} \quad dx/dt &= (a-x)^2 \frac{d \, 1/(a-x)}{dt} \\ &= v \end{aligned}$$

Extrapolating the 1/titre data vs. time data to zero time,

$$\begin{aligned} v_0 &= \lim_{x \rightarrow 0} \left\{ (a-x)^2 \frac{d \, 1/(a-x)}{dt} \right\} \\ &= a^2 \cdot \left[\frac{d \, 1/(a-x)}{dt} \right]_{t=0} \end{aligned}$$

By relating (a-x) to the sodium thiosulphate titre, the initial velocity from 1/titre data can be determined using the initial concentration of hypochlorous acid and the gradient of the 1/titre vs. time curve at zero time.

B. Discussion on log titre and 1/titre Graphical Data.

The general form of the log titre and reciprocal titre against time curves are shown in Figures 1 and 2 respectively. An explanation of the nature of these graphs should be possible in terms of the velocity equation and this is now given.

Assume that the general velocity equation is

$$dx/dt = k_1 (a-x)(b-x) + k_2 (a-x)^2 + k_3 (a-x)^2(b-x) \dots \text{Eqn. (1)}$$

where a = initial hypochlorous acid concentration

b = initial total olefin concentration

x = amount of hypochlorous acid used in time t.

Let T_0 = sodium thiosulphate titre at zero time.
 T = Sodium thiosulphate titre at time t
 n = normality correction factor such as that

$$T_0 \cdot n = (\text{HOCl})_0 = a$$

Then $a - x \propto T$
 $a \propto T_0$
 $x \propto T_0 - T$

and $dx/dt = -dT/dt$

Substituting these figures in equation (1), we get

$$\begin{aligned} -dT/dt &= k_1 n \cdot T(b - n(T_0 - T)) + k_2 n^2 T^2 + k_3 n^2 T^2 (b - (T_0 - T)) \\ &= nT \left\{ (k_1 b - nk_1 T_0) + T(nk_1 + nk_2 + nbk_3 - n^2 T_0 k_3) \right. \\ &\quad \left. + T^2 k_3 n^2 \right\} \end{aligned}$$

Let

$$-dT/dt = T(p + qT + rT^2) \quad \dots\dots\dots \text{Eqn. (2)}$$

where

$$\begin{aligned} p &= nbk_1 - n^2 T_0 k_1 \\ q &= n^2 (k_1 + k_2 + bk_3 - nT_0 k_3) \\ r &= n^3 k_3 \end{aligned}$$

From equation (2),

$$-\frac{d \ln T}{dt} = p + qT + rT^2 \quad \dots\dots\dots \text{Eqn. (3)}$$

Now $\ln T$ will be a linear function of time if, and only if,

$$q + rT = 0 ; \quad \text{since } T \neq 0$$

Taking the case of crotonic acid at 35° , investigation of the

relation $q + rT$ in the region of zero time showed that $q + rT = 0$ if

$$3a - b = 7 \times 10^{-3} \quad \dots\dots\dots \text{Eqn. (4)}$$

but this was for small values of a. This restriction on a immediately demands that b should be small also so that the equation (4) can be satisfied.

Summing up, the log titre vs. time curves will be nearly linear for reactions involving small initial concentrations of hypochlorous acid, and also small initial concentrations of crotonic acid plus sodium crotonate.

Consider the second derivative;

$$\frac{d^2 \ln T}{dt^2} = T(p + qT + rT^2)(q + 2rT) \quad \dots\dots\dots \text{Eqn. (5)}$$

Examine the sign of equation (5) for various values of a and b;

$$T > 0$$

$$q + 2rT = n^2(k_1 + k_2 + bk_3 + nk_3) > 0$$

$$\text{and} \quad p + qT + rT^2 > 0$$

Therefore,

$$\frac{d^2 \ln T}{dt^2} > 0 \quad \text{for all concentrations of reactants.}$$

Thus the log titre graphs will always be curved above the tangent to the curve at zero time, since the gradient is least at this point. (See Figure 1).

Consider now the 1/titre time curves :

From equation (2) ,

$$dT/dt = -T(p + qT + rT^2)$$

$$\text{Now} \quad \frac{d1/T}{dt} = -1/T^2 \cdot \frac{dT}{dt}$$

$$\begin{aligned} \text{Therefore,} \quad \frac{d1/T}{dt} &= (p + qT + rT^2)/T \\ &= q + p/T + rT \quad \dots\dots\dots \text{Eqn. (6)} \end{aligned}$$

Since $(p + qT + rT^2)$ is positive for all concentrations in the region investigated, $1/\text{titre}$ vs. time graphs will have positive slopes. Since for any particular run of a Series q is constant, the graph will be linear if,

$$p/T + rT = 0 \quad \text{for all } T$$

In the region of zero time, this relation, $p/T + rT$, will be zero if,

$$k_1(b-a) + a^2 k_3 = 0 \quad \dots\dots\dots \text{Eqn. (7)}$$

Again taking the example of crotonic acid at 35° and using the rate constants for that velocity equation, equation (7) reduces to

$$270 a^2 - a + b = 0 = f(a, b) \quad \text{say}$$

$$\text{Then} \quad \frac{\partial f(a, b)}{\partial a} = 540a - 1$$

Thus $270 a^2 - a$ has a minimum of -0.92×10^{-3} when $a = 1.85 \times 10^{-3}$ and since $b = 2.0 \times 10^{-3}$ at this value of a in the experimental work with crotonic acid, $f(a, b)$ will be greater than zero for all concentrations of the reactants in the experimental range.

Consider the second derivative:

$$\begin{aligned} \frac{d^2 l/T}{dt^2} &= \frac{d}{dT} \left(\frac{dl/T}{dt} \right) \cdot \frac{dT}{dt} \\ &= -T(p + qT + rT^2)(-p/T^2 + r) \\ &= -(rT^3 + qrT^2 - pq - p^2/T) \end{aligned}$$

It has always been noticed (See Figure 2) that the second derivative changes sign with increasing olefin concentration for constant hypochlorous acid concentration.

Examine the expression,

$$f(b) = rT^3 + qrT^2 - pq - p^2/T$$

for constant T_0 and for a particular value of T , to find out

for which values of b $f(b)$ changes sign.

$$\begin{aligned} \text{Now } \frac{\partial f(b)}{\partial b} &= rT^2 \frac{\partial a}{\partial b} - p \frac{\partial a}{\partial b} - q \frac{\partial p}{\partial b} - \frac{2p}{T} \frac{\partial p}{\partial b} \\ &= n^2 \left\{ rT^2 k_3 + 2n^2 T_0 k_1 k_3 - nk_1^2 - nk_1 k_2 \right. \\ &\quad \left. + \frac{2nT_0}{T} k_1^2 - b (2nk_1 k_3 + \frac{2}{T} k_1^2) \right\} \end{aligned}$$

Take, for example, the case of crotonic acid at 35° in which

$$(\text{HOCl})_0 = 2.0 \times 10^{-3} \text{ moles litre}^{-1}$$

$$\text{where } T_0 = 20$$

$$T = 15 \quad \text{say}$$

$$n = 10^{-4}$$

Then substitution gives

$$\frac{\partial f(b)}{\partial b} = (10.1 \times 10^{-3} - 3.49 b) \times 10^8$$

$$\text{Now this becomes zero if } b = 2.9 \times 10^{-3}$$

Examination of the second derivative showed that it was negative for values of b less than 2.9×10^{-3} , and positive for values of b greater than 2.9×10^{-3} . This was noticed in the B' Series where a change in the sign of the second derivative of the $1/\text{titre}$ vs. time curves occurred for B'1 and B'2. However, the value of b for which this changeover occurs is dependent on the value of the initial concentration of hypochlorous acid, and must be calculated separately for each Series.

An examination of the deviations of both log titre and $1/\text{titre}$ data from linearity showed that log titre data was to be favoured slightly and except where specified, the velocity determinations in this thesis were based on log titre vs. time

graphs and the relation derived in Appendix A (i).

C. Effect of Error in the Volumes Delivered by the Reactant

Flasks to the Reaction Flask on the Initial Concentrations.

Suppose that in the 50 ml. reactant flask, $(\text{HOCl}) = a \text{ moles lit.}^{-1}$

" " " " " " " $(\text{Olefin}) = b \text{ " " "}$

Then number of moles of hypochlorous acid present in

reaction flask on initial mixing assuming no error $= a/20$

Similarly, number of moles of olefin in flask $= b/20$

Total volume now present in reaction flask $= 100 \text{ ml.}$

Therefore,

$$(\text{HOCl})_o^{\text{Theor.}} = \frac{a \times 1000}{20 \times 100} = a/2 \text{ molar}$$

$$\text{and } (\text{Olefin})_o^{\text{Theor.}} = \frac{b \times 1000}{20 \times 100} = b/2 \text{ molar}$$

Suppose that there was an error of $\delta v \text{ ml.}$ of HOCl delivered

" " " " " " " $\delta w \text{ ml.}$ of Olefin "

$$\text{Number of moles of HOCl present in reaction flask} = \frac{a \times (50 - \delta v)}{1000}$$

$$= \frac{a}{20} (1 - \delta v/50)$$

$$\text{Number of moles of olefin present} = \frac{b}{20} (1 - \delta w/50)$$

$$\text{Total volume now present in reaction flask} = 100 - (\delta v + \delta w)$$

Therefore,

$$(\text{HOCl})_o^{\text{Actual}} = \frac{a/20 \cdot (1 - \delta v/50) \cdot 1000}{100 - (\delta v + \delta w)} \text{ molar}$$

$$(\text{Olefin})_o^{\text{Actual}} = \frac{b/20 \cdot (1 - \delta w/50) \cdot 1000}{100 - (\delta v + \delta w)} \text{ molar}$$

Thus the errors in the initial concentrations due to an error of δv ml. of hypochlorous acid and an error of δw ml. of olefin are:-

$$\text{Error}_{\text{HOCl}} = \frac{a/2 - a(50-\delta v)/(100-\delta v-\delta w)}{a/2} \cdot 100 \text{ per cent}$$

$$= \frac{\delta v - \delta w}{100-\delta v-\delta w} \cdot 100 \text{ per cent}$$

$$\text{Error}_{\text{Olefin}} = \frac{b/2 - b(50-\delta w)/(100-\delta v-\delta w)}{b/2} \cdot 100 \text{ per cent}$$

$$= \frac{\delta w - \delta v}{100-\delta v-\delta w} \cdot 100 \text{ per cent}$$

Note that there is not any error when $\delta v = \delta w$, and this would be the usual case. Experiments showed that δv and δw very rarely exceeded 0.5 ml. and the difference between them would in general, be less than this figure.

Thus it can be safely assumed that the error in the initial concentrations of either reactant would be less than, or at the most, equal to 0.5 per cent.

D. Integration of the Crotonic Acid Velocity Equation and
Calculation of $t_{x/a}$.

The general velocity equation (2.11) can be modified
 for constant pH to

$$dx/dt = k_1(a-x)(b-x) + k_2(a-x)^2 + k_3(a-x)^2(b-x) \quad \text{..... Eqn.(1)}$$

where, in terms of equation (2.11),

a = initial concentration of hypochlorous acid

b = " " " crotonic acid plus sodium crotonate

x = decrease in hypochlorous acid concentration in time t

$$k_1 = k_2^I$$

$$k_2 = k_2^{II}$$

and $k_3 = k_3^{II}/2.096$

Integration of Eqn. (1) and application of the boundary condition
 that at $t=0$, $x=0$, gives the equation,

$$t = 2.303/(a^2A + aB + C) \left\{ \log a/(a-x) + 1/2 \log \frac{Ax^2+Bx+C}{C} \right. \\ \left. + \frac{2aA + B}{2(B^2-4AC)^{1/2}} \log \frac{Bx+2C+x(B^2-4AC)^{1/2}}{Bx+2C-x(B^2-4AC)^{1/2}} \right\}$$

where

$$A = k_3$$

$$B = -(k_1+k_2+(a+b)k_3)$$

$$C = k_1b + k_2a + abk_3$$

Tables V and VIII were obtained by substituting suitably in the
 equation for t using the ratios $x/a = 0.1$ and 0.2 .

E. Integration of the Tiglic Acid Velocity Equation andCalculation of $t_{x/a}$.

The general velocity equation (3:15) for tiglic acid is of the form,

$$dx/dt = k_1(a-x)(b-x) + k_2(a-x)^2 \quad \text{..... Eqn.(1)}$$

where

a = initial concentration of hypochlorous acid

b = initial concentration of tiglic acid plus
sodium tiglactate

x = decrease in concentration of hypochlorous
acid in time t,

$$k_1 = k_2^I$$

$$k_2 = k_2^{II}$$

Integration of (1) and application of the boundary condition that at $t=0$, $x=0$, gives the equation,

$$t = 1/(B^2 - 4AC)^{1/2} \cdot 2.303 \log \frac{2Ax+B-(B^2-4AC)^{1/2}}{2Ax+B+(B^2-4AC)^{1/2}} \cdot \frac{B+(B^2-4AC)^{1/2}}{B-(B^2-4AC)^{1/2}}$$

where

$$A = k_1 + k_2$$

$$B = -(2ak_2 + (a+b)k_1)$$

$$C = abk_1 + a^2k_2$$

Tables XV and XVIII were constructed from values of $t_{x/a}$ derived by substitution in this equation.

F. The Variation of Dissociation Constant with Temperature.

(95)

Pitzer_Λ derived an equation for the change in the dissociation constant of weak acids with temperature as

$$\log K = A + B/T - 20 \log T$$

where A and B are constants., K is the dissociation constant at temperature T° absolute.

If sufficient ionisation data is not available for the determination of both A and B, the value of A can be taken as 53.78 which Pitzer found to be a close approximation.

This approximation for A was based on a constant figure for the entropy and heat capacity changes observed for weak acids in aqueous solution at temperatures near 25° . The value of B can be calculated using the known dissociation constant at given temperature.

(i) Crotonic Acid.

Substitution of the known dissociation constant for crotonic acid at 25° in Pitzer's equation gave the equation,

$$\log K = 53.78 - 2678.9/T - 20 \log T$$

At 35°

$$\log K = -4.689$$

i.e. $K = 2.046 \times 10^{-5}$

and the ratio of the dissociation constants at 35° and 25° ,

$$K_{35}/K_{25} = 1.008$$

(ii) Tiglic Acid.

Substitution of the known dissociation constant for tiglic acid at 25° in Pitzer's equation gave the equation,

$$\log K = 53.78 - 2776.2/T - 20 \log T$$

At 35°

$$\log K = -5.005$$

i.e. $K = 1.012 \times 10^{-5}$

and the ratio of the dissociation constants at 35° and 25°,

$$K_{35}/K_{25} = 1.06$$

(iii) β:β-dimethylacrylic Acid.

Substitution of the known dissociation constant for β:β-dimethylacrylic acid in Pitzer's equation gives the equation,

$$\log K = 53.78 - 2806.3/T - 20 \log T$$

At 35°

$$\log K = -5.102$$

i.e. $K = 0.791 \times 10^{-5}$

and the ratio of the dissociation constants at 35° and 25°

$$K_{35}/K_{25} = 1.04$$

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