STUDIES ON PRODUCT FORMATION IN SOME REACTIONS
INVOLVING METHYLENE INTERMEDIATES

PART ONE
VARIATION OF FORMATE YIELDS
IN THE HYDROLYSIS OF CHLOROFORM

PART TWO
THE DECOMPOSITION OF
DICHLOROFLUOROACETIC ACID

PART THREE
THE DECOMPOSITION OF
CHLORODIFLUOROACETIC ACID

PART FOUR
SOME REACTIONS OF METHYL
DICHLOROMETHYL ETHER

A THESIS

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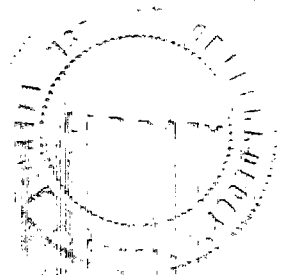
By

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TABLE OF CONTENTS

Page

PART ONE

Chapter

PART TWO

Chapter

PART THREE

PART FOUR

LIST OF TABLES

PART ONE

LIST OF ILLUSTRATIONS

PART ONE

SUMMARY

Part One

Previous studies on the hydrolyses of a number of haloforms have indicated that carbon monoxide and formate salts are the only products when the hydrolyses are carried out in alkaline aqueous solutions. In the work described in this part the yield of formate salts from the hydrolysis of chloroform was found to increase when either the temperature or the base concentration was increased. The formate yield was found to decrease, however, when the initial quantity of chloroform was in excess of its solubility in water. When water was replaced by deuterium oxide as the solvent, there appeared to be little or no change in the formate yield.

Two explanations are suggested to account for the effect of hydroxide concentration on the formate yield. The first of these assumes that the yield of formate compared to the yield of carbon monoxide is linearly dependent upon the hydroxide concentration. This assumption permits an estimate of the effectiveness of hydroxide in competition with water for the last intermediate common to the formation paths of both products. It was estimated that hydroxide reacts with such an intermediate 339 times faster than water. Since hydroxide is reported to be only about 30 times more effective than water in competing for dichloromethylene intermediates, the product determining step must involve an intermediate that is formed after dichloromethylene.

The second explanation assumes that more than one pair of product determining steps exist. The reactions suggested in this explanation represent an extension of a mechanism suggested by other workers for the hydrolysis of chloroform in acidic aqueous solutions. This explanation includes a path by which formic acid may be formed from chloroform in acidic solutions in addition to paths requiring the presence of hydroxide.

Previously reported formate yields from a number of haloforms and two trihaloacetic acids indicate the following: when bromine is the last halogen to be lost in the hydrolysis, the formate yield is lower than when chlorine is last; formate yields from compounds containing one or more fluorine atoms appear to be higher than the formate yield from chloroform under the same conditions.

The qualitative comparisons of formate yields from these compounds can be readily interpreted in terms of a generalized reaction sequence similar to the sequence suggested by the second explanation for the variation of formate yields from chloroform.

Part Two

The decomposition of dichlorofluoroacetic acid was studied in aqueous solutions. The effects of temperature, pH, added sodium fluoride, and ionic strength on the rate and products of the decomposition were determined. All of the observations were consistent with a reaction mechanism involving a first order decomposition of the dichlorofluoroacetate ion to carbon dioxide and a dichlorofluoromethide ion that is usually protonated to give dichlorofluoromethane but that often

loses a chloride ion to give the intermediate chlorofluoromethylene which is then hydrolyzed to a mixture of carbon monoxide and formic acid. Very low yields (< 1%) of fluoroform and chlorodifluoromethane were obtained even in the presence of saturated sodium fluoride.

Part Three

The decomposition of chlorodifluoroacetic acid in aqueous solutions produced carbon dioxide, carbon monoxide, oxalic acid, formic acid, chlorodifluoromethane, and fluoroform. In 1 $\underline{M}$ or stronger fluoride ion solutions trifluoroacetic acid appeared to become an important product. The addition of other halide ions to the solutions produced changes in the nature of the products that would be expected from reactions of the halide ions with difluoromethylene intermediates.

The mechanism of the decarboxylation reaction appears to be a concerted decomposition of the chlorodifluoroacetate ion to carbon dioxide, chloride ion, and difluoromethylene. This concerted mechanism is unlike the decarboxylation of other trihaloacetate ions which lose carbon dioxide to give a trihalomethide ion.

Part Four

Methyl dichloromethyl ether was prepared by the action of phosphorus pentachloride on methyl formate. This ether reacted very rapidly at room temperature with water or isopropyl alcohol. The rate of the reaction in isopropyl alcohol was estimated at 0°, -5°, and -14°. The rate of a second order reaction of the ether with potassium isopropoxide was also estimated in isopropyl alcohol at these temperatures.

Rates of reaction of methyl dichloromethyl ether with isopropyl alcohol, potassium isopropoxide, and potassium thiophenoxide were determined near $0°$ using 75% benzene - 25% isopropyl alcohol as a solvent.

The principal product of the reaction of the ether with potassium isopropoxide appeared to be methyldiisopropyl orthoformate, though a yield of about 0.6% of carbon monoxide was also obtained. In some cases the presence of small quantities of water in the solvent apparently causes the formation of potassium formate as a reaction product of the ether. Attempts to prepare and isolate an adduct of methoxychloromethylene and cyclohexene were unsuccessful.

The second order reactions between methyl dichloromethyl ether and potassium isopropoxide or potassium thiophenoxide observed in this work are believed to be interpreted best in terms of S_N2 displacements of chloride from the ether rather than mechanisms analogous to those operative in the hydrolysis of chloroform.

The mechanism of the first order solvolysis of methyl dichloromethyl ether was not elucidated, but the mechanism may be similar to an S_N1 mechanism proposed for the solvolysis of methyl chloromethyl ether in ethanol.

PART ONE

VARIATION OF FORMATE YIELDS IN

THE HYDROLYSIS OF CHLOROFORM

CHAPTER I

INTRODUCTION

The basic hydrolysis of chloroform has been reported to yield only carbon monoxide and formate as final products (1). In addition, this reaction has been shown to proceed by the mechanism outlined below (2,3).

$$CHCl_3 + OH^- \underset{}{\overset{fast}{\rightleftharpoons}} CCl_3^- + H_2O$$

$$CCl_3^- \overset{slow}{\longrightarrow} Cl^- + CCl_2$$

$$CCl_2 \underset{OH^-,\ H_2O}{\overset{fast}{\longrightarrow}} CO \text{ and } HCO_2^-$$
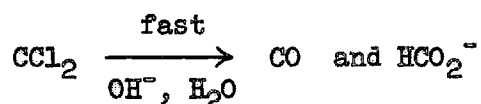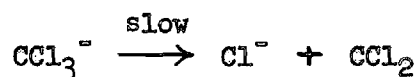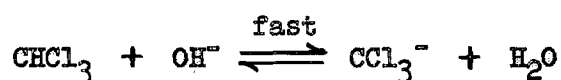
Since the third reaction in this series is fast compared to the preceding reaction, little information has been reported regarding the nature of the final steps leading to either carbon monoxide or formate. Hine has reported (2) formate yields from indirect measurements in a number of runs in 66 2/3% aqueous dioxane. These yields ranged from 3 to 50% without showing any pronounced trend. Hine, Dowell, and Singley (1) later reported mean values by two methods for the formate yields from several runs in water. These values were $14.51 \pm 0.13\%$ and

(1) J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., J. Am. Chem. Soc., 78, 479 (1956).

(2) J. Hine, ibid., 72, 2438 (1950).

(3) J. Hine and A. M. Dowell, Jr., ibid., 76, 2688 (1954).

$18.4 \pm 1.2\%$, but, since their kinetic expression was relatively insensitive to the formate yield, these workers subsequently used a value of 15% for all runs.

It has also been reported (2) that when sodium thiophenolate was used with sodium hydroxide and chloroform the yield of phenyl orthothioformate was independent of the hydroxide concentration and depended only on the concentration of thiophenolate relative to that of water.

In a study (3) of the competing abilities of various halide ions, hydroxide ion, and water for carbon dichloride intermediate it was found that this intermediate possesses sufficient stability that reaction does not occur with every collision. Instead the competition factors correlate well with the nucleophilicity constants reported by Swain and Scott (4).

Fells and Moelwyn-Hughes (5) have recently suggested the reactions below as reasonable paths leading to the products they observed from the hydrolysis of $CHCl_3$ in neutral or acidic solution;

$$CHCl_3 + H_2O \longrightarrow CHCl_2OH + HCl$$

$$CHCl_2OH \longrightarrow HCOCl + HCl$$

$$HCOCl + H_2O \longrightarrow HCO_2H + HCl$$

$$HCOCl \longrightarrow CO + HCl.$$
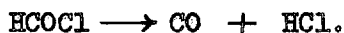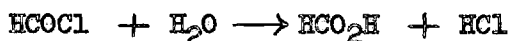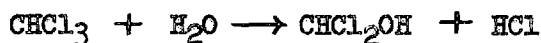
A similar first step was shown by Hine (2) to be unlikely in the

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(4) C. G. Swain and C. B. Scott, ibid., 75, 141 (1953).

(5) I. Fells and E. A. Moelwyn-Hughes, J. Chem. Soc., 398 (1959).

hydrolysis of $CHCl_3$ in alkaline solution. On the other hand, Hine and Langford have interpreted (6) the hydrolysis and chloride exchange (7) in acidic solution in terms of S_N2 mechanisms (8).

In most of the work cited here (1,2,5,6) on chloroform hydrolysis, some attempt has been made to determine the yields of carbon monoxide and formate. With one exception (1), all of these determinations were made from the amount of acid formed per mole of chloroform consumed as measured by changes in chloride concentration in the reaction solution. The yields of formate were below 25% in every case but one (2).

No systematic study of formate yields from $CHCl_3$ under varying hydrolytic conditions seems to have been carried out. This work was begun, consequently, with the idea that such a study might illuminate some details of the post-rate-determining steps in the hydrolysis of chloroform.

(6) J. Hine and P. B. Langford, J. Am. Chem. Soc., 80, 6010 (1958).

(7) J. Horiuti, K. Tanabe, and K. Tanaka, J. Res. Inst. Cat., Hokkaido Univ., 3, 119 (1955).

(8) J. Hine, Physical Organic Chemistry, McGraw-Hill Book Co., New York, N. Y., 1956, Chap. 5.

CHAPTER II

PROCEDURE

Formate yields were determined by a method that has been reported previously (1). A known volume of aqueous sodium hydroxide was allowed to stand in a thermostated bath for about one hour. A small, measured quantity of chloroform was then introduced into the alkaline solution by means of a calibrated syringe. The mixture was shaken until saturated with chloroform and then an aliquot of the solution was removed by pipet and titrated with standard hydrochloric acid. Samples were also withdrawn occasionally during the course of the reaction, but the majority of the measurements were made after the reaction had essentially reached completion. In this method the sample was titrated to the blue-yellow transition of a thymol blue indicator with hydrochloric acid. The solution was then evaporated to dryness at about 60° using a water aspirator. The residue was shaken with 10-15 ml. of absolute methanol and titrated to the yellow-red transition of thymol blue with standard p-toluenesulfonic acid in methanol. The quantity of formate was then taken as equivalent to the molar quantity of acid used in the latter titration, and the value of $\underline{f}$ was calculated from the following relation.

$$\underline{f} = \frac{3[HCO_2^-]}{-(\Delta[OH^-] + [HCO_2^-])}$$

Tests of the validity of the sodium formate determination by titration with p-toluenesulfonic acid were made in the following manner.

A solution containing a known amount of sodium formate was prepared in methanol. Aliquots of this solution were then titrated after dilution to 10 ml. with methanol. The titration was found to be accurate to within a mean deviation of 5% even in the presence of a five to one excess of sodium chloride over sodium formate over the range 7-122 micromoles sodium formate, i. e., more than the range covered in chloroform hydrolyses.

In another series of tests over the same range of formate concentration, alkaline formate solutions (0.05 to 0.33 M NaOH) were first titrated with dilute hydrochloric acid, evaporated to dryness, dissolved in methanol, and titrated with p-toluenesulfonic acid. The method was again found to be accurate to within a mean deviation of 5%.

Estimates of formate concentration by ultraviolet and infrared absorption were also tried, but these proved no more accurate and more tedious than the titration method.

Reagents.--Baker sodium hydroxide was used to prepare carbonate-free base by diluting a filtered, concentrated solution. Chloroform was purified by the method of Fieser (9) and distilled. The material used boiled over the range 60.0-60.1° (742 mm.). The purified chloroform was stored in a brown bottle under nitrogen, and periodic checks were made of its density and refractive index. When appreciable departures from the literature values appeared, the chloroform was repurified.

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(9) L. F. Fieser, Experiments in Organic Chemistry, 3rd ed., Heath Co., Boston, Mass., 1955, p. 283.

CHAPTER III

RESULTS

The original intent of this work was to study the effects, if any, of temperature, base concentration, and D_2O on the formate yield from chloroform hydrolysis. It can be seen from Table 1, however, that the amount of chloroform is also an important factor in some specific cases.

Table 1. Variation in Formate Yield

Run	Temperature[a] (°C.)	Average [OH⁻][b] (mole/l.)	Initial [CHCl₃] (mole/l.)	f
7	35	0.0445	0.0650	0.174 ± 0.007[d]
8	35	0.0437	0.0300	0.175 ± 0.001
9	35	0.0919	0.0516	0.333 ± 0.010
10	35	0.1799	0.1240	0.215 ± 0.023
11	35	0.1769	0.1240	0.234 ± 0.008
12	56 ± 1	0.1603	0.248	0.258 ± 0.006
13	27 ± 2	0.1654	0.248	0.177 ± 0.002
14	50	0.1967	0.496	0.291 ± 0.001
15	50	0.3518	0.496	0.426 ± 0.006
16	50	0.0934	0.496	0.164 ± 0.012
17[c]	50	0.1675	0.1240	0.337 ± 0.010
18	50	0.0125	0.1240	0.133[e]

[a]Temperature variations were within 0.2° unless otherwise indicated.

[b]Values given are one-half the sum of the initial and final base concentrations.

[c]Sodium formate was present initially in a concentration of 0.006 M.

[d]This value was averaged from two determinations.

[e]This value was obtained from a single determination.

None of the values of f given in Table 1 were determined until about 70% of the limiting reagent (hydroxide in all cases) had been consumed. Except in Runs 7 and 18, the reported value of f is a mean value from three to five determinations. The initial chloroform amounts given in this table are often greater than the solubility of chloroform in water at the temperatures used. This system was used to indicate the total quantity of chloroform in the reaction flask. The reported solubility of chloroform in water at 15° is 0.084 M (10) with little variation over the temperature range used in this work (11).

A previously reported (1) value for f of 0.145 ± 0.001 was determined by essentially the method used in this work in a solution initially 0.14 M in sodium hydroxide and 0.1 M in chloroform in 66 2/3% dioxane-water solution.

The validity of an indirect method as used here is, of course, somewhat open to question despite results of the tests reported earlier. There exists the possibility that sodium formate decomposes under the reaction conditions. That such decomposition is not significant is illustrated in Table 2.

A general picture of the factors affecting formate yields may be had from Table 1 where it is seen that the yield increases with increasing temperature and base concentration but decreases at the higher chloroform "concentrations." The reproducibility of the experiments is best illustrated by Runs 10 and 11.

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(10) Handbook of Chemistry and Physics, 32nd ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1950, p. 817.

(11) International Critical Tables, Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 387.

Table 2. Run 9

Time (sec.)	[OH⁻] mole/l.	$\underline{f}$
0	0.1615	--
67,500	0.0510	0.336
150,000	0.0320	0.354
322,000	0.0233	0.321
323,000	0.0232	0.321
340,000	0.0221	0.333

The effect of replacing water by deuterium oxide as solvent was also investigated. The results of this experiment are shown in Table 3 together with those from Run 9, which was made concurrently at the same temperature though at a somewhat higher base concentration.

Table 3. Effect of D_2O on $\underline{f}$

Run	Average [OH⁻]	Initial [CHCl₃]	$\underline{f}$
9 (H_2O)	0.0919	0.0516	0.333 ± 0.010
9 (D_2O)	0.0711	0.0573	0.266 ± 0.005

When the value of $\underline{f}/(1-\underline{f})$ in D_2O is plotted with values from Runs 7, 8, and 9 in H_2O against the average base concentrations in these runs as in Fig. 1, the points do not vary greatly from a straight line. This information would seem to indicate little or no distinction between H_2O and D_2O since a straight line relationship is also found in Fig. 2 for runs in water at 0.496 $\underline{M}$ initial chloroform concentration.

$$\frac{f}{1-f}$$

Average Hydroxide Concentration (mole/l.)
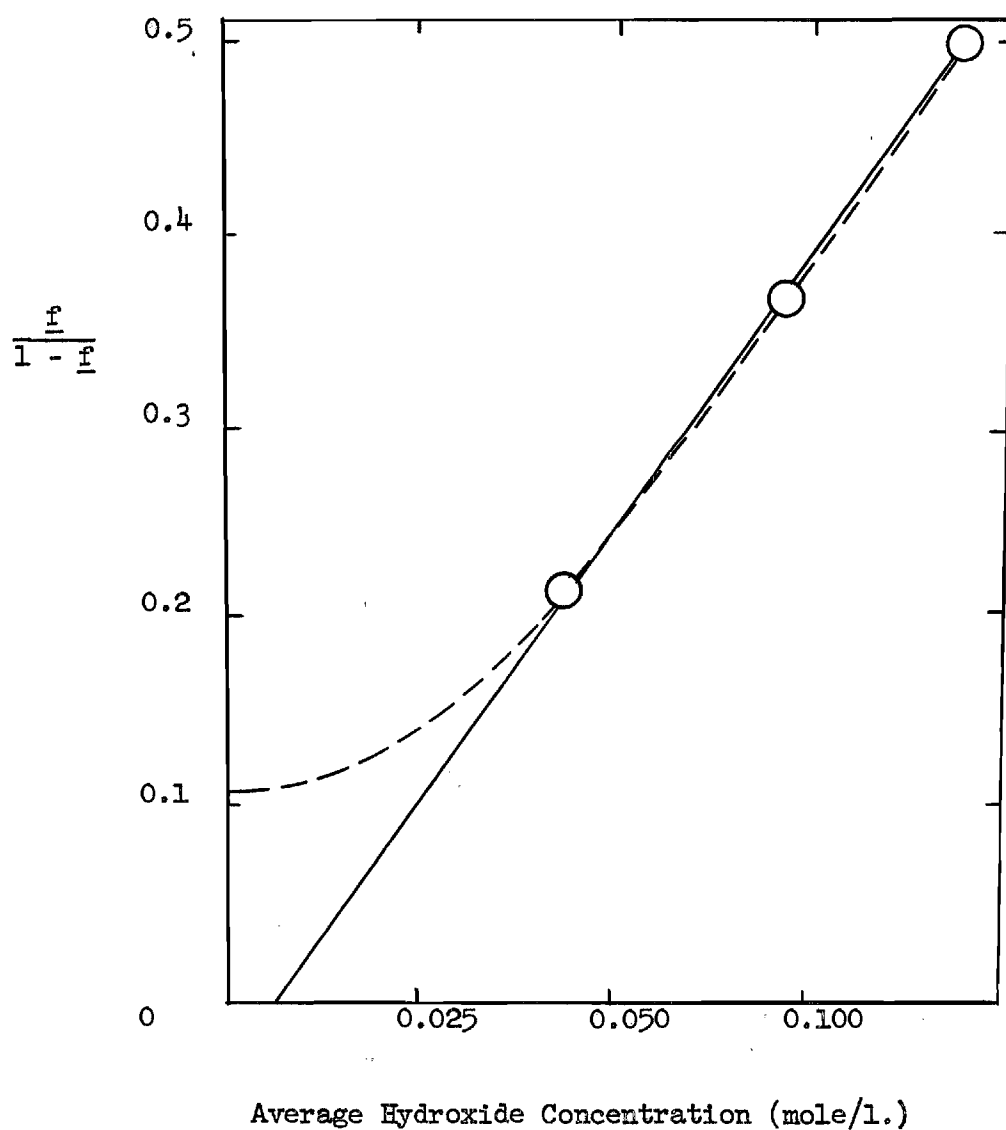
Figure 1. Variation of f with Base Concentration Using
0.05 M Initial Chloroform Concentration

Average Hydroxide Concentration (mole/l.)
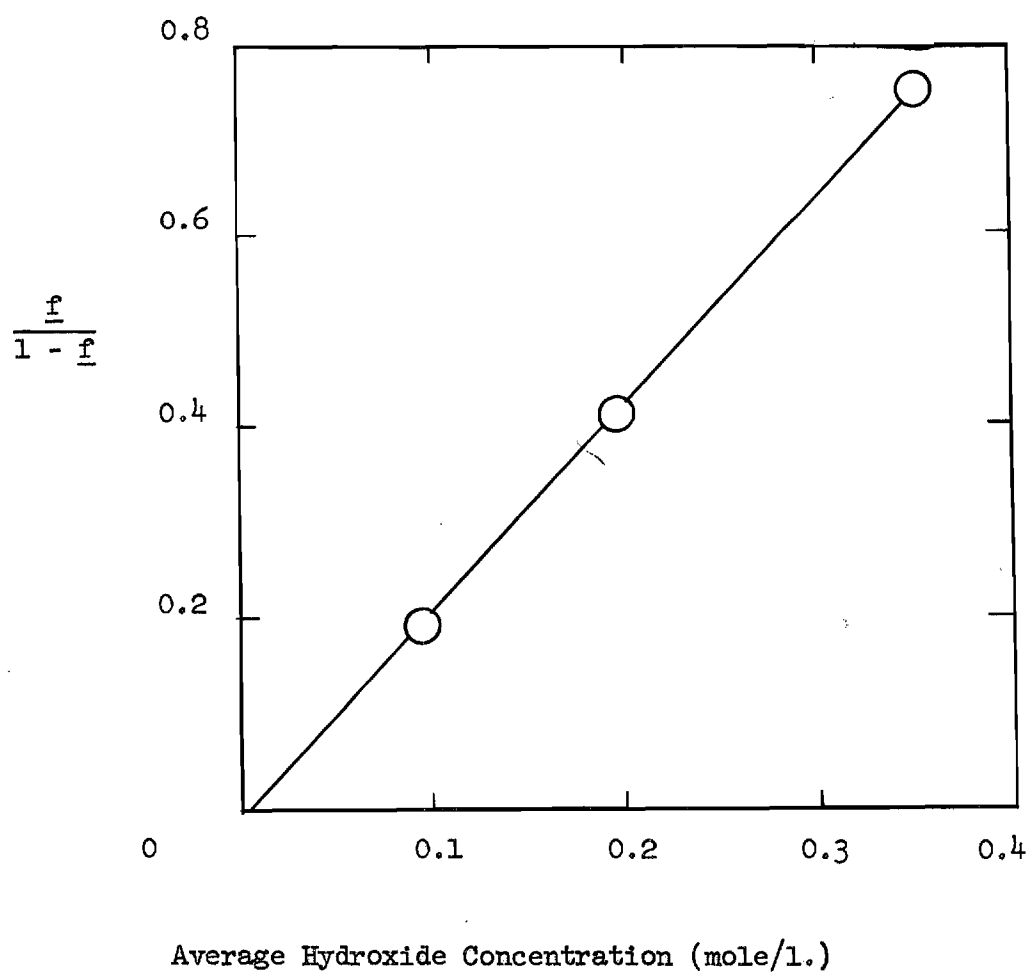
Figure 2. Variation of _f_ with Base Concentration Using
0.496 M̲ Initial Chloroform Concentration

CHAPTER IV

DISCUSSION AND CONCLUSIONS

From Table 1 and Figs. 1 and 2 it appears fairly well beyond question that higher formate yields are obtained by increasing the average hydroxide ion concentration in the hydrolysis of chloroform. It is also evident that the production of formate is favored by high temperature and low chloroform "concentration."

The dependence of formate yield on chloroform concentration may seem somewhat surprising. From Table 1 it is seen that little or no reduction in formate yield occurs in runs where the chloroform concentration was initially less than 0.065 $\underline{M}$. Furthermore, there seems to be little further reduction of formate yield when the initial chloroform concentration is increased beyond 0.1240 $\underline{M}$. Since the solubility of chloroform in water lies between these extremes, it seems possible that the effect may be caused by the presence of undissolved chloroform. This effect might then be caused by reaction of hydroxide at or near the interfaces of undissolved chloroform where the process of diffusion is unable to maintain as high a base concentration as exists in the solution as a whole. This explanation has as a principal drawback the high ionic mobility (12) and accompanying ease of diffusion of hydroxide ions. The half-life of chloroform in an initially saturated solution at 35° that is initially 0.3 $\underline{M}$ in base is about four hours (3).

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(12) F. Daniels, Outlines of Physical Chemistry, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 414.

Because of the effect of chloroform concentration on $\underline{f}$, an interpretation of the effect of base concentration on $\underline{f}$ will be based on comparisons between runs of equivalent initial chloroform concentrations.

The points in Figs. 1 and 2 appear to approximate straight lines. Probably the simplest interpretation of this fact is a competition between hydroxide and water for a particular intermediate. The sole product of the reaction of the intermediate with hydroxide is assumed to be formate and the sole product of the reaction of the intermediate with water is assumed to be carbon monoxide. It is also assumed that these are the only paths by which these products are formed.

From the data of Horiuti, Tanabe, and Tanaka (13) it has been estimated that hydroxide is only about 30 times more effective than water in competing for dichloromethylene intermediates. The slope of the curve in Fig. 1, however, indicates that, according to the mechanism proposed above, hydroxide is 339 times more effective than water in competing for the last intermediate common to the formation paths of both products. Thus,

$$\frac{d\left[HCO_2^-\right]}{d\ CO} = \frac{k_b\left[OH^-\right]}{k_w\ H_2O} = \frac{f}{1-f}$$

$$k_b/k_w = \text{slope x } [H_2O] = \frac{0.50 - 0.00}{0.0918 - 0.010} \times 55.5 = 339.$$

Consequently, this last common intermediate does not appear to be dichloromethylene.

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(13) J. Horiuti, K. Tanabe, and K. Tanaka, op. cit., pp. 147-184.

The last common intermediate suggested by Fells and Moelwyn-Hughes (5) is formyl chloride which decomposes to CO and HCl or reacts with water to give formate. These product determining steps were proposed for the acidic hydrolysis of $CHCl_3$, and no allowance was made for a reaction involving hydroxide that leads predominantly to formate.

From the dashed line in Fig. 1 it is seen that a curve whose slope increases rapidly at first may fit the points as well as a straight line. A more complex series of reactions is required if the dashed line is more representative of the actual situation. More than one product determining step seems necessary anyway since Hine and Langford (6) have found a value of f of 0.114 and Fells and Moelwyn-Hughes report data that permit an estimate of f of 0.21 for acidic hydrolyses of chloroform.

Table 4 contains a list of values for f that have been reported for a variety of haloforms. The initial haloform and base concentrations were not always reported for the alkaline hydrolytic experiments in which the formate yields were determined. Consequently, these values of f can only serve for qualitative comparisons. From this table it can be seen that replacing all chlorines in $CHCl_3$ by bromine decreases the value of f and replacement of one or more chlorines by fluorine increases the value of f. Since the value of f for $CHClBr_2$ is higher than that for bromoform and the same as that for chloroform, intermediates containing more than one halogen may not be involved in product determining steps. A comparison of f values for haloforms in Table 4 that contain fluorine indicates that the nature of the other halogen in the dihalomethylene (14)

(14)   J. Hine and S. J. Ehrenson, J. Am. Chem. Soc., 80, 824 (1958).

Table 4. Values of $\underline{f}$ for Various Haloforms

Haloform	Temperature ($^{\circ}$C.)	pH Range	$\underline{f}$	Reference
$CHCl_3$	35	alkaline	0.15	(1)[a]
$CHCl_3$	100	acidic	0.11	(6)
$CHClBr_2$	40	alkaline	0.16	(15)
$CHBr_3$	25	alkaline	0.08	(1,14)[a]
$CHFCl_2$	0	alkaline	0.72	(16)
$CHBrClF$	14	alkaline	0.63	(1)[a]
$CHFBr_2$	20	alkaline	0.54	(15)
$CHFI_2$	21	alkaline	0.34	(15)
$CClF_2CO_2H$	100	acidic	0.71	(17)
CCl_2FCO_2H	100	acidic	0.55	(17)

[a]These values were determined in 66 2/3% dioxane-water solution.

from these haloforms has some effect on the value of $\underline{f}$. The effect of halogens is apparently in the same direction regardless of whether the halogen is the last or next to last halogen to be lost. The order of ability to increase $\underline{f}$ is $I < Br < Cl < F$. This is the reverse of the ability of the halogens to stabilize methylene intermediates (14), but it is the order of bond strengths. This ability of the halogens to

(15) J. Hine, R. Butterworth, and P. B. Langford, J. Am. Chem. Soc., 80, 819 (1958).

(16) J. Hine and N. W. Burske, ibid., 78, 3337 (1956).

(17) J. Hine and D. C. Duffey, ibid., 81, 1129, 1131 (1959).

increase f is also essentially the reverse of the order of the effect of halogens on S_N2 reactivity of other halogens attached to the same carbon (18).

The reaction scheme of Fells and Moelwyn-Hughes (cf. p. 2), when modified as shown below, can be made to fit qualitatively the observations of this work and those reported in Table 4 on the variations of f in haloform hydrolyses. Reaction 1 in this sequence is probably applicable

$$CCl_2 + H_2O \text{ (or } OH^-) \xrightarrow[H_2O]{} CHCl_2OH \tag{1}$$

$$CHCl_2OH \xrightarrow[OH^-, H_2O]{} HCOCl + HCl \tag{2}$$

$$CHCl_2OH + OH^- \longrightarrow CHCl(OH)_2 + Cl^- \tag{3}$$

$$CHCl(OH)_2 \longrightarrow HCO_2H + HCl \tag{4}$$

$$HCOCl \longrightarrow CO + HCl \tag{5}$$

$$HCOCl + H_2O \text{ (or } OH^-) \longrightarrow HCO_2H + HCl \text{ (or } Cl^-) \tag{6}$$
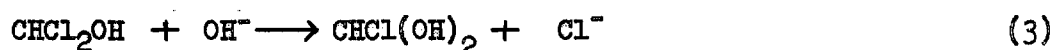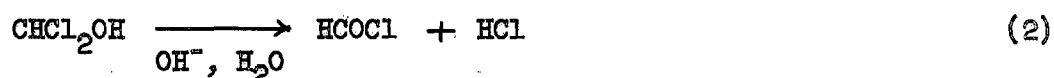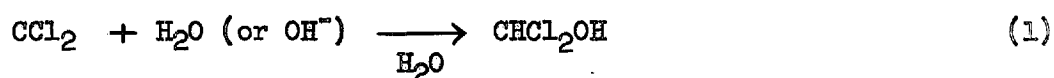
only in alkaline hydrolyses since dichloromethanol has been suggested (5) or implied (6) as the initial intermediate for acidic hydrolyses. Reaction 2 was suggested by Fells and Moelwyn-Hughes (5), but it may involve more than one step. The first step for Reaction 2 may be a dissociation to hydroxychloromethyl carbonium ion and chloride ion accompanied by sharing of a non-bonding electron pair on the oxygen analogous to the first step of the S_N1 reaction of α-haloethers (19,20) of proton removal

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(18) J. Hine, S. J. Ehrenson, and W. H. Brader, Jr., _ibid._, _78_, 2282 (1956).

(19) P. Ballinger, P. B. D. de la Mare, G. Kohnstam, and B. M. Prestt, _J. Chem. Soc._, 3641 (1955).

(20) Part Four of this thesis.

by hydroxide. Reaction 3 is analogous to the S_N2 reactions of α-haloethers (19,20). It might be expected that Reaction 3 would be more important for the alkaline hydrolysis of $CHFCl_2$ than for $CHCl_3$ since fluorine seems to decrease S_N2 reactivity less than chlorine (18). It might also be expected that a higher yield of formate would be observed in the alkaline hydrolysis of $CHFCl_2$ than is found in the decarboxylation of $CFCl_2CO_2H$ (17) in acidic solution. Both of these expectations are realized as judged by the data in Table 4. Reaction 4 may be a combination of steps also, but its occurrence is not surprising in view of the similarity to Reactions 2 and 6. The occurrence of Reaction 5 would also hardly be surprising in an aqueous medium since formyl chloride appears to be unstable even at -80° (21). Its decomposition is reported to be accelerated in aqueous solution and to give only small amounts of formic acid (21). The likelihood of Reaction 6 is probably greater in alkaline solution where water is replaced by hydroxide.

Conversion of CO to sodium formate by sodium hydroxide is probably of minor importance in this work. An initial rate constant for this conversion has been determined by Christiansen and Gjaldbaek (22) to be about 10^{-5} sec.$^{-1}$ in 1 $\underline{M}$ NaOH at 54°. The stability of sodium formate in alkaline solution was demonstrated in Table 2, while the stability of formic acid in dilute aqueous solutions has been shown by Barham and Clark (23).

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(21) K. B. Krauskopf and G. K. Rollefson, _J. Am. Chem. Soc._, _56_, 2542 (1934).

(22) J. A. Christiansen and J. C. Gjaldbaek, _Kgl. Danske Videnskab._, _Mat.-fys._, _20_, No. 3 (1942).

(23) H. N. Barham and L. W. Clark, _J. Am. Chem. Soc._, _73_, 4638 (1951).

Reaction sequences other than the one presented here may adequately account for the variations of $\underline{f}$ in haloform hydrolysis, but the available data would not seem to permit a choice between them. Consequently, the sequence presented is not intended to portray the only feasible post-rate-determining steps. Instead this sequence is intended as an example of what may be the minimum necessary complexity.

CHAPTER V

RECOMMENDATIONS

It is felt that values of f should be determined over a wider range of base concentrations than used in this work. It would also be desirable in continuation of this work to determine the nature of variations, if any, in formate yields for haloforms other than chloroform.

It seems likely that better correlations may be obtained in the variations of f if the formate yields are determined accurately during the early part of the reactions so as to allow extrapolation to zero reaction time where the initial base concentration may be used for comparisons rather than the averaged base concentrations used in this work.

The method of Hopton (24) should also be used in some cases to determine formate yields from haloform hydrolysis. This method, though somewhat more tedious than the one used in this work, has the advantage of utilizing the reducing properties of formic acid rather than its acidity and could, therefore, be applied to fluorine-containing haloforms without interference from NaF.

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(24) J. W. Hopton, Anal. Chim. Acta, 8, 429 (1953).

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PART TWO

THE DECOMPOSITION OF

DICHLOROFLUOROACETIC ACID

CHAPTER I

INTRODUCTION

The decomposition of trichloro-(1,2) and trifluoroacetic acids (3) has been investigated and found to be a unimolecular decomposition of the trihaloacetate anion to give a trihalomethide ion that is subsequently protonated.

$$CX_3CO_2^- \longrightarrow CO_2 + CX_3^-$$

$$CX_3^- + H_2O \longrightarrow CHX_3 + OH^-$$
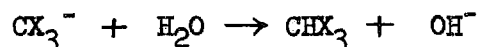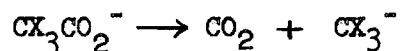
When the reaction of dichlorofluoroacetic acid was studied (3), halide ions were found in the solution after a short time. This observation was taken as evidence of hydrolysis prior to decarboxylation of the acid. The investigation was apparently abandoned at this point.

The work to be described here was undertaken in part as an extension of studies on the alkaline hydrolysis of dichlorofluoromethane (4) and also as a comparison with the decomposition of chlorodifluoroacetic acid to be described in a subsequent part of this thesis.

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(1) F. H. Verhoek, J. Am. Chem. Soc., 56, 571 (1934).

(2) R. A. Fairclough, J. Chem. Soc., 1186 (1938).

(3) I. Auerbach, F. H. Verhoek, and A. L. Henne, J. Am. Chem. Soc., 72, 299 (1950).

(4) J. Hine and N. W. Burske, ibid., 78, 3337 (1956).

CHAPTER II

PROCEDURE

Identification and Estimation of Gaseous Products.--In preliminary

studies a 40 ml. round-bottomed flask was fitted with a gas inlet tube,

immersed in an oil bath at about 100°, and used to contain 25 ml. of

the reaction solution. This flask was attached to the mercury-filled

gas buret of an Orsat apparatus through a 100 mm. water-cooled con-

denser. At intervals nitrogen was bubbled through the solution and

collected in the buret. The contents of the buret were then emptied into

a 10 cm. gas cell with sodium chloride windows. The contents of the

cell were analyzed on a Perkin-Elmer Model 21 Spectrophotometer with

sodium chloride optics.

This procedure proved only moderately satisfactory for quantita-

tive estimation of carbon dioxide; hence, this product was determined

in some runs by difference in volume after the gases had been passed

through a Fisher absorption pipet containing 36% aqueous potassium

hydroxide (5). Some $CHCl_2F$ was also absorbed in the alkaline solution,

but this quantity could be determined accurately by infrared analysis

in runs where the gases were not passed through alkaline solutions.

The difference in $CHCl_2F$ yield between runs where KOH absorption was

and was not used could then be subtracted from the total quantity of

gases absorbed by the KOH to give the yield of carbon dioxide.

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(5) P. W. Mullen, Modern Gas Analysis, Interscience Pub., Inc.,
New York, N. Y., 1955, p. 137.

The infrared absorption bands used to identify the reaction products are listed in Table 1 with their extinction coefficients.

Table 1. Infrared Absorption Peaks
and Extinction Coefficients

Compound	Wave Length (μ)	($1-mole^{-1}-cm^{-1}$)
Dimethyl oxalate	5.66	485 ± 15
" "	5.74	711 ± 13
" "	7.63	298 ± 4
" "	8.32	512 ± 1
" "	8.70	581 ± 17
" "	10.39	77 ± 1
" "	10.66	99 ± 1
" "	12.94	200 ± 9
CHF_3	7.26	140 ± 50
"	8.70	1500 ± 500
$CHFCl_2$	7.62	11.7 ± 0.9
"	8.04	48 ± 2
"	8.08	46 ± 4
"	9.23	209 ± 1
"	9.33	190 ± 10
$CHClF_2$	3.37	19.9 ± 0.5
"	4.59	6.0 ± 0.4
"	7.58	88.2 ± 2.7
"	7.63	88 ± 11
"	7.69	54.9 ± 2.4
"	8.84	206 ± 9
"	8.96	670 ± 100
"	9.04	336 ± 11
"	12.19	175 ± 12
"	12.35	203 ± 16
"	12.47	128 ± 9
CO_2	4.34	46^{a}
CO	4.65	20.3 ± 0.5

[a]For the resolution and scanning speed used, the value was not greater than 108 or less than 40.

The absorptions of dimethyl oxalate were determined in CS_2 solution. The extinction coefficients in Table 1 for the stronger bands were determined at optical densities of 0.05 to 1.5, but they are believed to be accurate to within 5% for optical densities of 0.2 to 0.7.

Chloride Analysis.--The solution was first titrated with standard aqueous sodium hydroxide to the phenolphthalein endpoint, reacidified with a few drops of dilute, chloride-free perchloric acid, and finally titrated with standard silver nitrate using the method of Mohr.

Formate Analysis.--The procedure of Hopton (6) was tested on a number of solutions containing the reaction products in appropriate concentrations, found satisfactory, and used without substantial modification.

Fluoride Analysis.--The fluoride determinations were carried out as described by Kolthoff and Sandell (7) using thorium nitrate with alizarin red as an indicator. Thorium also gives an insoluble oxalate salt, however, so an aliquot of the reaction solution was also treated with enough silver nitrate to precipitate essentially all of the oxalate and chloride. The precipitate was removed by filtration and the filtrate was titrated with standard thorium solution. Titration of the solution after removal of oxalate permitted the calculation of the fluoride content on the basis of between five and six fluoride atoms removed per atom of thorium required to turn the solution from yellow to pinkish-violet. The exact quantity of fluoride or oxalate removed per atom of thorium was determined by titration of solutions containing known quantities of sodium oxalate and/or potassium fluoride.

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(6) J. W. Hopton, Anal. Chim. Acta, 8, 429 (1953).

(7) I. M. Kolthoff and E. B. Sandell, Quantitative Inorganic Analysis, 3rd ed., Macmillan Co., New York, N. Y., 1952, p. 721.

<u>Oxalate Analysis</u>.--An estimate of the oxalate in a reaction solution was made in addition to that obtained from fluoride determinations. This method consisted of removal of oxalate from the solution by precipitation with a two-fold excess of silver nitrate. The resulting precipitate was washed, dried in an oven for about one-half hour at temperatures not exceeding 90°, and was finally dried overnight in an evacuated desiccator. The dried precipitate was then ground to a fine powder and heated under reflux for one to three hours with about 20 ml. of methyl iodide. All but about two ml. of the excess methyl iodide was removed by fractional distillation, and the pot residue was heated under reflux briefly with 25 ml. of carbon disulfide. The infrared spectrum of the carbon disulfide solution was then recorded, and the oxalate content was determined from the extinction coefficients listed in Table 1.

This procedure was first tested on solutions of known oxalate content and found satisfactory. Using this method, quantities of oxalate as small as 10^{-5} mole may be determined with fair accuracy.

<u>Kinetics by Titration</u>.--In contrast to the decomposition of other trihaloacetic acids, the rate of decomposition of $CFCl_2CO_2H$ may not be determined solely by following changes in acid concentration. As earlier workers have observed (3), the decomposition is complicated by the formation of halide ion in the reaction solution.

As a result, the reaction was followed by both acidimetric and argentometric titrations. The kinetic experiments were carried out using 250 ml. of a sodium acetate-buffered, aqueous solution of the acid contained in a 250 ml. volumetric flask. The flask was immersed

in a constant temperature bath where the temperature remained within
0.1° of the desired value during the time the reaction was allowed to
proceed. At intervals, a 15 ml. sample was withdrawn from the flask
and titrated to determine acid and chloride content.

Reagents.--Dichlorofluoroacetic acid was obtained from the Columbia
Organic Chemicals Co., Inc. The material was found to have a neutrali-
zation equivalent of 147.1 ± 0.8 (calc., 146.9) and was used without
further purification. C. P. methyl iodide was obtained from the Amend
Drug and Chemical Corp. Sodium perchlorate, used to study ionic
strength effects, was obtained from the G. F. Smith Co. Fluoroform
was supplied by E. I. du Pont de Nemours and Co., Inc. Other haloforms
were obtained from the Matheson Chemical Co. Merck reagent grade silver
nitrate and chloroacetic acid were used. All other reagents were C. P.
products of the Baker Chemical Co. All chemicals were used without
purification other than drying.

CHAPTER III

RESULTS

From preliminary experiments it was found that carbon dioxide and dichlorofluoromethane were evolved as major products of the decomposition of dichlorofluoroacetic acid, while considerable chloride was formed in solution as Auerbach, Verhoek, and Henne had observed previously (3). In addition, however, appreciable amounts of carbon monoxide and traces of chlorodifluoromethane and fluoroform were also found among the gaseous products.

The first two products are those to be expected from a decarboxylation reaction analogous to that of trichloroacetic acid. The other products could have been formed through subsequent reactions of an intermediate trihalomethide ion analogous to reactions occurring in the hydrolyses of a number of haloforms.

When the reaction solution was saturated initially with sodium fluoride at room temperature and then heated at $90 \pm 5^\circ$, the yield of CHF_2Cl and of CHF_3 was greatly increased although even in this experiment less than 3% of the dichlorofluoroacetic acid decomposed to give these two haloforms.

The results of studies on the gaseous decomposition products are summarized in Tables 2 and 3. The first order rate constants appearing in Table 3 are based on the quantity of carbon dioxide evolved as measured by infrared spectrum and are accurate only with a factor of two. The lowest value of k may result from incomplete dissociation

Table 2. Solutions for the Study
of Gaseous Decomposition Products

Initial $CFCl_2CO_2H$ (mmole.)	Initial NaOAc (mmole.)	Time (sec. x 10^{-3})	Temp. (°C)	Run
3.00^a	0.0	72	90 ± 5	1
3.09^a	0.0^c	11.7	90 ± 5	2
6.23^b	12.9	13.0	94.9 ± 0.1	3

[a]Initial volume of reaction solution was 25 ml.

[b]Initial volume of reaction solution was 100 ml.

[c]Solution was initially saturated with NaF (~ 1 $\underline{M}$).

Table 3. Gaseous Decomposition Products

Run	CO_2	CO	Products (micromoles)			(10^6) k (sec.$^{-1}$)
			$CHFCl_2$	CHF_2Cl	CHF_3	
1	360	39	480	2	2	1.8
2	244	19	77	0.3	1.5	7.1
3	433	73	412	0.5	0.5	5.5

of the acid in a 0.1 $\underline{M}$ unbuffered solution and the rather large temperature variations.

Further investigation of the decomposition products in solution led to the results reported in Table 4. In Experiment II of this table the reaction solution was treated with an excess of aqueous silver nitrate and again titrated for fluoride. After correcting for dilution, the quantity of fluoride remaining after this treatment was unchanged within the experimental error (2%). This information indicates the

Table 4. Soluble Products

Experiment	Chloride	Products (% yield) Fluoride	Formate
I	23.8	-	10.1
II	26.1	28.6	11.8

absence of oxalate among the reaction products. In another experiment oxalate was sought by conversion to its dimethyl ester. This method showed that oxalate was not formed in a yield of more than 0.05%, if at all.

Another sample of dichlorofluoroacetic acid was refluxed for 195 hours in 6.5 $\underline{M}$ aqueous KF. The solution was then tested for oxalate by conversion to the dimethyl ester, and again the existence of any oxalate in the solution was questionable and could not have exceeded a yield of 0.3%.

From the data in Table 3 it is evident that much of the decomposition reaction is in essence a loss of carbon dioxide accompanied by formation of dichlorofluoromethane. To evaluate the importance of this reaction path, the reaction in Experiment II of Table 4 was allowed to go essentially to completion while the overall yields of CO_2, CO, and $CHFCl_2$ were determined by infrared analysis of the gases not absorbed by 36% aqueous KOH. The results of this analysis are reported in Table 5. This experiment was carried out for 62 hours at reflux. The numbers in the table are in mmoles.

Since no evidence was obtained to indicate products that contained the carboxylate carbon atom of the starting acid, it is assumed

Table 5. Gaseous Decomposition
Products (mmoles.)

$CFCl_2CO_2H$	NaOAc	Absorbed by KOH	Unabsorbed CO_2	CO	$CHFCl_2$
4.02	8.4	4.67	0.09	0.61	2.13

that CO_2 is produced in quantitative yield. Haloforms other than $CHFCl_2$ were produced in negligible amounts, and the rapidity of the alkaline hydrolysis of this haloform would indicate that some was absorbed by the KOH solution. Hence, $CHFCl_2$ is apparently produced in 71.6% yield based on the calculation below:

$$\frac{2.13 + (4.67 + 0.09 - 4.02)}{4.02} \times 100 = 71.6\%.$$

The fate of the <u>alpha</u>-carbon of $CFCl_2CO_2H$ may thus be accounted for completely within the combined experimental errors as shown below:

$$(CO) + (HCO_2^-) + (CHFCl_2) = 15.2\% + 11.8\% + 71.6\% = 98.6\%.$$

A check on the yields of carbon monoxide and formate is provided by the data in Table 4. In Experiment II the yields of chloride and fluoride are 26.1% and 28.6%, respectively, compared with a combined yield of 27.0% for carbon monoxide and formate.

From the preceding information on the products of $CFCl_2CO_2H$ decomposition, a procedure was developed for kinetic studies in which it was necessary only to determine the acid and chloride content of the

reaction solution at intervals. In this procedure the observed products are assumed to be formed according to the following stoichliometric equations:

$$CFCl_2CO_2H \longrightarrow CO_2 + CHFCl_2$$

$$CFCl_2CO_2H + H_2O \longrightarrow 2HCl + HF + CO_2 + CO$$

$$CFCl_2CO_2H + 2H_2O \longrightarrow 2HCl + HF + CO_2 + HCO_2H.$$
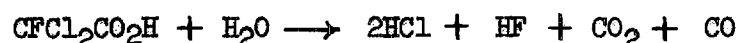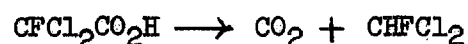
It is not necessary to specify the reaction mechanisms since the stoichiometry is not dependent on the mechanisms by which the products are formed. Thus, the concentration of chloride ion formed is a function of the amounts of dichlorofluoroacetic acid that has reacted and the amount of dichlorofluoromethane that has been formed as shown in Equation 1:

$$[Cl^-] = 2(\triangle[CFCl_2CO_2H] - [CHFCl_2]). \tag{1}$$

Similarly, the change in the total acid concentration may be expressed as shown in Equation 2:

$$\triangle [H^+] = (2 + \underline{f}) (\triangle[CFCl_2CO_2H] - [CHFCl_2]) - [CHFCl_2], \tag{2}$$

$$\text{where} \quad \underline{f} = [HCO_2^-] / ([HCO_2^-] + [CO]). \tag{3}$$

From Equations 1 and 2 the following equation may be obtained for the yield of dichlorofluoromethane:

$$\frac{[CHFCl_2]}{\triangle [CFCl_2CO_2H]} = 1 - \frac{1}{3 + \underline{f} - 2\triangle[H^+] / [Cl^-]}. \tag{4}$$

Analyses for the formate and carbon monoxide produced gave $\underline{f}$ values ranging from 0.44 to 0.66. An intermediate value of 0.50 has been used here in all calculations. An error of 20% in this value would change the calculated dichlorofluoromethane yield by less than 2% in the range of the observations made in this work.

The rate constants determined by this method are reported in Table 6.

Table 6. Decomposition Rates Determined by Titration

Run	Temp. (^{o}C)	Initial pH	$\dfrac{[CHFCl_2]}{\triangle[CFCl_2CO_2H]}$	Initial Ionic Strength	$10^6 \, k$ (sec.$^{-1}$)
9	71.3	5.02	0.72	0.77	0.18 ± 0.05
8	81.0	4.70	0.74	0.08	0.780 ± 0.006
1	90.5	5.02	0.75	0.17	3.39 ± 0.19
2	"	"	0.74	0.77	3.34 ± 0.17
3	"	"	0.73	1.37	3.25 ± 0.14
4	"	"	0.71	1.97	2.72 ± 0.06
5	94.8	4.77	0.75	0.11	7.02 ± 0.25
6	"	"	0.74	0.34	6.50 ± 0.06
7	"	6.25	0.63	0.89	6.97 ± 0.56

Because of the inaccuracy of carbon dioxide determinations used, a precise comparison of rate constants by titration and CO_2 evolution was not possible. From an experiment at 94.9°, however, which is reported in Table 2 and Table 3, a rate constant may be obtained from the

quantity of $CHFCl_2$ observed. In this run the nominal initial ionic strength was 0.10. Consequently, if the ratio of haloform to acid reacted is taken as 0.75, the value indicated by Table 6 for low ionic strengths, a first order rate constant of 7.12×10^{-6} sec.$^{-1}$ is obtained from the evolution of $CHFCl_2$. This value is in excellent agreement with the values reported in Table 6 at a slightly lower mean temperature. The temperature deviations during a run did not exceed 0.1°.

CHAPTER IV

DISCUSSION AND CONCLUSIONS

From the preceding experimental data it is possible to elucidate the various phases of $CFCl_2CO_2H$ decomposition with considerable clarity. First, it is clear that the slowest step in the reaction, as with other trihaloacetic acids, is the loss of CO_2 from the trihaloacetate anion leaving a trihalomethide ion.

The fate of the trihalomethide ion in this case appears to be three-fold. In solutions of pH 5 or less about three out of every four trihalomethide ions are protonated, presumably either by water or hydronium ions. In a 1 $\underline{M}$ solution of NaF, however, only about two-thirds of these intermediates eventually give rise to the haloform, and in a solution of pH 6.25 only a 63% yield of $CHFCl_2$ was obtained. An explanation of such decreases in haloform yield possibly rests on the accompanying decrease in hydronium ion concentration although it is not certain that the differences observed are large enough to be significant.

Horiuti, Tanabe, and Tanaka (8) observed in the deuterium exchange of chloroform in solutions of various acidities that at pH 5, or less, proton removal is effected by the base water, but at pH 6, or greater, proton removal by hydroxide becomes significant. Protonation of the trichloromethyl anion is thus effected predominantly by hydronium ions below pH 5 and predominantly by water above pH 6. An analogous situation may exist in the protonation of dichlorofluoromethide ions

(8) J. Horiuti, K. Tanabe, and K. Tanaka, $\underline{J}$. Research Inst. Catalysis, Hokkaido Univ., $\underline{3}$, 119, 147 (1955).

such that a considerable decrease in hydronium ion concentration favors increased decomposition of the dichlorofluoromethide ions to give products other than dichlorofluoromethane.

The data presented here are insufficient to permit an estimate of the amount of $CHFCl_2$, if any, that is formed and subsequently undergoes hydrolysis. Such a reaction probably accounts for a portion of the formic acid and CO observed, but since a dichlorofluoromethyl anion is the expected intermediate for the hydrolysis as well as the decarboxylation, some of the hydrolysis products are undoubtedly formed directly.

Hine and Burske (4) have reported that 7.8% of the trihalomethyl anions formed during the deuterium exchange of $CHFCl_2$ in alkaline solution decomposed to give formate and CO at 0°. At 20.2°, however, 9.4% of the intermediates decomposed in preference to reprotonation. Since these values indicate an increase in the fraction of dichlorofluoromethide ions decomposing as the temperature increases, it is conceivable that the fraction may be as high as 30% at 100° so that no subsequent hydrolysis of $CHFCl_2$ is required. The supposition that subsequent hydrolysis of $CHFCl_2$ contributes little to the total yield of carbon monoxide and formate is supported by the observation that nitrogen flushing, which probably removes a considerable portion of the dissolved $CHFCl_2$, had little or no effect on the yield of $CHFCl_2$ as determined from the ratio $(CHFCl_2)/\triangle(CFCl_2CO_2H)$.

When logarithms of the rate constants in Table 6 are plotted against the reciprocals of the corresponding temperatures, the slope of the curve indicates an activation energy of 40.8 ± 2.1 kcal./mole. Using this activation energy, the entropy of activation is 21.5 ± 2.0 e.u. as

calculated from the absolute rate equation (9).

$$k = \frac{kT}{h} \; e^{-\Delta H^{\ddagger}/RT} \; e^{\Delta S^{\ddagger}/R}$$

Auerbach, Verhoek, and Henne (3) found activation energies of 42.0 ± 0.5 and 31.6 kcal./mole for the decomposition of sodium trifluoro-acetate and sodium trichloroacetate, respectively, in ethylene glycol. The value for sodium trichloroacetate in water was 36.2 kcal./mole (1). The activation energy for $CFCl_2CO_2H$ decomposition as would be expected, lies between the values reported for CCl_3CO_2Na and CF_3CO_2Na even though these values may not be directly comparable.

The absence of significant S_N2 (10) reactivity by dichloro-fluoroacetic acid is indicated by the absence of oxalate among the decomposition products. It seems probable that even small amounts ($<1\%$) of chlorodifluoromethane and fluoroform do not result from reactions of the type below:

$$CFCl_2CO_2^- + F^- \longrightarrow CF_2ClCO_2^- + Cl^-$$

$$CF_2ClCO_2^- + F^- \longrightarrow CF_3CO_2^- + Cl^-$$

$$CF_3CO_2^- + H_2O \longrightarrow CO_2 + OH^- + CHF_3.$$
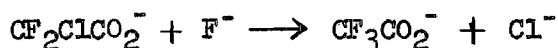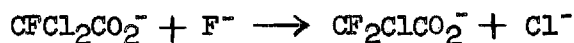
This conclusion is supported by the failure of a 1 M NaF solution to

(9) S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes, McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.

(10) For an explanation of the term S_N2, see J. Hine, Physical Organic Chemistry, McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 93-113.

increase the yield of CHF_2Cl and CHF_3 above 2%. Further evidence in support of this conclusion is provided by the preponderance of fluoroform over chloroform in the presence of added fluoride despite the much slower rate of decarboxylation of trifluoroacetic acid compared either to CF_2ClCO_2H or to $CFCl_2CO_2H$. Consequently, the small amounts of CHF_2Cl and CHF_3 observed among the decomposition products of $CFCl_2CO_2H$ are apparently derived by further reaction of the intermediate dichlorofluoromethide ion by a series of reactions similar to that shown below:

$$CFCl_2^- \longrightarrow CFCl + Cl^- \tag{4}$$

$$CFCl + F^- \longrightarrow CF_2 + Cl^- \tag{11}$$

$$CF_2 + F^- \longrightarrow CF_3^- \tag{12}$$

$$CF_3^- + H_2O \longrightarrow CHF_3 + OH^- \tag{13}$$

$$CF_2 + H_2O + Cl^- \longrightarrow CHF_2Cl + OH^-. \tag{14}$$
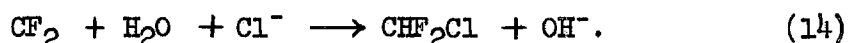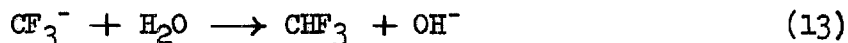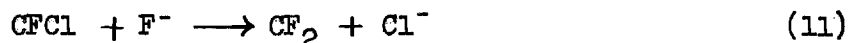
Since there is good evidence that the transformation of CHF_2X to CF_2 by the action of hydroxide ion is a concerted one-step process (13,14), it seems quite probable that a process of the reverse type, the reaction of chloride ions with CF_2, should also be concerted, yielding CHF_2Cl in a single step, as shown in the last reaction above. Since the CF_2Cl^- anion seems ordinarily to have no real existence as an

(11) J. Hine and S. J. Ehrenson, J. Am. Chem. Soc., 80, 824 (1958).

(12) J. Hine and K. Tanabe, ibid., 79, 2654 (1957).

(13) J. Hine and J. J. Porter, ibid., 5493 (1957).

(14) J. Hine and P. B. Langford, ibid., 5497 (1957).

intermediate, decomposing as it is formed, it seems improbable that it is an intermediate in the reaction of fluoride ions with CClF to give CF_2 and that this, too, is a concerted process as written above. On the other hand, the formation of fluoroform in good yield in the decarboxylation of trifluoroacetic acid (3) suggests that CF_3^- can be a real intermediate, and it is so shown above.

The greater yield of fluoroform compared to chlorodifluoromethane observed in this work is probably a result of the greater bond strength of the C-F bond compared to the C-Cl bond.

CHAPTER V

RECOMMENDATIONS

Of interest in continued pursuance of the work presented here is an investigation of the solubility and hydrolysis rate on dichlorofluoromethane in acidic aqueous media at various temperatures.

Further study of the decomposition of $CFCl_2CO_2H$ seems unnecessary at this point. This work has indicated, however, a definite desirability in developing a quantitative technique for measuring carbon dioxide by infrared absorption spectra. Such a procedure would be relatively free from the errors inherent in analysis by gas absorption methods and have a further advantage of requiring only a small quantity of carbon dioxide.

APPENDIX

Table 7. Description of Reaction Solutions

Run	Initial $CFCl_2CO_2H$ (mole/l.)	Initial NaOAc (mole/l.)	Temp. ($^\circ$C.)	Initial Ionic Strength	pH
1	0.0585	0.161	90.5	0.17	5.02
2	0.0573	0.161	90.5	0.77	5.02
3	0.0568	0.161	90.5	1.37	5.02
4	0.0574	0.161	90.5	1.97	5.02
5	0.0547	0.112	94.8	0.11	4.77
6	0.1619	0.336	94.8	0.34	4.77
7	0.0274	0.847	94.8	0.89	6.25
8	0.0455	0.080	81.0	0.08	4.70
9	0.0573	0.161	71.3	0.77	5.02

Table 8. Run 1

$AgNO_3$ = 0.1356 $\underline{M}$ $\Delta[H^+]/[Cl^-]$ = -0.23 $CHFCl_2$ = 75%

Time (sec.)	ml. of $AgNO_3$[a]	10^6k (sec.$^{-1}$)
0	0.31	--
23,040	0.59	3.76
65,850	0.92	3.17
91,430	1.17	3.36
111,950	1.44	3.83
159,900	1.64	3.31
248,400	2.09	3.22

[a]15 ml. samples were titrated in all runs.

Table 9. Run 2

$AgNO_3$ = 0.1356 $\underline{M}$ $\triangle[H^+]/[Cl^-]$ = -0.20 $CHFCl_2$ = 74%

Time (sec.)	ml. of $AgNO_3$	$10^6 k$ (sec.$^{-1}$)
0	0.30	--
65,850	1.00	3.67
91,430	1.17	3.42
111,950	1.33	3.39
159,900	1.60	3.19
248,400	2.12	3.33
347,100	2.41	3.03

Table 10. Run 3

$AgNO_3$ = 0.1356 $\underline{M}$ $\triangle[H^+]/[Cl^-]$ = -0.14 $CHFCl_2$ = 73%

Time (sec.)	ml. of $AgNO_3$	$10^6 k$ (sec.$^{-1}$)
0	0.33	--
65,850	0.97	3.36
91,430	1.21	3.39
111,950	1.37	3.36
159,900	1.61	3.06
248,400	2.12	3.11

Table 11.   Run 4

AgNO$_3$ = 0.1356 $\underline{M}$ $\triangle[H^+]/[Cl^-]$ = 0.00   CHFCl$_2$ = 71%

Time (sec.)	ml. of AgNO$_3$	$10^6 k$ (sec.$^{-1}$)
0	0.31	--
65,850	0.90	2.69
91,430	1.13	2.81
111,950	1.28	2.78
159,900	1.54	2.64
248,400	2.06	2.67

Table 12.   Run 5

AgNO$_3$ = 0.1356 $\underline{M}$ $\triangle[H^+]/[Cl^-]$ = -0.22   CHFCl$_2$ = 75%

Time (sec.)	ml. of AgNO$_3$	$10^6 k$ (sec.$^{-1}$)
0	0.12	--
49,700	1.09	7.63
66,270	1.27	7.08
134,600	2.01	7.11
158,100	2.07	6.36
181,100	2.31	6.89
231,200	2.58	6.94
232,300	2.62	7.22

Table 13. Run 6

AgNO$_3$ = 0.1356 $\underline{M}$ $[H^+]/[Cl^-]$ = -0.18   CHFCl$_2$ = 74%

Time (sec.)	ml. of AgNO$_3$	10^{6}k (sec.$^{-1}$)
0	0.23	--
49,700	2.78	6.49
66,270	3.53	6.61
134,600	5.63	6.47
158,100	6.22	6.55
181,100	6.65	6.55
231,200	7.36	6.30
232,300	7.48	6.53

Table 14. Run 7

AgNO$_3$ = 0.1356 $\underline{M}$ $[H^+]/[Cl^-]$ = 0.41   CHFCl$_2$ = 63%

Time (sec.)	ml. of AgNO$_3$	10^{6}k (sec.$^{-1}$)
0	0.19	--
49,700	0.91	7.69
66,270	1.08	7.55
134,600	1.50	6.44
181,100	1.81	6.94
231,200	1.91	6.16
232,300	1.94	6.39

Table 15. Run 8

AgNO$_3$ = 0.0501 $\underline{M}$ [H$^+$]/[Cl$^-$] = -0.13   CHFCl$_2$ = 73%

Time (sec.)	ml. of AgNO$_3$	10^6k (sec.$^{-1}$)
0	0.28 ± 0.02	--
143,400	1.09 ± 0.03	0.772
234,500	1.59 ± 0.01	0.784
315,100	1.98 ± 0.01	0.784

Table 16. Run 9

AgNO$_3$ = 0.1356 $\underline{M}$ [H$^+$]/[Cl$^-$] = -0.04   CHFCl$_2$ = 72%

Time (sec.)	ml. of AgNO$_3$	10^6k (sec.$^{-1}$)
0	0.12	--
260,100	0.28	0.18

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12. Hine, J., and K. Tanabe, *ibid.*, 79, 2654 (1957).

13. Hine, J., and J. J. Porter, *ibid.*, 5493 (1957).

14. Hine, J., and P. B. Langford, *ibid.*, 5497 (1957).

PART THREE

THE DECOMPOSITION OF

CHLORODIFLUOROACETIC ACID
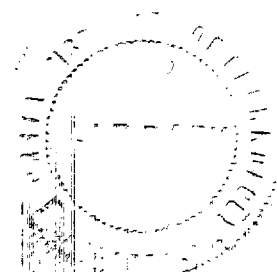
CHAPTER I

INTRODUCTION

A number of haloforms including chloroform (1), dichlorofluoro-
methane (2), and dibromofluoromethane (3,4) have been found to undergo
base-catalyzed deuterium exchange in accordance with the reactions illus-
trated below:

$$CDX_3 + OH^- \longrightarrow HOD + CX_3^-$$

$$CX_3^- + H_2O \longrightarrow CHX_3 + OH^- .$$
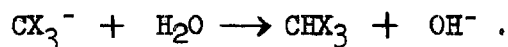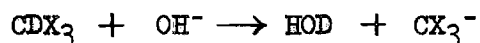
When deuterated bromodifluoromethane was subjected to the same
treatment, however, the deuterium content of the unreacted haloform was
found to increase slightly as the reaction progressed (5).

It has been shown that $CHClF_2$ (6), like $CHCl_3$ (7) and a number
of other haloforms, gives a reaction with base that involves the

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(1) J. Hine, R. C. Peek, Jr., and B. D. Oakes, *J. Am. Chem. Soc.*,
76, 827 (1954).

(2) J. Hine and N. W. Burske, *ibid.*, 78, 3337 (1956).

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(1958).

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79, 1406 (1957).

(5) J. Hine and P. B. Langford, *ibid.*, 79, 5497 (1957).

(6) J. Hine and J. J. Porter, *ibid.*, 5493 (1957).

(7) J. Hine, *ibid.*, 72, 2438 (1950).

formation of dihalomethylene intermediates, but the rate of formation of difluoromethylene from $CHClF_2$ was many times faster even than the anticipated rate of chlorodifluoromethide ion formation. Since this carbanion is analogous to the precursors of dihalomethylenes in the hydrolyses of other haloforms, it was felt that $CHClF_2$ may not hydrolyze by the same mechanism followed by $CHCl_3$. In fact, the ease of formation of CF_2 intermediates from $CHClF_2$ and $CDBrF_2$ and the lack of deuterium exchange with $CDBrF_2$ caused Hine and Langford (5) to propose a concerted α-dehydrohalogenation as the first step in the hydrolysis of haloforms containing two fluorine atoms.

It is still possible, of course, the chlorodifluoromethide ions are actually formed during the hydrolysis of $CHClF_2$, but they always lose chloride, or bromide in the case of $CHBrF_2$, in preference to reprotonation by water.

In this work it was decided to generate the chlorodifluoromethide ion, if such existed, under conditions more favorable toward its protonation. For this purpose the study of the decomposition of chlorodifluoroacetic acid was undertaken.

Fairclough (8) and Verhoek (9) have observed that the decomposition of trichloroacetic acid in protonic solvents takes place according to the reaction scheme shown below where the second step is rate-controlling. Such a mechanism,

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(8) R. A. Fairclough, J. Chem. Soc., 1186 (1938).

(9) F. H. Verhoek, J. Am. Chem. Soc., 56, 571 (1934).

$$CCl_3CO_2H \longrightarrow CCl_3CO_2^- + H$$

$$CCl_3CO_2^- \longrightarrow CCl_3^- + CO_2$$

$$CCl_3^- + H_2O \longrightarrow CHCl_3 + OH^- ,$$
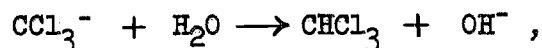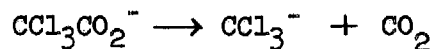
has been found to hold also for other trihaloacetic acids including CBr_3CO_2H (8), $CClBr_2CO_2H$ (10), $CClBrFCO_2H$ (10), CF_3CO_2H (11), and CCl_2FCO_2H (12).

Auerbach, Verhoek, and Henne (11) have observed that halide ions were formed rapidly in heated solutions of sodium chlorodifluoroacetate. These workers accounted for their observation by a hydrolysis of the acid that competed with decarboxylation. They reached the same conclusion in the case of dichlorofluoroacetic acid. This acid has since been found (12) to undergo decarboxylation as a first step invariably within experimental error. It was thought, therefore, that the same situation might also prevail with chlorodifluoroacetic acid.

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(10) L. H. Sutherland and J. G. Aston, _ibid._, _61_, 241 (1939).

(11) I. Auerbach, F. H. Verhoek, and A. L. Henne, _ibid._, _72_, 299 (1950).

(12) Part Two of this thesis.

CHAPTER II

PROCEDURE

The reaction techniques and analytical methods employed in this work have been described in Part Two of this thesis on the decomposition of dichlorofluoroacetic acid.

Reagents.--Sodium chlorodifluoroacetate, obtained from the Custom Chemical Co., was found to contain some $CFCl_2CO_2Na$ and other impurities. The salt was purified by the following procedure: 35-40 g. of the salt was dissolved in 100 ml. concentrated sulfuric acid. The resulting solution was distilled at 40 mm. through a 200 mm. column packed with tantalum heligrids until the pot temperature reached 115°, and the head temperature was 55°. The pot residue was diluted several fold with ice and water and then extracted with three 50 ml. portions of ether. The ether was removed from the combined extracts with the water pump leaving a residue of about 2 g. This residue still possessed a strong odor of ether and did not freeze at 0°. It was discarded. The distillate from the fractionation at reduced pressure was refractionated through the same column to give about 10 g. of distillate, b. p. 114-115° (740 mm.). This material melted sharply within the range 25-26° and had a neutralization equivalent of 130.5 ± 0.5. It was used as the chlorodifluoroacetic acid without further purification. The reported values for chlorodifluoroacetic acid are: m. p. 22.9°; b. p. 121.5° (13). The calculated neutralization equivalent is 130.5.

(13) Beilstein's Handbuch der organischen Chemie, Vol. II, 4th ed., Julius Springer, Berlin, Germany, 1920, p. 201.

In later experiments chlorodifluoroacetic acid was obtained from the Columbia Organic Chemicals Co. This product was used without further purification since it melted at 25-26° and had a neutralization equivalent of 131 ± 1.

Other materials used in this work were reagent grade with the exceptions of sodium fluoride and sodium bromide which were of technical grades. Sodium iodide was obtained from Merck and Company, Inc.; lithium bromide was obtained from the Baker Chemical Corp.; bromodifluoromethane was supplied by E. I. du Pont de Nemours and Co., Inc.; difluoroiodomethane was prepared by Hine and Langford (5).

Solubility of Chlorodifluoromethane.--A 40 ml. vessel was used to contain 25 ml. of an aqueous solution that had been buffered at pH 4.7 with sodium acetate-acetic acid. The solution was first cooled in a dry ice-acetone bath while the vessel was evacuated. It was then warmed to 0° with ice-water mixtures while the system was filled with $CHClF_2$ to a pressure of 742 mm. More of the haloform was added occasionally until the pressure remained constant for 15 minutes. The volume of $CHClF_2$ taken up by the solution was then calculated from the combined pressure drops. The solution was then immersed in a bath at 97° while the system was attached to a mercury manometer. The decrease in solubility of $CHClF_2$ on going to the higher temperature was then calculated from the increase in pressure once corrections had been made for changes in the vapor pressure of the aqueous solution alone.

CHAPTER III

RESULTS

In view of the observations made (11) on a previous study of the decomposition of chlorodifluoroacetic acid, experiments were first carried out to determine the nature and yields of the decomposition products.

Gaseous Products.--The gaseous products, as identified by infrared absorption, were carbon dioxide, carbon monoxide, formic acid, chloro-difluoromethane, and fluoroform. When lithium bromide or sodium iodide was added, bromodifluoromethane or difluoroiodomethane was observed among the products in an amount comparable to the yield of fluoroform in the absence of added salts. The results of the experiments on gaseous decomposition products are summarized in Table 1. No infrared absorption bands were observed that could not be attributed to these products. All experiments in Table 1 were carried out at or near the boiling point of the aqueous solution using 25 ml. of solution. An explanation of the data in this table is dependent on other factors that will be considered in subsequent sections.

Products in Solution.--In accordance with the observation of Auerbach, Verhoek, and Henne (11), experiments were carried out to determine the yield of chloride from chlorodifluoroacetate decompositions. The results of these experiments are reported in Table 2. All of the solutions were buffered with sodium acetate and the estimated methodical

Table 1. Gaseous Decomposition Products
from $CClF_2CO_2H$ in Aqueous Solutions at 100°

Experiment	Initial CF_2ClCO_2H (mmole.)	Initial NaOAc (mmole.)	Elapsed Time (sec.)	Added Salt	Molarity of Added Salt	Products (μ-moles.)			
						CO_2	CO	CHF_2Cl	CHF_3
1	4.31	0.0	17,570	None	-	137	8	1.4	0.1
2	3.3	0.0[a]	86,460	"	-	370	84	4.1	12
3	1.32	4.7	311,500	"	-	396	156	3.6	6.6
4	2.63	3.8	420,600	"	-	791[b]	121	11.3	9.3
5	2.92	6.0	650,700	"	-	1622[b]	227	21.3	23.5
6	3.3	0.0	39,600	NaCl	2.6	140	22	11	0.1
7	2.94	6.3	78,120	KF	2.2	57.2[b]	6.1	1	47.2
8	3.3	0.0	64,800	NaF	1.0	86	21	0.3	19.2
9	3.3	0.0	72,000	LiBr	1.3	116	40	3	0.1
10	3.3	0.0	68,400	NaI	2.6	370	64	5.0	2.2

[a]The solution was initially neutralized with NaOH.

[b]CO_2 was measured in these runs by absorption with 36% KOH.

Table 2. Chloride Yield from CF_2ClCO_2H

Temp. ($^{\circ}$C.)	Time (hrs.)	Chloride Yield (%)
71.6 ± 0.1	149.9	5.7
97.1 ± 0.1	146.5	61.7
99 ± 1	135	76.6
99 ± 1	181	82.0
99 ± 1	192	89.5
99 ± 1	238	95.4
99 ± 1	285	95.5
99 ± 1	324	98.8
99 ± 1	350	98.3

experimental error in chloride yield based on the initial quantity of CF_2ClCO_2H was 0.7%.

From Table 2 the maximum yield of chloride would appear to be in the range 98-99%. The fate of the remaining 1-2% of the chloride is apparently the formation of CHF_2Cl in accordance with the data of Table 1.

In Table 1 there is also an indication that the presence of added fluoride ion decreases the rate of formation of all of the gaseous products except fluoroform. This seemingly anomalous behaviour was investigated further through the effect of added fluoride ion on the chloride yield from the decomposition. The results of these experiments appear in Table 3. The data from this table indicate a great increase in the rate of chloride formation in the presence of added fluoride in contrast to the data of Table 1 which shows a considerable decrease in the rate of CO_2 evolution when fluoride ion was present. The virtually quantitative yield of chloride reported in Table 3 is in

Table 3. Effect of Added Fluoride on Chloride Yield

Temp. ($^{\circ}$C.)	Added NaF or KF (moles/l.)	Time (hrs.)	Chloride Yield (%)
97.2 ± 0.1	1.0	92.7	78.3
94.9 ± 0.1	2.3	92.1	92.5
99 ± 1	2.2	22	83.6
99 ± 1	1.4	115	100.4
99 ± 1	3.2	164	99.6

agreement with the data in Table 1 where the observed CHF_2Cl probably resulted largely from decomposition of CF_2ClCO_2H prior to preparation of the reaction solution.

The conflicting observations on rates of CO_2 and chloride formation in the presence of added fluoride were taken as evidence of another major decomposition product(s) which contained the carbon dioxide moiety but did not contain chloride. A conceivable product fitting this description is trifluoroacetic acid which could arise from a nucleophilic attack by fluoride on the chlorodifluoroacetate anion or acid. Trifluoroacetic acid was found to decompose to an extent not greater than 2% under the conditions of these experiments in accordance with the observations of other workers (11).

To check for the presence of trifluoroacetic acid among the reaction products, a 2.3 $\underline{M}$ solution of KF containing CF_2ClCO_2H and NaOAc was heated at 94.9° for 92.1 hours. In this time 92.5% of the available chloride had been liberated. A portion of this reaction solution was made alkaline with a slight excess of aqueous NaOH, and

the water was removed with the water pump. The residue was shaken with
ethylene glycol, and the resulting mixture was heated at 165° for 2.25
hours during which time a 16.0% yield of CHF_3 was obtained. In this time
there was little dimunition in the rate of evolution as would be expected
from a half-life of about 24 hours for CF_3CO_2H at this temperature (11).
The half-life of CF_2ClCO_2H at this temperature is probably much less than
ten minutes. Only fluoroform and carbon dioxide were found among the
gaseous products from the glycol solution. Consequently, at least 8%
of the initial CF_2ClCO_2H was converted to CF_3CO_2H though the correct
yield is probably very much higher.

In Experiment 5 of Table 1 after 180.9 hours when the yield of
carbon dioxide was 55.4%, the chloride yield was 81.8%. In Experiment
3 of this table after 86.5 hours when the yield of carbon dioxide was
only 30%, the yield of chloride was 55.1%. This information served to
indicate the presence of still another decomposition product. This
product was identified as oxalic acid. The yields of oxalate, as deter-
mined by conversion to its dimethyl ester, in a number of experiments
are reported in Table 4. The yields in this table are based on the
amount of chloride produced in the same time. The mean yield of oxalate
over the pH range 4.2 to 5.4 is $23 \pm 3\%$. The experimental error was
about 2%.

Since trifluoroacetate has been found among the decomposition
products in the presence of added fluoride, several experiments were
carried out to enable an estimation of the effect of added fluoride on
oxalate yields. The results of these experiments are summarized in
Table 5. Under the conditions of these experiments there is negligible
decomposition of trifluoroacetate to give oxalate.

Table 4. Oxalate Yields

Expt.	Initial pH	Temp. (°C.)	Time (hrs.)	Oxalate Yield (%)
1	1.0	99 ± 1	135	43
2	1.1	99 ± 1	180	42
3	4.2	99 ± 1	145	23
4	4.3	77 ± 2	458	22
5	4.3	77 ± 2	458	24
6	4.5	99 ± 1	457	28
7	4.7	99 ± 1	238	20
8	4.9	99 ± 1	457	19
9	5.0	99 ± 1	191	27
10	5.4	99 ± 1	324	23

Table 5. The Effect of Fluoride on Oxalate Yield

Added Fluoride (moles/l.)	Reaction Time (hrs.)	Temp. (°C.)	Oxalate Yield (%)
1.4	115	99 ± 1	21
3.2	164	99 ± 1	18
2.3	92.1	94.9 ± 0.1	13

In addition to chloride and oxalate, several runs were made in which the yields of fluoride and formate were determined in the absence of added salts. The results of these determinations are shown in Table 6. The yields are based on chloride.

To give an overall picture of the distribution of decomposition products of chlorodifluoroacetic acid, in a single experiment all products were determined and the yields are presented in Table 7. In this table

Table 6. Yields of Fluoride and Formate

Expt.	Time (hrs.)	Fluoride (%)	Formate (%)
1	238	55	25.0
2	191	25	24.8
3	180.8	67	24.2
4	135	87[a]	28.3
5	350	88[a]	11.4[b]
6	285	--	--

[a]These yields were determined after the solution had stood at room temperature for several months.

[b]This low yield is attributed to prolonged refluxing at pH 3.6.

Table 7. Percentage Yields of Decomposition Products

CO_2	Oxalate	CO	Formate	CHF_2Cl	CHF_3
67 ± 2	34 ± 3	10 ± 1	24 ± 1	1.0 ± 0.2	1.0 ± 0.2
69 ± 2	--	8 ± 1	--	0.4 ± 0.1	1.1 ± 0.1

the oxalate yield was determined using thorium nitrate and may be somewhat high. The analysis is based on the sum of the chloride and chlorodifluoromethane yields since these accurately represent the quantity of acid that has decomposed in the elapsed time. The reaction time in the first run in Table 7 was 180.8 hours. The second run was allowed to react for only 25.7 hours. From this table it is seen that the carboxyl carbon is completely accounted for within the experimental error, but the fate of the α-carbon of the starting acid has been determined only

about 70% of the time. It is of interest that in the same experiments
the fluoride yield was 67%. Both of the experiments reported in Table 7
were carried out at reflux using a buffered solution of pH 4.8 initially.

It is evident from Table 1 that the discrepancy in the yield of
products containing the α-carbon of CF_2ClCO_2H is not due to absorption of
haloforms and CO along with CO_2 in the 36% KOH solution since the yields
of these products are essentially the same when this treatment is
omitted.

On the other hand it may be argued that the haloforms and CO,
once formed, largely remain dissolved in the reaction solution. To check
this possibility, several experiments were carried out to determine the
solubility and stability of chlorodifluoromethane in solutions typical
of those used in the study of CF_2ClCO_2H decomposition.

The solubility of chlorodifluormethane in a buffered solution of
pH 4.7 and ionic strength 0.19 under an atmosphere of CHF_2Cl is shown in
Table 8. During a reaction, of course, the partial pressure of CHF_2Cl

Table 8. Solubility of CHF_2Cl in Aqueous Acid

Temp. (°C.)	Pressure of CHF_2Cl Above Soln. (mm.)	Solubility (mole/l.)
0	742	0.028 ± 0.005
97	1324	0.013 ± 0.003
97	742	0.007 ± 0.003

above the solution is very low. Hence, the solubility would be considerably lower than reported in Table 8. This lowered solubility was generally reduced still further by boiling the solution or passing nitrogen through it.

Nevertheless, the stability of CHF_2Cl was studied as follows. A buffered, acidic (pH 5.0) solution was prepared in an ampoule and saturated with CHF_2Cl under an atmosphere of CHF_2Cl. The ampoule was then sealed and heated at 97.2° for 72 hours. After this time less than 20% of the initial CHF_2Cl had reacted as measured by chloride formation.

The action of fluoride ion on CHF_2Cl was tested similarly using 1.6 M NaOH solution saturated with NaF. After heating for one-half hour in an ampoule at 100°, 10% of the CHF_2Cl had been converted to CHF_3. No other gaseous products could be positively identified.

In another experiment a 0.0043 M solution of perchloric acid was made 10 M in KF and treated as before. After heating at 100° for 48 hours, the solution had become alkaline and 19% of the CHF_2Cl had been converted to CHF_3. Again no carbon monoxide could be found among the gases.

Kinetics.--Since chloride is formed in nearly quantitative yield in the decomposition of CF_2ClCO_2H, the rate of decomposition was followed by titration of the liberated chloride. Such a procedure would be expected to give rate constants that are somewhat low since about 1% of the initial acid gives CHF_2Cl. The mean deviation of rate constants during a run exceeded this error, but even so the rate constants in Table 9 have been obtained by dividing the observed rate constants by 0.99. For example, the data from one run is summarized in Table 10.

Table 9. Decomposition Rates by Chloride Titration

Run	Initial CF_2ClCO_2H (mole/l.)	Initial pH	Temperature ($^oC.$)	10^8k (sec.$^{-1}$)
-	--[a]	--[b]	99 $\pm$ 1	301 $\pm$ 27
2	0.0507	5.5	97.2 $\pm$ 0.1	216 $\pm$ 15
3	0.0909	4.0	97.2 $\pm$ 0.1	185 $\pm$ 10
1	0.0479	5.0	97.1 $\pm$ 0.1	186
-	0.3000	4.3	77 $\pm$ 2	16.3 $\pm$ 0.2
5	0.0706	4.5	74.9 $\pm$ 0.1	10.8 $\pm$ 0.9
4	0.1046	4.7	71.6 $\pm$ 0.1	9.0 $\pm$ 0.6

[a]Initial concentrations ranged from 0.0528 to 0.2888.

[b]The initial pH ranged from 4.6 to 5.2.

Table 10. Decomposition of Aqueous Sodium

Chlorodifluoroacetate at 97.1^o (Run 1)

$[CF_2ClCO_2H]_o$ = 0.0479 $[NaOAc]_o$ = 0.1355 $\frac{\Delta [H^+]}{[Cl^-]}$ = 2.4

Time (sec.)	Vol. NaOH[a] per 5 ml.	$CF_2ClCO_2^-$	10^8k (sec.$^{-1}$)
0	4.98	0.00000	-
21,600	5.43	0.00180	178
83,400	6.61	0.00653	177
128,400	7.34	0.00946	172
173,400	8.04	0.01226	171
262,200	9.37	0.01760	175
433,800	11.20	0.02492	170
527,400	12.02	0.02820	169

[a]Molarity of NaOH was 0.04807.

An effort was made to determine quantitatively the effect of added fluoride on the rate of chloride formation. The results of these experiments are reported in Table 11.

Table 11. Effect of Added Fluoride on Rate

of Chloride Formation

Initial CF_2ClCO_2H (mole/l.)	Concentration of Fluoride (mole/l.)	Temperature (^{o}C)	10^8k (sec.$^{-1}$)
0.0270	0.95	97.3 ± 0.1	354
0.0589	1.10	97.2 ± 0.1	446 ± 13
0.0596	2.32	94.9 ± 0.1	1300 ± 150[a]
0.1175	2.17	99 ± 1	2328

[a]Estimated by extrapolation to zero time.

In a number of experiments it was found that the rate of decomposition could be followed by the change in titratable acids since the ratio $\Delta[H^+]/\Delta[Cl^-]$ remained fairly constant during the course of the several reactions where it was determined. The rate constants determined by this method are reported in Table 12 as well as in Table 10. The value obtained from a number of runs for $\Delta[H^+]/\Delta[Cl^-]$ was 2.4 ± 0.3, and the mean value has been used in the calculation of the rate constants in Table 12. The rate constants in this table should, in theory, agree with those determined by titration of liberated chloride.

Table 12. Decomposition Rates by Acid Titration

Run	Initial CF_2ClCO_2H (mole/l.)	Initial pH	Temperature ($^\circ$C.)	$10^8 k$ (sec.$^{-1}$)
–	0.1578	4.6	99 $\pm$ 1	386
–	0.2888	5.0	99 $\pm$ 1	352
–	0.2295	5.0	99 $\pm$ 1	344
–	0.0528	5.2	99 $\pm$ 1	277
–	0.0330	5.4	97.3 $\pm$ 0.1	230[a]
6	0.0574	4.2	97.2 $\pm$ 0.1	218 $\pm$ 6[b]
3	0.0909	4.0	97.2 $\pm$ 0.1	208 $\pm$ 5
2	0.0507	5.5	97.2 $\pm$ 0.1	208 $\pm$ 11
1	0.0479	5.0	97.1 $\pm$ 0.1	173 $\pm$ 3
–	0.3000	4.3	77 $\pm$ 2	20.4 $\pm$ 0.5[c]
5	0.0706	4.5	74.9 $\pm$ 0.1	15.6 $\pm$ 1.3
4	0.1046	4.7	71.6 $\pm$ 0.1	14.4 $\pm$ 0.5

[a] The reaction solution was initially 0.78 $\underline{M}$ in NaBr.

[b] The reaction solution was initially 1.64 $\underline{M}$ in NaCl.

[c] $\Delta[H^+]/\Delta[Cl^-]$ was taken as 2.4 though the value observed at 77° was 3.01 $\pm$ 0.02 in two experiments.

CHAPTER IV

DISCUSSION AND CONCLUSIONS

From the preceding results it is evident that in aqueous solutions of chlorodifluoroacetic acid where the acid is essentially all in the form of its anion, the predominant decomposition path has as its first step the loss of carbon dioxide from the anion. Decarboxylation is accompanied, however, by considerable hydrolysis yielding oxalate, and, in the presence of 1 $\underline{M}$ or stronger fluoride concentrations, a reaction leading to the formation of trifluoroacetate becomes quite significant if not predominant.

All of these reactions are quite evidently first order in chlorodifluoroacetate anion. At pH $\backsim$ 1, however, where a fair portion of the acid is probably undissociated, there is a considerable increase in the oxalate yield. This increase, from about 23 to 42%, may be attributed to a preferential attack by water on the free acid.

In the absence of large quantities of added fluoride, less than 15% of the starting acid is converted to trifluoroacetate, and when the reaction is carried out in a solution of pH $>$4, at least 65% of the starting acid undergoes decarboxylation. The nature of this decarboxylation appears to be a concerted disintegration of the anion to chloride, carbon dioxide, and difluorocarbene as indicated below.

$$CF_2ClCO_2^- \longrightarrow \left[Cl\ldots CF_2 \ldots CO_2 \right]^- \longrightarrow Cl^- + CF_2 + CO_2$$
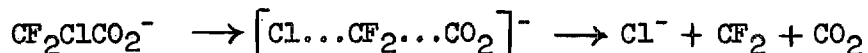
In support of a concerted decarboxylation, as opposed to a step-wise mechanism where the trihalomethide ion is first formed, a very low yield ($<2\%$) of chlorodifluoromethane was observed. Even this low yield of the haloform could be greatly decreased or increased by adding large amounts of NaF or NaCl, respectively, indicating that the chloro-difluoromethane is formed by subsequent reaction of difluorocarbene. The yield of fluoroform is affected in the opposite manner by addition of these salts.

In Fig. 1 it is shown that, when the effect of substituting fluorine for chlorine atoms in CCl_3CO_2H on the decarboxylation rate at 70° is considered, each fluorine appears to decrease the rate by about 100-fold in the series CCl_3CO_2H - $CFCl_2CO_2H$ - CF_3CO_2H. The rate of decarboxylation of CF_2ClCO_2H, however, is more than 30 times faster than predicted by this relationship. When chlorine is replaced by bromine, a regular increase in decarboxylation rate is observed for each chlorine replaced in all the cases where data are available. Further-more, a smooth relationship exists for the analogous rates of carbanion ion formation, as measured by deuterium exchange, from haloforms of the type $CHCl_nBr_{3-n}$ where all of the data are available (4). These observations indicate that the effect of fluorine substitution is consistent and that CF_2ClCO_2H does indeed decarboxylate by a different mechanism than that of other trihaloacetic acids.

Since the formation of CF_2 intermediates in the hydrolysis of CHF_2Cl is reported to be the result of a concerted loss of HCl (5,6), by the principle of microscopic reversibility the formation of CHF_2Cl as a product of the decarboxylation of CF_2ClCO_2H in alkaline solution must
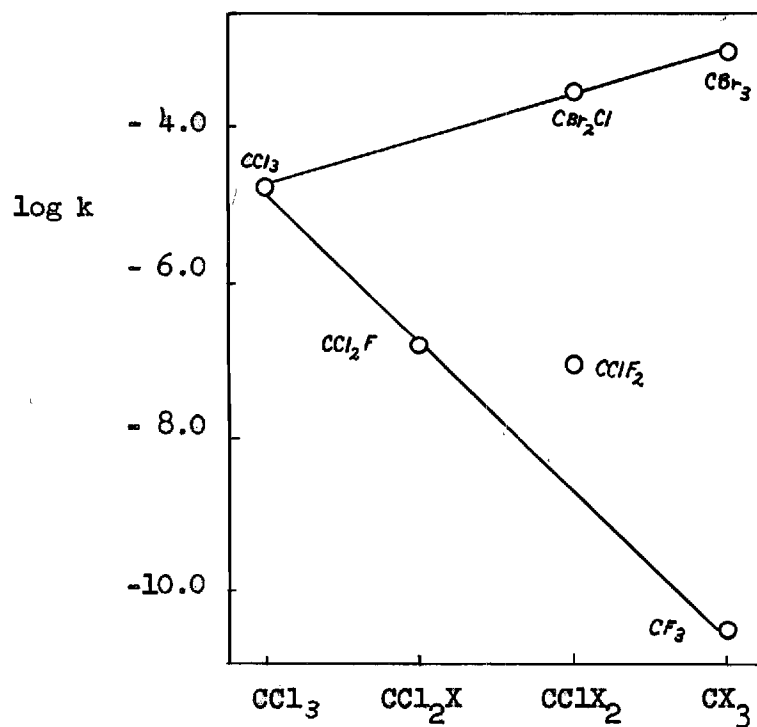
Figure 1. Decarboxylation Rates of Trihaloacetic

Acids in Water at 70° (14)

(14) J. Hine and D. C. Duffey, J. Am. Chem. Soc., 81, 1131 (1959).

occur by a concerted third order reaction of difluorocarbene with chloride ion and water. Since these decarboxylations were carried out in solutions of various acidities, however, hydronium ions may have replaced water to some extent as the proton donor. The use of hydronium ions as proton donors probably does not affect the concerted mechanism for the formation of CHF_2Cl from CF_2.

It was observed during the course of this work that the purified chlorodifluoroacetic acid decomposed slightly over long periods of time at room temperature in the dark. Chlorodifluoromethane was the only haloform product of this decomposition observed in the vapor phase. In most of the experiments reported in Table 1 no precautions were taken to exclude this small quantity of CHF_2Cl so it may be considered as having been reported among the products.

In Experiment I, however, the reaction solution was heated to boiling while nitrogen was bubbled through it for five minutes before the collection of product gases was begun. The first analysis of the gaseous products was then made after 3240 seconds. This analysis showed 46.7 micromoles of carbon dioxide and 0.3 micromole of CHF_2Cl. The amount of CHF_3 and CO in the sample was too small to detect, if any was present at all. The lower limits of detection for these gases are 0.05 and 0.7 micromole, respectively, for the method used. The sensitivity of the spectrophotometer was increased for this analysis by flushing the monochromator housing with nitrogen which had been treated to remove CO_2. Consequently, the values found for carbon dioxide in this experiment are believed to be accurate to within 10% This experiment was carried out to confirm similar observations made in other runs.

From these observations and other data reported in Table 1 it is seen that, while the yields of CHF_2Cl and CHF_3 in the absence of added salts are always very low, a consistent pattern of variation for the ratio of these haloforms has been demonstrated. In strongly acidic (pH ∿ 1) solutions CHF_2Cl is formed even when the chloride concentration is very low. The appearance of this product may result either from a slight tendency for the decarboxylation to proceed by a step-wise mechanism or from the relative abundance of an excellent proton donor in the form of hydronium ion. In such solutions, and perhaps in less acidic solutions also, the yield of fluoroform is greatly decreased relative to that of CHF_2Cl during the very early part of the reaction. This decrease may be explained by several factors. The fluoroform, being the product of a step-wise mechanism, is less sensitive to an increase in acidity. Consequently, when the probability of a third order combination is increased, the greater nucleophilicity of chloride over fluoride permits a preference for the formation of chlorodifluoromethane. In addition, the low concentration of fluoride in these solutions is probably reduced still further by hydrolysis to HF which attacks the glass vessel and does not participate in the capture of difluorocarbene. A similar reduction of F^- concentration would, of course, be expected for any solution of equivalent acidity.

In less acidic solutions of pH 4 - 5 the ratio of fluoroform to chlorodifluoromethane is three or more early in the reaction, but the ratio decreases as the reaction progresses and is nearly unity toward the end of the reaction (cf. Experiments 2, 3, 4, and 5 in Table 1). This decrease could be attributed to the possibility that the

chloride ion concentration continues to increase while the fluoride ion concentration rapidly reaches a point beyond which it increases more slowly due to the conversion of fluoride to HF. This explanation is supported by an experiment carried out at 94.9° using a solution initially 0.0596 $\underline{M}$ in CF_2ClCO_2H, 0.0876 $\underline{M}$ in NaOAc, and 2.32 $\underline{M}$ in KF. After less than a day the acid concentration had decreased to a constant value though only about half of the available chloride had been liberated at this time. In another experiment a 10 $\underline{M}$ KF solution was initially made 0.004 $\underline{M}$ in acid with $HClO_4$ and then heated at 100° for two days. At this time the solution had become more than 0.013 $\underline{M}$ in base.

Of considerable interest here are the effects of added salts on the haloform yields as shown in Table 1. In this table it may be assumed that the reported quantities of carbon dioxide, though possibly of rather poor accuracy, are at least comparable. On this basis, then, in 2.6 $\underline{M}$ NaCl 8% of the difluorocarbene intermediates are converted to chlorodifluoromethane while in 1 $\underline{M}$ NaF 22% of these intermediates are converted to fluoroform. These figures cannot be directly compared, however, since the fluoride solution was probably much less acidic due to the buffering action of NaF. It is interesting, nonetheless, that a several hundred-fold increase in chloride concentration causes only an eight-fold increase in the CHF_2Cl yield, and a comparison of Experiments 3 and 6 of Table 1 shows that a 13-fold increase in fluoroform yield is caused by about a 20-fold increase in fluoride concentration. Again, a direct comparison of these results is misleading since at such high concentrations as used in these experiments the possibilities of ion-pair formation and solvation effects increase the complexity of the

reaction processes beyond the accuracy of the data. Nevertheless, a similar surprisingly high preference of fluoride for difluorocarbene has been reported by Hine and Tanabe (15).

Qualitatively, a large increase in CHF_2Cl is brought about in the decomposition of chlorodifluoroacetic acid by the addition of large quantities of NaCl, just as a large increase in fluoroform yield is brought about by the addition of large quantities of NaF. The addition of these salts also causes a decrease in the yield of the other haloform as would be expected. In this discussion it should be remembered that while the quantity of haloform in the vapor phase is reported accurately in Table 1 the yields of these haloforms is low enough to allow the possibility of an appreciable fraction remaining in solution undetected.

On the whole the effects of added salts on haloform products and yields are those to be expected from attack by halide on a difluoro-carbene intermediate rather than reaction with chlorodifluoroacetate anion prior to decarboxylation. Also, since added fluoride causes a large decrease in the yield of CHF_2Cl, even the small amount of this haloform produced in the absence of added salts apparently results predominantly from a concerted recombination rather than protonation of a chlorodifluoromethyl anion formed by decarboxylation of the chlorodifluoroacetate anion.

In Table 12 it is seen that NaBr and NaCl have very little effect on the rate of decarboxylation of CF_2ClCO_2H. If the decarboxylation

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(15) J. Hine and K. Tanabe, J. Amer. Chem. Soc., 80, 3002 (1958); ibid., 79, 2654 (1957).

were proceeding by means of an α-lactone, the addition of large quantities of chloride would be expected to slow the reaction by a mass law effect. This, however, does not seem to be the case. Also, the addition of large quantities of bromide would be expected to increase the reaction rate if the bromide were capable of performing a nucleophilic displacement of chloride to give $CF_2BrCO_2^-$, which presumably decarboxylates faster than $CF_2ClCO_2^-$.

The appearance of oxalate as a reaction product in the decomposition of CF_2ClCO_2H is not without precedent since Hazeldine obtained good yields of oxalic acid from CF_2ClCO_2Ag at lower temperatures (16). In this case, water presumably displaces Cl^- from $CF_2ClCO_2^-$ and even more easily from the acid itself to give an intermediate that is readily converted to oxalate.

In the absence of large quantities of added fluoride, trifluoroacetic acid does not appear as a major product, but from Table 11 it is seen that added fluoride increases the rate of chloride formation to a degree somewhat greater than proportional to the concentration of added fluoride. This type of phenomenon has been observed previously in reactions between ions of like charge (17).

An overall summary of the decomposition paths of chlorodifluoroacetic acid is presented in the reactions below.

$$CF_2ClCO_2H + 2H_2O \longrightarrow Cl^- + 2HF + H^+ + (CO_2H)_2$$

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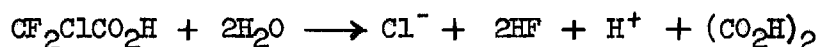
(16) R. N. Hazeldine, _J. Chem. Soc._, 4259 (1952).

(17) A. V. Kiss and P. Vass, _Z. physik. Chem._, 160, 290 (1932); A. N. Kappanna, _J. Ind. Chem. Soc._, 6, 419 (1929); ibid., 8, 541 (1931).

$$CF_2ClCO_2H \longrightarrow CF_2ClCO_2^- + H^+$$

$$CF_2ClCO_2^- + 2H_2O \longrightarrow Cl^- + 2HF + (CO_2H)_2$$

$$CF_2ClCO_2^- + F^- \longrightarrow Cl^- + CF_3CO_2^-$$

$$CF_2ClCO_2^- \longrightarrow CF_2 + Cl^- + CO_2$$

$$CF_2 + F^- + H_2O \longrightarrow CHF_3 + OH^-$$

$$CF_2 + Cl^- + H_2O \longrightarrow CHF_2Cl + OH^-$$

$$CF_2 + H_2O \longrightarrow CO + 2HF$$

$$CF_2 + 2H_2O \longrightarrow HCO_2H + 2HF$$
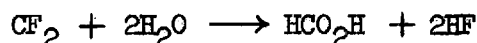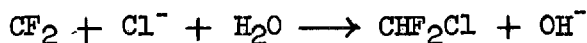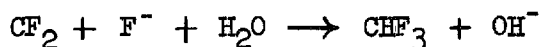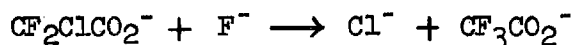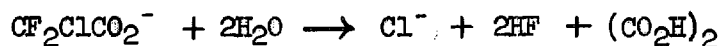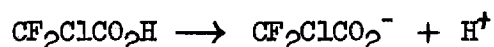
The data in Tables 10 and 12 as plotted in Fig. 2 may be used to evaluate the heat of activation for the decomposition reaction as a whole from the equation (18)

$$k = \frac{kT}{h} \, e^{-\Delta H^{\ddagger}/RT} \, e^{\Delta S^{\ddagger}/R}.$$

The heat of activation thus determined was 32.2 ± 2.0 kcal./mole, and the entropy of activation was 1.7 ± 3 e.u. These quantities were not determined for individual decomposition paths except in the case of decarboxylation for which the heat of activation was 32.2 kcal./mole and the entropy of activation was 1.2 e.u. In the latter calculation it was assumed that the oxalate yield is independent of temperature as

(18) S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes, McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.
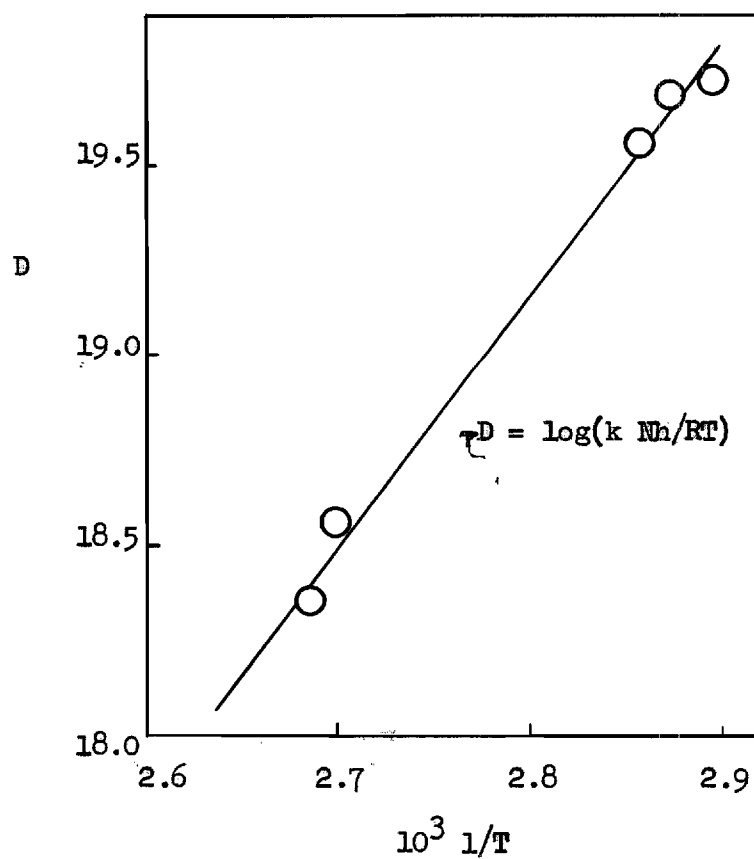
Figure 2. Variation of Decomposition Rate of
CF_2ClCO_2H with Temperature

indicated in Table 4. This assumption is probably not entirely justified, and, in fact, the ratio $\triangle[\text{H}^+] / \triangle[\text{Cl}^-]$ indicated an increasing oxalate yield at lower temperatures similar to that found by Hazeldine (16) for $CClF_2CO_2Ag$. The activation energy for CF_2ClCO_2H decomposition is considerably lower than would be expected by comparison with activation energies of other trihaloacetic acids toward decarboxylation, but this fact is evidence that chlorodifluoroacetic acid may decarboxylate by a mechanism different from that of other trihaloacetic acids. Some support for the concerted mechanism of decarboxylation for chlorodifluoroacetic acid is also furnished by the very low entropy of activation. The data of Auerbach, Verhoek, and Henne (11) permit the calculation of entropies of activation of 10.9 e. u. and 12.5 e. u. for CF_3CO_2Na and CCl_3CO_2Na, respectively, in ethylene glycol. The data of Fairclough (8) permit the calculation of an entropy of activation of 26.6 e. u. for the decarboxylation of CCl_3CO_2Na in water.

CHAPTER V

RECOMMENDATIONS

The results of this study of the decomposition of chlorodifluoro-acetic acid are insufficient to account quantitatively for the fate of all the starting material in all cases. Along this line it is felt that a more detailed study of the effects of added fluoride would be of value. It was noted in many experiments, particularly those with added fluorides, that an appreciable quantity of insoluble solids appeared in the reaction flask as the reaction progressed. These solids were quite insoluble in water and charred somewhat on being heated to high temperatures. An investigation of this residue seems warranted since the material could contain products of the chlorodifluoroacetic acid that would account for the remainder of the starting material.

APPENDIX

Table 13. Run 2

$[CF_2ClCO_2H]_o$ = 0.0507 $\underline{M}$ Initial pH = 5.46

NaOH = 0.04807 $\underline{M}$ Temperature = 97.2°

$AgNO_3$ = 0.05936 $\underline{M}$ 10 ml. samples

Time (sec.)	NaOH (ml.)	$AgNO_3$ (ml.)	$10^8 k$ (sec.$^{-1}$) by chloride	$10^8 k$ (sec.$^{-1}$) by acid
0	10.53	-	-	-
44,390	12.85	0.86	239	217
131,450	16.75	2.08	213	215
212,500	19.02	2.92	197	192

Table 14. Run 3

$[CF_2ClCO_2H]_o$ = 0.0909 $\underline{M}$ Initial pH = 4.00

NaOH = 0.04807 $\underline{M}$ Temperature = 97.2°

$AgNO_3$ = 0.05936 $\underline{M}$ 10 ml. samples

Time (sec.)	NaOH (ml.)	$AgNO_3$ (ml.)	$10^8 k$ (sec.$^{-1}$) by chloride	$10^8 k$ (sec.$^{-1}$) by acid
0	18.64	-	-	-
44,390	22.54	1.29	199	202
131,450	29.13	3.15	175	200
212,500	35.10	4.86	180	212

Table 15. Run 4

$[CF_2ClCO_2H]_0$ = 0.1046 $\underline{M}$ Initial pH = 4.74

NaOH = 0.04820 $\underline{M}$ Temperature = 71.6°

$AgNO_3$ = 0.05936 $\underline{M}$ 10 ml. samples

Time (sec.)	NaOH (ml.)	$AgNO_3$ (ml.)	$10^8 k$ (sec.$^{-1}$) by chloride	$10^8 k$ (sec.$^{-1}$) by acid
0	21.66	0.22	-	-
90,430	22.34	0.38	9.9	14.3
190,200	23.13	0.50	8.6	15.3
366,200	24.17	0.83	9.7	13.7
540,000	25.46	1.00	8.3	14.1

Table 16. Run 5

$[CF_2ClCO_2H]_0$ = 0.0706 $\underline{M}$ Initial pH = 4.46

NaOH = 0.0766 $\underline{M}$ Temperature = 74.9°

$AgNO_3$ = 0.0501 $\underline{M}$ 15 ml. samples

Time (sec.)	NaOH (ml.)	$AgNO_3$ (ml.)	$10^8 k$ (sec.$^{-1}$) by chloride	$10^8 k$ (sec.$^{-1}$) by acid
0	13.82	0.35	-	-
81,000	14.22	0.51	9.4	14.2
170,400	14.82	0.77	12.0	17.5
249,000	15.21	0.91	11.0	15.1

Table 17. Run 6 with Added NaCl

$[CF_2ClCO_2H]_0$ = 0.05745 $\underline{M}$ Initial pH = 4.2

NaOH = 0.0766 $\underline{M}$ Temperature = 97.2°

$[NaCl]_0$ = 1.64 $\underline{M}$ 15 ml. samples

Time (sec.)	NaOH (ml.)		$10^8 k$ (sec.$^{-1}$)
0	11.25	0.03	-
21,600	12.54	0.02	227
68,400	15.06	0.01	223
106,300	16.78	0.09	216
159,300	18.90	0.04	211

Table 18. Run 7 with Added NaF

$[CF_2ClCO_2H]_0$ = 0.05894 $\underline{M}$ $[NaF]_0$ = 1.10 $\underline{M}$

$AgNO_3$ = 0.05936 $\underline{M}$ Temperature = 97.2°

$[NaOAc]_0$ = 0.4323 $\underline{M}$ 10 ml. samples

Time (sec.)	$AgNO_3$ (ml.)	$10^8 k$ (sec.$^{-1}$)
0	0.93	-
87,200	4.08	438
169,200	6.08	432
246,500	7.66	460
333,700	8.71	459

Table 19. Run 8 with Added KF

$[CF_2ClCO_2H]_0$ = 0.0596 $\underline{M}$ $AgNO_3$ = 0.2019 $\underline{M}$

$[NaOAc]_0$ = 0.0876 $\underline{M}$ Temperature = 94.9°

$[KF]_0$ = 2.32 $\underline{M}$ 15 ml. samples

Time (sec.)	$AgNO_3$ (ml.)	$10^8 k$ (sec.$^{-1}$)
0	0.00	-
79,700	2.62	1124
153,000	3.59	1087
230,400	3.90	924
308,700	4.03	778
331,600	4.11	792

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13. _Beilstein's Handbuch der organischen Chemie_, vol. II, 4th ed., Julius Springer, Berlin, 1920, p. 201.

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15. Hine, J., and K. Tanabe, _J. Am. Chem. Soc._, 80, 3002 (1958); _ibid._, 79, 2654 (1957).

16. Hazeldine, R. N., _J. Chem. Soc._, 4259 (1952).

17. Kiss, A. v., and P. Vass, _Zeitschrift fur physikalische Chemie_, 160, 290 (1932); Kappanna, A. N., _Journal of the Indian Chemical Society_, 6, 419 (1929); _ibid._, 8, 541 (1931).

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PART FOUR

SOME REACTIONS OF METHYL

DICHLOROMETHYL ETHER

CHAPTER I

INTRODUCTION

Extensive studies of the susceptibility toward nucleophilic attack of a number of halogenated methanes have been reported in the literature, and the observation has been made that halogens tend to decrease the ease with which other halogens attached to the same carbon are displaced in S_N2 reactions (1,2). Chloroform, however, reacts faster and by a mechanism different from that by which methylene chloride and carbon tetrachloride are hydrolyzed in basic solutions.

The greater reactivity of chloroform (3,4) and some other haloforms has been attributed to the ease with which these molecules undergo an α-dehydrohalogenation to give a dihalomethylene intermediate. The dihalomethylene then reacts rapidly to give formic acid, or its salts, and carbon monoxide. These, particularly formate, are likely products also from successive S_N2 displacements of chloride by hydroxide. The essential mechanistic difference between the basic solvolyses of haloforms and that of other halogenated methanes probably results from the ability of halogens to increase the acidity of the

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(1) J. Hine, S. J. Ehrenson, and W. H. Brader, Jr., J. Am. Chem. Soc., 78, 2282 (1956).

(2) J. Hine, Physical Organic Chemistry, McGraw-Hill Book Co., Inc., New York, N. Y., 1956, Chap. 5.

(3) J. Hine, J. Am. Chem. Soc., 72, 2438 (1950).

(4) I. Fells and E. A. Moelwyn-Hughes, J. Chem. Soc., 398 (1959).

haloform hydrogen while they decrease the susceptibility of other

halogens attached to the same carbon toward nucleophilic displacement.

Thus, the attacking species acts preferentially as a base by removing

a proton rather than displacing halide from the haloform.

An intermediate that has been suggested in the basic hydrolysis

of chloroform is dichloromethanol, which would also be the first product

of an S_N2 displacement of chloride by hydroxide (4,5).

The analogous intermediate in the basic methanolysis of chloro-

form would be methyl dichloromethyl ether. If this compound is a

common intermediate in the formation of all of the solvolysis products

by all significant paths, then it must react more rapidly than chloro-

form and give rise to the same distribution of products.

Since a preparation of methyl dichloromethyl ether had already

been reported (6), tests to determine if this ether is an intermediate

in the methanolysis of chloroform seemed feasible insofar as reaction

rate and product distribution were concerned.

Further interest in methyl dichloromethyl ether results from the

possibility that this ether may react by either a mechanism analogous

to that of chloroform or by an S_N2 mechanism, or perhaps both mechanisms

simultaneously.

Should the reaction of methyl dichloromethyl ether with water or

alcohols and base proceed by a mechanism analogous to that of chloroform

with water and base, the rate of the reaction of the dichloro ether

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(5) Part One of this thesis.

(6) L. R. Evans and R. A. Gray, J. Org. Chem., 23, 745 (1958).

would provide interesting comparisons to the reactivities of the halo-
forms. Information of this sort would seem particularly worthwhile if
it permitted comparisons of the ability of the methoxy group to stabilize
carbanions and methylenes with the abilities of the halogens to perform
these tasks in haloform solvolysis reactions (7,8,9).

Should methyl dichloromethyl ether solvolyze by an S_N2 mechanism,
a comparison of the second order reactions of the monochloro- (10,11)
and dichloromethyl ethers would provide another example of the effect
of chlorine on the S_N2 reactivity of other halogens attached to the
same carbon.

(7) J. Hine and S. J. Ehrenson, J. Am. Chem. Soc., 80, 824 (1958).

(8) J. Hine, N. W. Burske, M. Hine, and P. B. Langford, ibid., 79, 1406 (1957).

(9) J. Hine and P. B. Langford, ibid., 5497 (1957).

(10) R. Leimu and P. Salomaa, Acta Chem. Scand., 1, 353 (1947).

(11) P. Ballinger, P. B. D. de la Mare, G. Kohnstam, and B. M. Prestt, J. Chem. Soc., 3641 (1955).

CHAPTER II

PROCEDURE

Preparation of Methyl Dichloromethyl Ether.--The procedure of Fischer
and Wecker (12) was followed on a reduced scale, first to prepare ethyl
dichloromethyl ether, and later to prepare methyl dichloromethyl ether.
Attempts to isolate the ethyl compound from the reaction mixture were
unsuccessful probably because it boils at a temperature near the boiling
point of phosphorus oxychloride, which is presumably the other major
product of the expected reaction of ethyl formate with phosphorus
pentachloride.

In the preparation of methyl dichloromethyl ether 25 ml. of
methyl formate was added drop-wise to 39 g. of phosphorus pentachloride
contained in a 200 ml., round-bottomed flask immersed in an ice-water bath.
The reaction was sufficiently vigorous at first to cause slow refluxing
of the ester. After the addition of the ester was completed, the con-
tents of the reaction vessel were heated under total reflux until the
temperature in the distilling head attached to the flask reached 58-60°.
Distillation was then begun and continued until the head temperature
reached 106°. The distillate, amounting to about 35 ml., was fractionated
through a 200 mm. column packed with tantalum heligrids. The portion
boiling at 82.4-83.2° (736 mm.) was collected and found to have a density
of 1.263 g./ml. at 30° and a refractive index of 1.4264 (n_D^{25}) which

(12) H. Fischer and G. Wecker, Z. physiol. Chem., 272, 1 (1941);
C. A., 37, 3102 (1943).

agree fairly well with the values reported by Evans and Gray (6) who have prepared methyl dichloromethyl ether by chlorinating methyl chloromethyl ether. These workers observed a boiling range of 82-84° and a refractive index of 1.4353 (n_D^{20}). The molar refractivity (Mr_D) calculated for methyl dichloromethyl ether is 22.81. The value obtained for the ether as prepared in this work is 23.22 if d_4^{25} is taken as 1.270. The yield of methyl dichloromethyl ether by the method employed in this work varied from 55% to 75% based on phosphorus pentachloride.

The ultraviolet spectrum of the ether in isooctane solution revealed a single weak maximum at 216 mμ; phosphorus oxychloride, however, absorbs strongly below 225 mμ. The infrared spectrum of the gaseous ether is shown in Fig. 1 (Appendix).

Reactivity of Methyl Dichloromethyl Ether.--A vigorous exothermic reaction took place when the ether was added to 10 ml. of 5.1 $\underline{M}$ sodium hydroxide. Some bubbling occurred, and the final solution was acidic to phenolphthalein. This solution was diluted to 200 ml. with water, and two 10 ml. aliquots were withdrawn and titrated first with 0.1221 $\underline{M}$ sodium hydroxide to the phenolphthalein endpoint then with 0.448 $\underline{M}$ silver nitrate using Mohr's method. For each aliquot 2.24 ± 0.01 ml. of sodium hydroxide and 4.50 ± 0.01 ml. of silver nitrate were required. These titrations indicate the presence of 93% of the calculated quantity of chloride. About 2.6 mmole. of base was consumed per mmole. of ether. Both of these analyses are somewhat low for the pure ether; a fact that may be attributed to some loss of hydrogen chloride.

When 7.0 mmole. of the ether was added to 40 ml. of 0.174 $\underline{M}$ potassium isopropoxide at room temperature, a white precipitate was

formed at once. The solution was acidic toward methyl red when a sample
was withdrawn after five minutes and titrated with potassium isopropoxide.
The total base consumption at this time was 20.0 mmole. No further
increase in acidity occurred on boiling the solution for one hour.

In another experiment 2.66 mmole. of the ether was added to 50 ml.
of 0.163 M isopropoxide solution. A sample was withdrawn after less than
three minutes and titrated with 0.148 M p-toluenesulfonic acid in isopropyl
alcohol. For neutralization of a 15 ml. sample, 5.35 ml. of the acid was
required. This indicates that the ether had consumed 5.51 mmole. of
base. The ultraviolet spectrum of the diluted reaction solution showed
a single maximum at 228 mμ. This spectrum was duplicated using solutions
of the ether in isopropyl alcohol or in water and a solution of methyl
formate in isopropyl alcohol.

In a dry ice-acetone bath at approximately -75° one mmole. of the
ether had not consumed 0.3 mmole. of isopropoxide in 90 minutes. Another
experiment carried out in a brine-ice bath at -14 ± 1°, using 0.48 g. of
methyl dichloromethyl ether in 40 ml. of 0.174 M potassium isopropoxide
in isopropyl alcohol, indicated that the rate of base consumption was
measurable at this temperature (cf. Table 9, Appendix). The rate of
disappearance was followed by withdrawing 4.00 ml. samples into chilled
pipets. The samples were then titrated to the methyl red endpoint with
p-toluenesulfonic acid. The reaction solution turned pink in 355 minutes.
A final sample was withdrawn and titrated with potassium isopropoxide
after the solution had been acidic for 845 minutes. To neutralize a
4.00 ml. sample at this time required 0.50 ml. of 0.165 M isopropoxide.

Experiments were also carried out at -5° and 0° (cf. Tables 7 and 8, Appendix). In these runs 25 ml. of isopropyl alcohol solutions containing 0.33, 0.65, and 1.63 mmole. of potassium isopropoxide and one drop methyl red indicator solution were cooled for several minutes in a dry ice-acetone bath. About 0.06 ml. of methyl dichloromethyl ether was then added, and the solution was transferred to a bath at -5° or 0°. The time required for the solutions to become acidic (pink) was observed, but the reactions were allowed to proceed for an additional measured length of time. The solutions were then titrated with standard potassium isopropoxide, diluted to about 100 ml. with water, and titrated with standard silver nitrate solution using the method of Mohr. The data collected in this way permitted estimates, which are reported in Table 1, of both first and second order reaction rate constants.

Additional experiments were carried out at temperatures near 0° using a solvent composed of three parts benzene and one part isopropyl alcohol as measured by volume at room temperature. In these experiments the reaction solution was contained in 250 ml. three-necked flasks fitted with two burets and a mechanical stirrer. The burets were used to contain standard solutions of potassium isopropoxide and p-toluenesulfonic acid in the mixed solvent. About 0.25 ml. of methyl dichloromethyl ether was dissolved in 50 ml. of the benzene-isopropyl alcohol solvent, containing five or six drops of methyl red indicator, to make up the initial reaction solutions. Measured volumes of isopropoxide solution were then added and allowed to react for a measured time; the solutions were then neutralized with p-toluenesulfonic acid. The reaction solutions were also allowed to become acidic occasionally for a measured time and then were neutralized with standard isopropoxide

solution. From the data collected in this way both the first and second
order rate constants could be determined. The initial concentration of
the ether was determined in the following manner: The final reaction
solution was extracted twice with 25 ml. portions of water; two 40 ml.
aliquots of the water solution were titrated with standard silver nitrate;
the initial quantity of ether was then taken to be half the quantity of
chloride found by the silver titrations.

The rates of reaction of methyl dichloromethyl ether with potas-
sium thiophenoxide and a mixture of thiophenoxide and isopropoxide were
determined in the same way as the reaction of the ether with isopropoxide
alone (cf. Tables 5 and 6, Appendix). The initial and final thiophenoxide
concentrations were determined by titration of aliquots with methanolic
0.010 $\underline{M}$ iodine (13).

The reactivities of methyl chloromethyl ether and methyl dichloro-
methyl ether toward sodium iodide in acetone were studied briefly. The
reactions of both ethers appeared to be too rapid to measure at room
temperature using a concentrated iodide solution (14), but at -5°, while
the reaction of the monochloro ether was essentially complete in 12 min-
utes, the dichloro ether had reacted only the extent of about 71 ± 10%.
The degree of completion of these reactions was determined by the quantity
of chloride precipitated in the specified time. The density of methyl
chloromethyl ether was assumed to be 1.0 g./ml. In these experiments
there was little clouding of the solution containing methyl dichloromethyl
ether until 15 seconds had elapsed, while a heavy precipitate appeared

(13) J. Hine and J. J. Porter, J. Am. Chem. Soc., 79, 5493 (1957).

(14) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, The Systematic
Identification of Organic Compounds, 4th ed., John Wiley and Sons, Inc.,
New York, N. Y., 1956, p. 158.

within three seconds after the addition of methyl chloromethyl ether.

For these reactions 0.05 ml. of each ether was added by syringe to 5.0 ml. of acetone containing 0.15 g. of sodium iodide. The precipitates were collected, washed with acetone, and dissolved in water. The aqueous solutions were then titrated with 0.58 M silver nitrate. These titrations indicated 0.55 mmole. of chloride from the dichloro ether and 0.62 mmole. from the monochloro ether.

Reaction Products of Methyl Dichloromethyl Ether with Isopropoxide.--
Approximately one mole of potassium isopropoxide was dissolved in 500 ml. of 1:1 benzene-isopropyl alcohol contained in a one l. three-necked flask equipped with a mechanical stirrer, dropping funnel, and gas outlet. The flask was cooled in a brine-ice bath at -5° for one-half hour. Twenty-four g. (0.21 mole) of methyl dichloromethyl ether was then added drop-wise with stirring over 15 minutes during which time the emerging gases were collected over a saturated salt solution. The reaction mixture was stirred for an additional one-half hour with occasional nitrogen flushing. The yield of carbon monoxide from this experiment was found by infrared analysis to be somewhat less than 0.6%. Fractionation of the lower boiling liquids from the reaction mixture gave about three ml. of material boiling over the range 33-61°. This fraction was found by its infrared spectrum to contain some methyl isopropyl ether and possible traces of methyl formate and acetone, but the major constituent of this fraction was benzene. The yield of methyl isopropyl ether did not seem to differ greatly from that of carbon monoxide. The only other isolated product of the reaction was obtained by concentration of

the higher boiling liquids from the reaction mixture. A colorless liquid, d_4^{27} 0.842, n_D^{25} 1.3950, was obtained that distilled over the range 58.3-58.5° (10 mm.). Thirteen g. of this material was collected.

For comparison, a sample of triisopropyl orthoformate was prepared by adding chloroform to a 1 $\underline{M}$ solution of potassium isopropoxide in isopropyl alcohol. The properties observed for this sample were: b.p. 165° (740 mm.), 57.5-59.5° (10 mm.); n_D^{25} 1.3979; d_4^{25} 0.85 ± 0.02. The reported (15) values for this compound are: b.p. 166-168°; n_D^{25} 1.3980; d_4^{25} 0.8600. The calculated molar refractivity was 53.3; the observed value was 53.9.

When the infrared spectrum of this triisopropyl orthoformate was compared to that of the product obtained from isopropoxide and methyl dichloromethyl ether, the two spectra were identical except that the spectrum of triisopropyl orthoformate contained three additional bands of moderate intensity (cf. Figs. 2 and 3, Appendix). A second fractionation had no effect on the spectrum of the reference compound.

Four ml. of methanol was then boiled with 15 ml. of triisopropyl orthoformate and a trace of anhydrous hydrogen chloride for 20 hours. The solution rapidly underwent a series of pronounced color changes from yellow to red to green and finally returning to yellow after which no further changes were observed. Fractionation of the solution at 20 mm. gave ten ml. of a fraction (b.p. 71.2-72.7°) having no spectral absorptions noticeably different from those of triisopropyl orthoformate. A lower boiling fraction (b.p. 55.8-56.9°), however, had an infrared absorption spectrum virtually identical with the spectrum of the product obtained from methyl dichloromethyl ether in isopropoxide solution. The boiling point of

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(15) P. P. T. Sah and T. S. Ma, J. Am. Chem. Soc., 54, 2965 (1932).

trimethyl orthoformate at 20 mm. was estimated to be 30° from the reported (15) value of $105-107^{\circ}$ at atmospheric pressure. An increase in boiling point at 20 mm. of 14° for each methyl group replaced by an isopropyl group in trimethyl orthoformate was estimated by taking one-third of the temperature difference between the boiling points of tri-methyl and triisopropyl orthoformates at 20 mm. These estimates indicate the methyl diisopropyl orthoformate should boil at about 58° at 20 mm.

From this evidence the product is assumed to be fairly pure methyl diisopropyl orthoformate. Thus, the mixed orthoester was obtained in a yield of about 40%. Since the isolation techniques were not designed for quantitative estimates, it is probable that the orthoformate is produced in much higher yield and may represent the only major product.

Chloroform Reaction with Sodium Methoxide in Methanol.--Chloroform (12.3 mmole.) was dissolved in about 50 ml. of methanol containing 12.0 mmole. of sodium methoxide. This solution was boiled in a partially evacuated system for 23.3 hours. The gases were then analyzed for carbon monoxide. An additional amount of sodium methoxide (30 mmole.) was then added, and the reaction was allowed to continue as before for another 7.5 hours. The reaction was stopped at this point, and the gases were again analyzed by infrared spectrum. The solution was also analyzed for base and chloride. At this time 5.8 mmole. of base remained. The chloride concentration indicated that 78.2% of the chloroform had reacted. The quantity of base consumed per mole of chloroform is thus 3.76 mole. Such a high base consumption is most readily explained by the presence of a small quantity of water in the methanol. The carbon monoxide produced could only account for 6.0% of the chloroform that had reacted. From the

observations of Gjaldbaek (16) the quantity of carbon monoxide remaining in the solution under these conditions is estimated to be less than 0.5% of that in the vapor phase.

Reaction of Methyl Dichloromethyl Ether with Cyclohexene and Potassium t-Butoxide.--In one experiment one-half the quantities specified by Doering and Hoffman (17) for preparing 7,7-dichlorobicyclo[4,1,0]heptane were used in an attempt to prepare 7-methoxy-7-chlorobicyclo[4,1,0]-heptane. Only about ten grams of high boiling (b.p. 47-58° at 17-10 mm.) material was obtained. When the procedure of Doering and Hoffman was modified by filtering the reaction mixture instead of extracting it with water, about the same amount of material boiling over the same range was isolated as before. In both of these experiments chloroform was replaced with an equivalent quantity of methyl dichloromethyl ether.

The material isolated from both experiments had a density of about 1.2 g./ml. at 25°, gave a precipitate with aqueous silver nitrate, and had virtually identical infrared spectra in carbon disulfide solution (cf. Fig. 4, Appendix). No further identification of these materials was attempted.

Reagents.--Eastman White Label methyl formate and phosphorus pentachloride from Merck and Co. and the Baker Chemical Co. were used in the preparation of methyl dichloromethyl ether. Isopropyl alcohol from the Will Corp. was distilled from sodium isopropoxide and then from sodium iso-propoxide and isopropyl benzoate. Purified metallic potassium was

(16) J. C. Gjaldbaek, Kgl. Danske Videnskab., Mat.-fys. Medd., 24, No. 13 (1948).

(17) W. von E. Doering and A. K. Hoffman, J. Am. Chem. Soc., 76, 6162 (1954).

obtained from the Baker Chemical Co. p-Toluenesulfonic acid monohydrate (Eastman White Label) was dried by vacuum sublimation. "Thiophene-free" benzene from the Matheson Co. was fractionally distilled from metallic sodium. Thiophenol was obtained from the Matheson Co. and used without further purification. Methyl isopropyl ether was prepared from C. P. methyl iodide (Amend Drug and Chemical Corp.) and potassium isopropoxide in isopropyl alcohol. The ether boiled over the range 30.3-30.7 (738 mm.). The refractive index was 1.3596 (n_D^{25}). Eastman White Label cyclohexene was fractionally distilled, b.p. 82° (742 mm.), from metallic sodium: n_D^{25} 1.4439, d_4^{25} 0.802. t-Butyl alcohol was dried over magnesium sulfate and fractionally distilled. It had a melting point of 25-26°. Methyl chloromethyl ether was obtained from the Matheson Co. and used without further purification. Acetone was dried over potassium carbonate and fractionally distilled twice. U. S. P. sodium iodide from Merck and Co. was used in acetone solution.

CHAPTER III

RESULTS

Reaction Rates in Isopropyl Alcohol.--From experiments carried out in
brine-ice baths, it was possible to calculate approximate rate constants
at several temperatures for the first order reaction of methyl dichloro-
methyl ether with isopropyl alcohol and for the second order reaction of
the ether with potassium isopropoxide in isopropyl alcohol. These rate
constants are reported in Table 1. It was assumed in all cases that
methyl diisopropyl orthoformate and potassium formate were the sole reac-
tion products. The first order constants are believed to be accurate to
well within a factor of two. The second order rate constants at -14°
were calculated from Equation 1, assuming a value for r of 2.0 in the
basic solutions thus,

$$k = \frac{2.303}{t(\underline{r}E - B)} \log \frac{B}{E} \cdot \frac{(E - x)}{(B - \underline{r}x)} \tag{1}$$

where E is the initial concentration of the dichloro ether in moles/liter,
B is the initial concentration of potassium isopropoxide in moles/liter,
x is the concentration of orthoformate at time t (in seconds), and $\underline{r}$ is
the mole ratio of isopropoxide consumed per mole of ether. The second
order rate constants calculated in this way are believed to be accurate
only within a factor of three. Use of the above equation implies that
the rate determining step is the initial reaction of the ether with an

isopropoxide molecule, but no choice between the S_N2 and α-elimination mechanisms is required.

The first order rate constants (k_1) in Table 1 were calculated from the data in Tables 7, 8, and 9 (see Appendix) by assuming the amount of acid generated during a recorded time interval in an initially neutral solution was equivalent to three times the quantity of methyl dichloromethyl ether that reacted during this time.

Table 1. Rate Constants for CH_3OCHCl_2 Reactions

in Isopropyl Alcohol

Temperature ($^{\circ}$C.)	k_1 (sec.$^{-1}$)	k_2 (l. mole^{-1}sec.$^{-1}$)
-14 ± 1	6.7×10^{-6}	$3.9 \pm 0.7 \times 10^{-3}$
-5 ± 2	$2.1 \pm 0.3 \times 10^{-5}$	9×10^{-3}
0 ± 1	5.4×10^{-5}	5×10^{-2}

In order to evaluate the second order rate constants (k_2) at -5° and 0°, Equation 2 was derived, as shown below, from the rate law for competing first and second order reactions,

$$\frac{dx}{dt} = k_1(E - x) + k_2(E - x)(B - \underline{r}x),$$

where k_1 and k_2 are the first and second order rate constants, respectively, and all other quantities are defined as in Equation 1. The

above expression may be rearranged to

$$\frac{dx}{(E - x)\left[(k_1/k_2) + B - rx\right]} = k_2 dt$$

and integrated to give

$$\frac{2.303}{B + (k_1/k_2) - rE} \log \frac{(k_1/k_2) + B - rx}{(E - x)} = k_2 t + C.$$

The constant C is evaluated by setting t and x equal to zero. The following equation is then derived by rearranging and combining the logarithmic terms:

$$k_2 t = \frac{2.303}{rE - B - (k_1/k_2)} \log \frac{[B + (k_1/k_2)](E - x)}{E[B + (k_1/k_2) - rx]} .$$

At the time when the reaction solution has become neutral, B is equal to rx so that substitution of one of these terms for the other in the above expression gives Equation 2:

$$k_2 t = \frac{2.303}{rE - B - (k_1/k_2)} \log \frac{[B + (k_1/k_2)](E - x)}{E(k_1/k_2)} . \tag{2}$$

Using the values for k_1 from Table 1 at -5° and 0° in Equation 2, the values for k_2 at these temperatures were estimated by the method of successive approximations. In these runs r was assumed to have a value of 2.0 in basic solution and 3.0 in acidic solution. The values obtained for k_2 at -5° were 0.06, 0.0057, and 0.0023 l. mole^{-1}sec.$^{-1}$ The decrease in the rate constants is believed to be due at least in part to the

presence of reactive impurities, an explanation which is supported by the data on the first order solvolysis in benzene-isopropyl alcohol. The geometric mean of these values is reported in Table 1. The value for k_2 at $0°$ in Table 1 was estimated from a single point.

Reaction Rates in Benzene-Isopropyl Alcohol Solution.--First order rate constants for the reaction of methyl dichloromethyl ether in a solvent composed of 75% benzene and 25% isopropyl alcohol, as measured by volume at room temperature, were determined in a number of experiments. These experiments were carried out using a solution containing a known amount of ether and several drops of methyl red indicator solution in the mixed solvent. The solution rapidly turned pink, but was allowed to stand for a measured length of time. It was then titrated to an orange color with standard isopropoxide solution and the process was repeated. Corrections were made for dilution resulting from the addition of the isopropoxide solution.

The rate constants were found to be as high as 12.5×10^{-6} sec.$^{-1}$ at less than 1% reaction. The values dropped rapidly at first, however, and fairly constant values were obtained after about 3% reaction. Values for the first order constant from one run are reported in Table 2. These values were calculated using a value for r of 2.93. This value was determined at the end of the reaction by adding an excess of base and titrating the unused portion with p-toluenesulfonic acid.

Experiments were also carried out that permitted the calculation of second order rate constants for the reaction of methyl dichloromethyl ether with isopropoxide in the mixed benzene-isopropyl alcohol solvent. In two runs at $0.5 \pm 0.2°$ and $0.8 \pm 0.3°$ values of 0.049 ± 0.024 l. mole^{-1} sec.$^{-1}$ and 0.0415 ± 0.0067 l. mole^{-1}sec.$^{-1}$ were obtained.
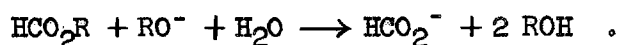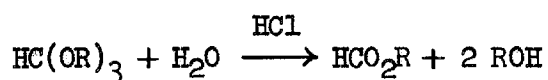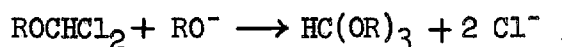
Table 2. First Order Reaction Rate in

Benzene-Isopropyl Alcohol at $2 \pm 2^{\circ}$

Time (sec.)	Total Volume of i-PrOK (ml.)[a]	$10^6 k$ [b] (sec.$^{-1}$)
0	0.00	---
14,700	1.25	6.8
22,500	1.85	6.7
31,800	2.60	6.9
75,000	5.57	7.3

[a]The concentration of isopropoxide was 0.511 $\underline{M}$.

[b]Rate constants are based on 2.31 mmole. of ether initially present in 50 ml. of solution.

Reaction Products.--Samples of the gas mixtures over the reaction solutions of the ether and isopropoxide contained only carbon monoxide and benzene. No propylene or methyl formate was found in these samples. In calculating the rate constants from all runs it was assumed that ortho-formates, methanol, and formate were the only organic products or the formation of the true products required no more isopropoxide than mixtures of these products. In some reactions where the solution was occasionally allowed to become acidic, as many as 2.93 moles of isopropoxide were consumed per mole of methyl dichloromethyl ether. In cases where the solution was not allowed to become acidic, this ratio tended to be considerably lower. It is believed that the high ratio of base consumed is accounted for by the presence of small quantities of water that participate in the overall reaction as indicated by the following series of reactions:

$$\text{ROCHCl}_2 + \text{RO}^- \longrightarrow \text{HC(OR)}_3 + 2\ \text{Cl}^-$$

$$\text{HC(OR)}_3 + \text{H}_2\text{O} \xrightarrow{\ \text{HCl}\ } \text{HCO}_2\text{R} + 2\ \text{ROH}$$

$$\text{HCO}_2\text{R} + \text{RO}^- + \text{H}_2\text{O} \longrightarrow \text{HCO}_2^- + 2\ \text{ROH}\quad.$$

These reactions provide a means for the consumption of a maximum of three moles of base per mole of ether. The presence of potassium formate would not have been detected by any of the titrations performed on the reaction solutions.

The quantities of carbon monoxide and methyl formate observed among the reaction products of methyl dichloromethyl ether and excess potassium isopropoxide were always low. An observed 0.6% yield of carbon monoxide seemed to correspond roughly to the yield of methyl isopropyl ether from the same reaction. The yield of methyl formate from this reaction was less than 5%. The only major product obtained from the reaction was an orthoformate ester that was isolated in about 40% yield. In this experiment the reactants were present in much higher concentration than in kinetic runs where it is conceivable that sufficient water was present for potassium formate to become the principal product.

Reaction of Methyl Dichloromethyl Ether with Thiophenoxide.--The rate of reaction of the dichloro ether with potassium thiophenoxide in benzene-isopropyl alcohol solution was studied at $0.8 \pm 0.5°$ in the same way as the reaction of the ether with isopropoxide. The second order rate constant was calculated to be 0.051 ± 0.015 l. mole^{-1}sec.$^{-1}$. The value of $\underline{r}$ in this case was found to be 2.13. In another experiment both thiophenoxide and isopropoxide were placed in a benzene-isopropyl alcohol

solution of methyl dichloromethyl ether. The rate of disappearance of base titratable with p-toluenesulfonic acid was followed as before. The combined second order rate constant for the reactions of thiophenoxide and isopropoxide at $0.8 \pm 0.5°$ was found to be 0.067 ± 0.015 l. mole^{-1} sec.$^{-1}$.

In this experiment the base concentration was always sufficiently high during the reaction to keep the thiophenol in the form of its potassium salt. The total quantity of isopropoxide added during the course of the reaction was three times that of thiophenoxide. The ratio of thiophenoxide consumed to ether consumed was 0.85, assuming a value for r of 2.0.

Since the initial and final concentrations of thiophenoxide were determined, the use of a value of 2.0 for r permits the calculation from Equation 1 of a second order rate constant of 0.038 l. mole^{-1}sec.$^{-1}$ for the reaction of only thiophenoxide with methyl dichloromethyl ether in the presence of isopropoxide.

CHAPTER IV

DISCUSSION AND CONCLUSIONS

In this work it has been found that methyl dichloromethyl ether reacts rapidly with potassium isopropoxide both in isopropyl alcohol and in benzene-isopropyl alcohol solution with a net consumption of between two and three moles of isopropoxide per mole of ether. Second order reaction rate constants have been calculated for this reaction and an apparently similar reaction of the ether with potassium thiophenoxide by assuming the reactions are first order in each reactant. These second order rate constants are of approximately equal magnitude.

The rate of a first order reaction of the ether was also determined and found to be small in comparison to the rate of the second order reaction.

The reactions of methyl chloromethyl ether and methyl dichloromethyl ether with sodium iodide in acetone were found to be extremely rapid though the dichloro ether seems to react less than half as fast as the monochloro ether at -5°.

Ballinger and coworkers (11) have found the rate constant for the first order solvolysis of methyl chloromethyl ether to be 1.42×10^{-2} sec.$^{-1}$ in ethanol at 0.0°. The corresponding value for the dichloro ether in isopropyl alcohol was found in this work to be about 4.1×10^{-5} sec.$^{-1}$. The 350-fold decrease in apparent S_N1 reactivity effected by replacing a second hydrogen by chlorine is surprising in

view of Hine and Lee's observation that S_N1 reactivity in one series of chloro compounds was increased 10-fold by replacement of a second hydrogen by chlorine (18). A decrease in S_N1 reactivity might be caused by changing from ethanol to isopropyl alcohol as a solvent, but, since a change from methanol to ethanol causes about an 8-fold decrease in the solvolysis rate of $\underline{t}$-butyl chloride at 25° (19), the change to isopropyl alcohol from ethanol would not be expected alone to cause more than a small part of the observed 350-fold decrease in rate. The rate constant for methyl chloromethyl ether of 8.9×10^{-6} sec.$^{-1}$ in 90% ether-10% ethanol solution at 0.0°, however, was only slightly greater than the rate constant for methyl dichloromethyl ether in 75% benzene-25% isopropyl alcohol solution at $2 \pm 2^\circ$ ($k_1 = 6.9 \pm 0.2 \times 10^{-6}$ sec.$^{-1}$).

The second order reaction of methyl chloromethyl ether with sodium ethoxide in ethanol has been found to have a rate constant of 0.47 l. mole^{-1}sec.$^{-1}$ at 0.0° (11). The rate constant for the corresponding reaction of methyl dichloromethyl ether in isopropyl alcohol has been found in this work to be 0.05 l. mole^{-1}sec.$^{-1}$ at $0 \pm 1^\circ$. A decrease of about this magnitude might be expected from the observations of Hine, Ehrenson, and Brader (1) if the reactions of both ethers proceed by an S_N2 mechanism and differences in the solvents are ignored. Solvent differences are probably of minor importance here since the change from isopropyl alcohol to 75% benzene-25% isopropyl alcohol seems to cause only a slight increase in the second order reaction rate constants for the reaction of methyl dichloromethyl ether.

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(18) J. Hine and D. E. Lee, ibid., 73, 22 (1951).

(19) J. Hine, Physical Organic Chemistry, McGraw-Hill Book Co., New York, N. Y., 1956, p. 135.

If the reaction of methyl dichloromethyl ether with isopropoxide does indeed proceed by an S_N2 mechanism, then the reaction of this ether with thiophenoxide ions would be expected to proceed even more rapidly since this reagent has been found to be from twenty to ten thousand times more reactive than methoxide in S_N2 displacement reactions (1,20).

In this work the rate of the reaction of the dichloro ether with thiophenoxide was found to be probably not more than twice as fast as, and possibly even somewhat slower than, the reaction of the ether with isopropoxide. In an experiment permitting direct competition between isopropoxide and thiophenoxide the quantity of thiophenoxide consumed during the reaction was essentially the amount predicted from the rate of reaction of thiophenoxide in the absence of isopropoxide. This observation is in contrast to the situation found for the reactions of several haloforms with thiophenylate or thiocresylate (2,13,21). These haloforms were found to react at a negligible rate with thiophenoxide alone, but in the presence of alkoxide the reactions proceeded readily to give the orthothioformate ester as virtually the sole product of total halide displacement. The use of thiophenoxide as a base for proton removal seems no more likely with methyl dichloromethyl ether than with some of the haloforms studied. Consequently, it is concluded that the reaction with thiophenoxide proceeds by an S_N2 mechanism. In addition, the reaction of methyl dichloromethyl ether with isopropoxide also seems to
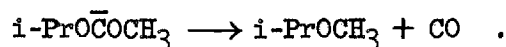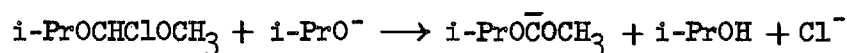
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(20) J. Hine, C. H. Thomas, and S. J. Ehrenson, _J. Am. Chem. Soc._, 77, 3886 (1955).

(21) J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., _ibid._, 78, 479 (1956).

follow an S_N2 mechanism since the rate of thiophenoxide disappearance is not enhanced by the presence of isopropoxide. It is conceivable, however, that a methoxychloromethylene may be too unstable to react preferentially with thiophenoxide ions that are present in low concentration compared to the isopropyl alcohol.

A further indication of the susceptibility of methyl dichloro-methyl ether toward S_N2 attack is found in the reaction of the ether with sodium iodide in acetone. This reaction was very fast even at -5°, but it was still apparently not more than half as fast as the reaction of methyl chloromethyl ether.

The appearance of a small amount of carbon monoxide in the reaction of methyl dichloromethyl ether with isopropoxide in benzene-isopropyl alcohol solution may result from the decomposition of methyl formate (22), which seems to persist in the starting ether despite repeated fractionations. The appearance of methyl isopropyl ether in the same reaction, however, could serve to indicate that a part of the reaction proceeds through steps such as shown below:

$$i\text{-PrOCHClOCH}_3 + i\text{-PrO}^- \longrightarrow i\text{-Pro}\bar{\text{C}}\text{OCH}_3 + i\text{-PrOH} + \text{Cl}^-$$

$$i\text{-Pro}\bar{\text{C}}\text{OCH}_3 \longrightarrow i\text{-PrOCH}_3 + \text{CO} \quad .$$

An analogous methylene intermediate has been mentioned for the dehydra-tion reaction of alcohols with chloroform and alkali (23). The absence

(22) J. A. Christiansen and J. C. Gjaldbaek, Kgl. Danske Videnskab., Mat.-fys. Medd, 20, No. 3 (1942).

(23) J. Hine, E. L. Pollitzer, and H. Wagner, J. Am. Chem. Soc., 75, 5607 (1953).

of propylene among the products makes the above reactions seem somewhat less likely since this olefin was found in a 30% yield in the reaction of chloroform with isopropoxide in isopropyl alcohol. The carbon monoxide yield from this reaction of chloroform was 42% (23).

However, since the carbon monoxide yield from chloroform and sodium methoxide was only 6%, there may be some tendency for the reaction of methyl dichloromethyl ether with isopropoxide to proceed through steps such as shown before leading to the formation of carbon monoxide. Such a tendency is apparently small and it is believed that the available data are best interpreted in terms of successive S_N2, or an S_N2 followed by an S_N1, displacements of chloride in the reactions of methyl dichloromethyl ether isopropoxide and thiophenoxide.

CHAPTER V

RECOMMENDATIONS

In this work some difficulty has been encountered in comparing the results of Ballinger, de la Mare, Kohnstam, and Prestt on methyl chloromethyl ether with those obtained on methyl dichloromethyl ether in the experiments reported here. Experiments permitting closer comparison of these reactions of the two ethers seem desirable.

No experiments were carried out in this work to establish whether methyl dichloromethyl ether undergoes first order solvolysis by an S_N1 mechanism or an S_N2 displacement chloride by the solvent. Work along this line appears of some value.

In general in this work it has been found that the reactions of methyl dichloromethyl ether in isopropyl alcohol were difficult to follow accurately probably because of the presence of water in the solvent. It is felt that better results would be possible if greater pains were taken to remove water from the solvents and to exclude atmospheric moisture from contact with the ether.

A study of the solvolysis of methyl trichloromethyl ether or methyl trifluoromethyl ether might also be of interest in a comparison of reactivities of various halo ethers.

APPENDIX

Table 3. Reaction of CH_3OCHCl_2 with Potassium Isopropoxide

in Benzene-Isopropyl Alcohol

TosOH = 0.208 M   r = 2.38

Initial Volume = 50 ml.   Temperature = 0.5 ± 0.2°

Elapsed Time (sec.)	Initial Ether (mole/l.)	Initial i-PrOK (mole/l.)	Final Vol. TosOH Added (ml.)	k (1. mole^{-1}sec.$^{-1}$)
193	0.05177	0.02423	1.80	0.0562
2160	0.04043	0.03178	0.70	0.0156
540	0.02492	0.05275	4.39	0.0761

Table 4. Reaction of CH_3OCHCl_2 with Potassium Isopropoxide

in Benzene-Isopropyl Alcohol

TosOH = 0.257 M   r = 2.69

Initial Volume = 50 ml.   Temperature = 0.8 ± 0.3°

Elapsed Time (sec.)	Initial Ether (mole/l.)	Initial i-PrOK (mole/l.)	Final Vol. TosOH Added (ml.)	k (1. mole^{-1}sec.$^{-1}$)
456	0.04776	0.05670	1.37	0.0517
340	0.02570	0.05308	5.61	0.0390
1032	0.01237	0.04089	5.81	0.0339

Table 5. Reaction of CH_3OCHCl_2 with Potassium Thiophenoxide

in Benzene-Isopropyl Alcohol

TosOH = 0.262 $\underline{M}$ r = 2.13

Initial Volume = 50 ml.   Temperature = $0.8 \pm 0.5°$

Elapsed Time (sec.)	Initial Ether (mole/l.)	Initial PhSK (mole/l.)	Final Vol. TosOH Added (ml.)	k (1. mole^{-1}sec.$^{-1}$)
320	0.05140	0.07420	4.23	0.0497
152	0.02127	0.01087	1.55	0.0815
2340	0.01522	0.01383	0.60	0.0342
4500	0.00808	0.01164	0.75	0.0367

Table 6. Reaction of CH_3OCHCl_2 with PhSK and i-PrOK

in Benzene-Isopropyl Alcohol

TosOH = 0.254 $\underline{M}$ r = 2.0 (assumed)

Initial Volume = 50 ml.   Temperature = $0.8 \pm 0.5°$

Elapsed Time (sec.)	Initial Ether (mole/l.)	Initial PhSK i-PrOK (mole/l.)	Final Vol. TosOH Added (ml.)	k (1. mole^{-1}sec.$^{-1}$)
128	0.05605	0.06465	6.56	0.0530
200	0.02475	0.06068	11.00	0.0825

Table 7. CH_3OCHCl_2 with Isopropoxide in Isopropyl Alcohol

Temperature = -5 ± 2°   i-PrOK = 0.165 M

Initial Isopropoxide (mmole.)	0.33	0.65	1.63
Initial CH_3OCHCl_2 (mmole)	1.37	1.08	1.04
Time Required to Consume Base (sec.)	600	5,400	28,800
Total Reaction Time (sec.)	31,220	31,820	32,170
Vol. of i-PrOK Required for Neutralization (ml.)	10.34	5.20	2.20

Table 8. CH_3OCHCl_2 with Isopropoxide in Isopropyl Alcohol

Temperature = 0 ± 1°   i-PrOK = 0.165 M

Initial Isopropoxide (mmole.)	0.33	0.65	1.63
Initial CH_3OCHCl_2 (mmole.)	0.67	0.61	0.80
Time Required to Consume Base (sec.)	2,400	2,400	21,410
Total Reaction Time (sec.)	19,210	19,500	20,600
Vol. of i-PrOK Required for Neutralization (ml.)	3.90	3.05	6.20[a]

[a]Since this sample had not turned pink in the allowed reaction time, 10 ml. of 0.148 M TosOH was added, and the solution was then back-titrated with i-PrOK.

Table 9. CH_3OCHCl_2 with Isopropoxide in Isopropyl Alcohol

Temperature = -14 ± 1°   Initial i-PrOK = 0.165 $\underline{M}$

Initial ether = 0.105 $\underline{M}$ TosOH = 0.148 $\underline{M}$

Time (sec.)	Vol. TosOH[a] (ml.)	Vol. 0.174 $\underline{M}$ i-PrOK[a] (ml.)	10^3k (1. mole^{-1}sec.$^{-1}$)
3,400	0.85	---	4.66
12,000	0.25	---	3.53
13,800	0.13	---	4.27
21,300	0.08	---	3.31
72,000	--	0.50	--[b]

[a]These volumes were required to neutralize 4 ml. of the reaction solution.

[b]A first order rate constant was calculated from this point and found to be 6.7 x 10^{-6} sec.$^{-1}$ as reported in Table 1.
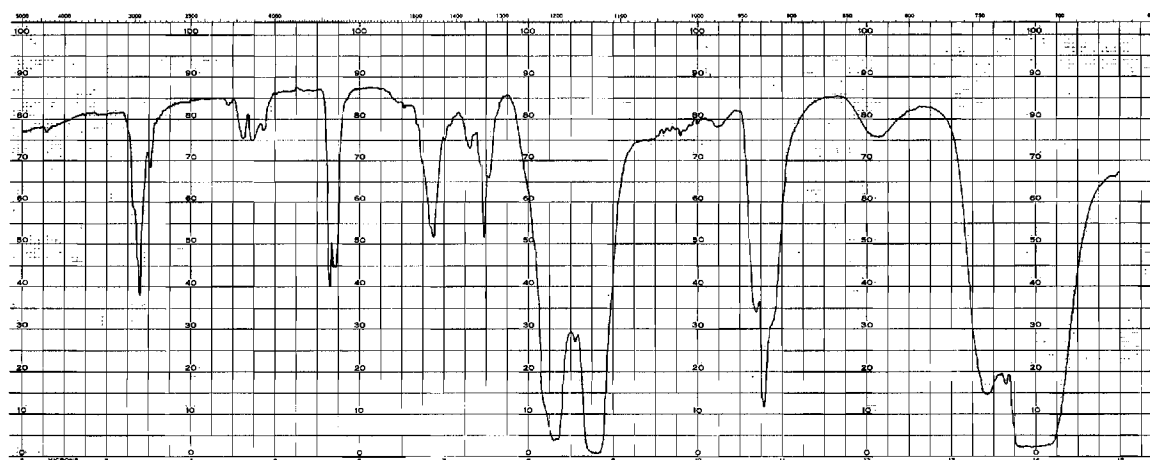
Figure 1. Infrared Spectrum of Methyl Dichloromethyl Ether
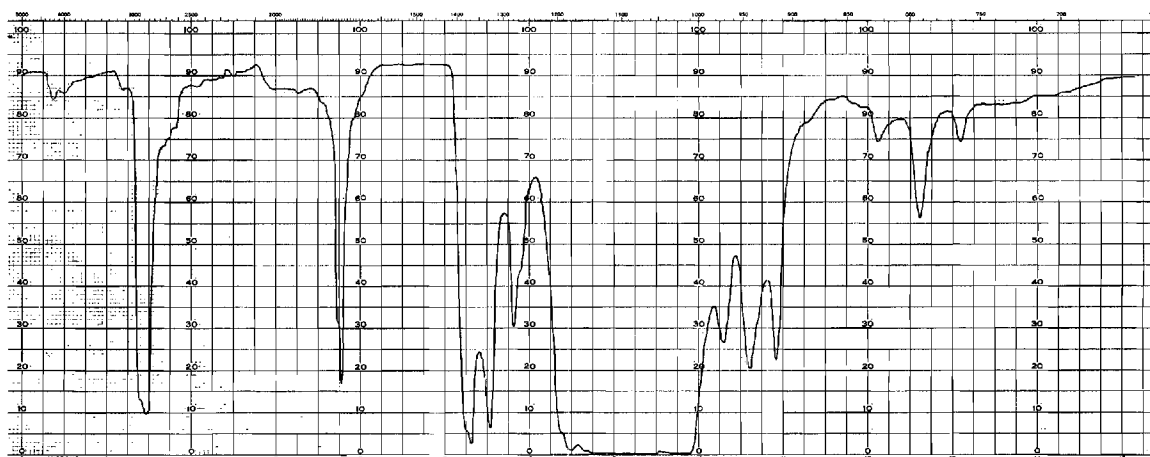(gas at 10 mm., 10 cm. cell thickness)

Figure 2. Infrared Spectrum of Triisopropyl Orthoformate
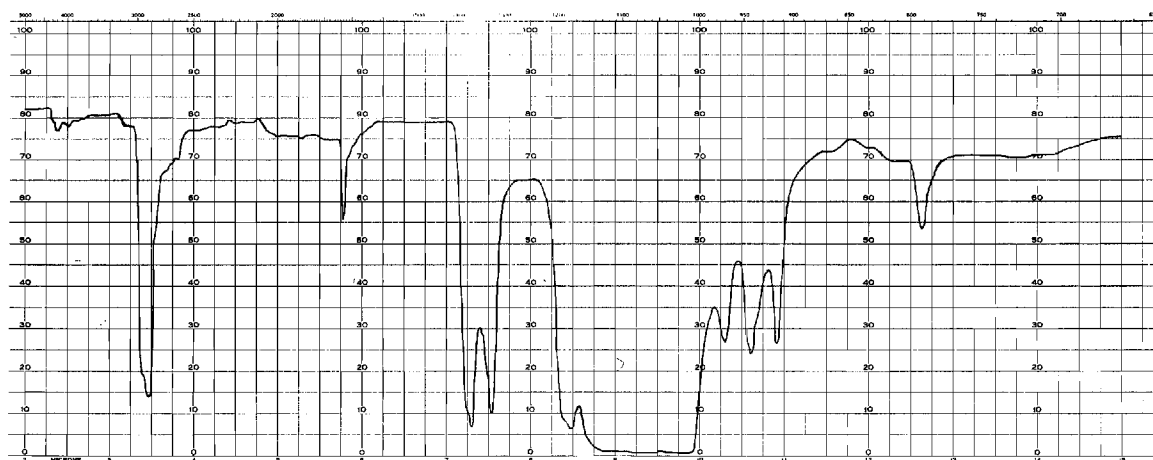(5% by vol. in carbon disulfide,
0.51 mm. cell thickness)

Figure 3. Infrared Spectrum of Methyl Diisopropyl Orthoformate
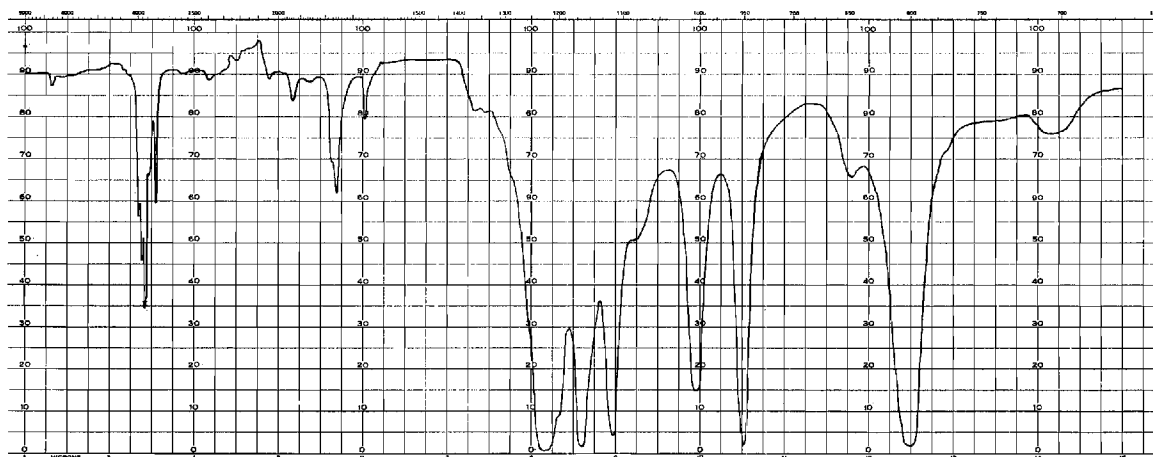(5% by vol. in carbon disulfide, 0.51 mm. cell thickness)

Figure 4. Infrared Spectrum of High Boiling Material from Reaction
of Methyl Dichloromethyl Ether with Cyclohexene and
Potassium t-Butoxide (2% by vol. in carbon disulfide,
0.51 mm. cell thickness)

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VITA

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