previous example. The total conversion to telomer was 68% on a weight basis. The composition of the product was approximately 21%, $n = 1$; 18%, $n = 2$; and 61% $n > 2$. A representative fraction of the telomer $n = 2$ had a neutral equivalent of 229 (calcd. 225 for diphenylbutylamine), demonstrating that it was substantially pure amine free from hydrocarbon contamination (contrast with the neutral equivalent of 248 for the amine obtained in the previous example which used acetic acid as solvent).

Telomerization of Styrene with Formaldehyde in Acetic Acid.—To a solution of 60 g. (2 moles) of formaldehyde introduced as paraformaldehyde and 68 g. (1 mole) of boron fluoride in 700 ml. of acetic acid was added 560 ml. (5 moles) of styrene. A clear solution was obtained. The exothermic reaction which occurred increased the temperature from 25° to 40° in spite of ice-bath cooling. The reaction mixture was held at 25° for 72 hours, and the reaction was terminated by adding ice, water and 200 ml. of 20 *M* sodium hydroxide. The organic layer was separated, washed with water, and dried over calcium sulfate. After distillation of the solvent, the product was fractionally distilled under reduced pressure. The telomer $n = 1$ (208 g., 35% of the product) had b.p. 117° (2.8 mm.)-140° (0.6 mm.) and $n^{25}\mathrm{D}$ 1.4971-1.5189. The telomer $n = 2$ (98 g., 17% of the product) had b.p. 141° (0.6 mm.)-196° (0.8 mm.) and $n^{25}\mathrm{D}$ 1.5189-1.5349. The residue (285 g., 48% of the product) consisted of telomers containing an average of five styrene units (*Anal.* Found: C, 81.35; H, 7.45; sapn. equiv., 313; mol. wt., 606). The glycol diacetates obtained in this synthesis were contaminated with varying quantities of the simple styrene–acetic acid telomers. In addition, there may have been some unsaturated products corresponding in structure to the loss of an acetic acid molecule from a glycol diacetate. The presence of these unsaturated compounds was indicated by the high refractive indices of certain of the fractions.

Diphenylpentanediol.[16]—One of the fractions (b.p. 183–188° (0.6 mm.) $n^{25}\mathrm{D}$ 1.5341) representative of the telomers $n = 2$ was selected for hydrolysis to the glycol. Its analysis confirmed its identity as the diacetate of a C_{17} glycol.

Anal. Calcd. for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11; sapn. equiv., 170.2. Found: C, 75.15; H, 7.19; sapn. equiv., 194.8.

An 18.3-g. sample of this glycol diacetate was saponified by heating for nine hours with 50 ml. of 20 *M* sodium hydroxide and 200 ml. of ethanol. The ethanol was distilled, and toluene was added to facilitate the separation of the glycol from the aqueous alkali. After distillation of the toluene, the glycol was distilled, b.p. 200° (0.5 mm.). The diphenylpentanediol (11 g.) was a clear, very viscous liquid.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.87; hydroxyl equiv., 128. Found: C, 79.74; H, 8.06; hydroxyl equiv., 145.

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[16] D. D. Coffman and E. L. Jenner, U. S. Patent 2,555,918 (1951).

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

Carbon Dihalides as Intermediates in the Basic Hydrolysis of Haloforms. III. Combination of Carbon Dichloride with Halide Ions[1]

BY JACK HINE AND ARTHUR M. DOWELL, JR.

RECEIVED JANUARY 4, 1954

Additional evidence has been found in support of the proposal that carbon dichloride is an intermediate in the basic hydrolysis of chloroform. Since sodium fluoride, nitrate and perchlorate, at concentrations up to 0.16 *N* have an identical effect on the reaction rate, within experimental error, this effect is believed to be due to the concentration and not the identity of the anions present. At the same concentrations, however, sodium chloride, bromide and iodide all decrease the reaction rate. In the case of sodium chloride this is due to a "mass-law effect" produced by the recombination of carbon dichloride with chloride ions. Bromide and iodide ions combine with carbon dichloride to form carbanions which are changed to dichlorobromomethane and dichloroiodomethane, the latter compound having been isolated. The rate "constants" obtained in the presence of bromide and iodide ions climb as the reaction proceeds, in agreement with expectation since the new haloforms arising in these reactions are more reactive than chloroform. Excellent agreement is found between the magnitude of the decrease in the rate of chloroform hydrolysis produced by the various halide ions (NaI > NaBr > NaCl) and the *nucleophilic constants* of the halide ions given by Swain and Scott. These data rule out all of the alternative mechanisms which have been suggested.

Introduction

Considerable evidence has been presented to show that the alkaline hydrolysis of chloroform consists of a relatively rapid reversible formation of the trichloromethyl anion, followed by the rate-controlling loss of a chloride ion to give the reactive intermediate carbon dichloride, which is then rapidly transformed into the final products, carbon monoxide and formate ion (mechanism I).[2]

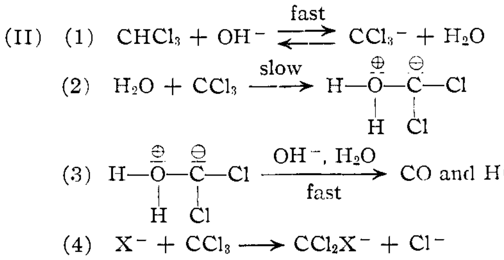
$$\text{(I)}\quad (1)\quad \mathrm{CHCl_3 + OH^-} \overset{\text{fast}}{\rightleftarrows} \mathrm{CCl_3^- + H_2O}$$

$$(2)\quad \mathrm{CCl_3^-} \xrightarrow{\text{slow}} \mathrm{Cl^- + CCl_2}$$

$$(3)\quad \mathrm{CCl_2} \xrightarrow[\text{fast}]{\mathrm{OH^-,\ H_2O}} \text{CO and } \mathrm{HCO_2^-}$$

$$(4)\quad \mathrm{CCl_2 + X^-} \longrightarrow \mathrm{CCl_2X^-}$$

While it could not be ruled out unequivocally, a number of arguments were advanced to show the improbability of an alternate mechanism (II) in which the trichloromethyl anion is decomposed by a nucleophilic attack by water.



$$\text{(II)}\quad (1)\quad \mathrm{CHCl_3 + OH^-} \overset{\text{fast}}{\rightleftarrows} \mathrm{CCl_3^- + H_2O}$$

$$(2)\quad \mathrm{H_2O + CCl_3} \xrightarrow{\text{slow}} \mathrm{H{-}\overset{\oplus}{O}{-}\overset{\ominus}{C}{-}Cl}\ \text{(with H below O and Cl below C)}$$

$$(3)\quad \mathrm{H{-}\overset{\ominus}{O}{-}\overset{\ominus}{C}{-}Cl} \xrightarrow[\text{fast}]{\mathrm{OH^-,\ H_2O}} \text{CO and } \mathrm{HCO_2}$$

$$(4)\quad \mathrm{X^- + CCl_3} \longrightarrow \mathrm{CCl_2X^- + Cl^-}$$

The possibility that the reaction involves a rate-controlling S_N2 attack[3] by the hydroxide ions on chloroform (mechanism III) has been shown to be

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[1] From a Ph.D. thesis submitted by Arthur M. Dowell, Jr., to the Graduate School of the Georgia Institute of Technology. For Part II see J. Hine, R. C. Peek, Jr., and B. D. Oakes, THIS JOURNAL, **76**, 827 (1954).

[2] J. Hine, *ibid.*, **72**, 2438 (1950).

[3] For the significance of the terms S_N1 and S_N2 see C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. VII.

highly unlikely in view of the fact that the related formation of phenylorthothioformate from sodium thiophenoxide and chloroform is powerfully catalyzed by hydroxide ions.[2]

$$\text{(III)} \qquad CHCl_3 + OH^- \xrightarrow{\text{slow}} CHCl_2OH + Cl^-$$

$$CHCl_2OH \xrightarrow[\text{fast}]{OH^-,\ H_2O} CO \text{ and } HCO_2^-$$

It may be noted that in the carbon dichloride mechanism (I), the nucleophilic attack on carbon occurs after the rate-controlling step of the reaction, while in mechanism II the rate-controlling step is itself a nucleophilic attack. For this reason, the two mechanisms lead to different predictions concerning the effect of introducing additional nucleophilic anions. If carbon dichloride is actually being formed, a nucleophilic reagent would certainly be expected to enter the molecule by combination with its highly electron-deficient carbon atom, as shown in step 4 of mechanism I. The intermediate CCl_2X anion could then react further in various ways, depending upon the nature of X. In the case where X is a chloride ion, step 4 becomes simply a reversal of step 2, re-forming the trichloromethyl anion. Since this anion will remove a proton from the solvent much more rapidly than it will undergo any other reaction, the net result is the diversion of carbon dichloride, which would otherwise have been hydrolyzed, back to the starting material, chloroform. Therefore, to the extent to which chloride ion combines with carbon dichloride, the reaction will be slowed by a "mass-law effect."[4] On the other hand, if mechanism II is operative any CCl_2X anions formed should be due to nucleophilic attack on the trichloromethyl anion (mechanism II, step 4), since it seems very unlikely that a nucleophilic displacement of a water molecule from the intermediate $H_2\overset{\oplus}{O}–\overset{\ominus}{C}Cl_2$ would be able to compete with the deprotonation of this oxonium acid by the hydroxide ion and water molecules present (or its rearrangement to $HOCHCl_2$). Therefore, if X is chloride ion no kinetic effect at all will result from the operation of mechanism II, since the products of step 4 will be identical to the reactants.

Attempts to determine the effect of various salts on the rate of the base-catalyzed decomposition of chloroform were made earlier, but these were unsuccessful since measurable effects were found only at salt concentrations so high that the possibility of their being merely specific salt effects could not be eliminated.[2] The previous work having been done in 66²/₃ per cent. dioxane solution, we decided to make measurements in aqueous solution since "salt effects" usually tend to remain "ionic strength effects" over wider concentration ranges in pure water.

Discussion of Results

TABLE I

RATE CONSTANTS FOR THE BASIC HYDROLYSIS OF $CHCl_3$ AT 35° IN THE PRESENCE OF ADDED SALTS[a]

Run[b]	Added salt	$k \times 10^4$ (sec.$^{-1}$ mole^{-1} l.)
1A	0.080 N NaCl	2.15 ± 0.04[c]
1B	.080 N $NaClO_4$	2.29 ± .03
1C	.080 N NaI	1.39[d]
2A	.080 N NaCl	2.16 ± .03
2B	.080 N $NaClO_4$	2.35 ± .01
3A	.080 N NaBr	1.95[d]
3B	.080 N NaF	2.39 ± .01
3C	.080 N $NaNO_3$	2.38 ± .03
4A	.080 N NaBr	1.95[d]
4B	.080 N NaF	2.37 ± .02
4C	.080 N $NaNO_3$	2.39 ± .02
5A	.160 N NaCl	1.98 ± .04
5B	.160 N $NaNO_3$	2.32 ± .02
6A	.160 N NaCl	2.06 ± .02
6B	.160 N $NaClO_4$	2.37 ± .06
6C	.160 N NaF	2.32 ± .07
7	.160 N NaI	1.00[d]
8A	1.50 N $NaClO_4$ + 0.200 N NaCl	1.54 ± .03
8B	1.50 N $NaClO_4$ + 0.200 N NaBr	1.26[d]
8C	1.70 N $NaClO_4$	1.98 ± .07

[a] The initial chloroform concentration was about 0.031 M in all runs. The initial sodium hydroxide concentrations were about 0.019, 0.035 and 0.031 N in the presence of 0.080, 0.160 and 1.70 N added salts. The sodium hydroxide solutions used with the 0.160 N added salts contained a small amount of added Ba^{++} ion to show that no carbonate was picked up during the reaction. This fact may have an effect on any direct comparison of the data at different salt concentrations. [b] All runs with the same numbers were made in the same constant temperature bath at the same time using the same reagents, etc. [c] Average deviation. [d] Initial rate constant (extrapolated).

From Table I it may be seen that the basic hydrolysis of chloroform proceeds at the same rate, within experimental error, in the presence of equal concentrations of sodium fluoride, sodium nitrate and sodium perchlorate at ionic strengths up to 0.20. Since these are salts whose anions would be expected to have the least ability to combine with carbon dichloride, it is believed that the reaction rate in the presence of these salts is simply equal to the rate of formation of carbon dichloride. The equality of rate for these three salts shows that the rate of formation of carbon dichloride is independent of the *nature* of the anions present at this concentration.[5] In the presence of salts, such as sodium chloride, bromide and iodide, whose anions would be more likely to combine with carbon dichloride, the rate of the basic hydrolysis is considerably diminished. There is no reason to attribute this to a decrease in the rate of formation of carbon dichloride in view of the previously described insensitivity of this rate to changes in the nature of the anion. Instead, in these cases, the decrease in the rate of disappearance of alkali (the variable actually measured experimentally) must be due to combination of these halide ions with carbon dichloride, thus reverting to haloform, an intermediate which would otherwise have been hydrolyzed. Mechanisms II and III offer no explanation for this effect.

This interpretation is supported by four other

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[4] For an investigation of "mass-law effects" in S_N1 reactions see L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 979 (1940), and preceding papers.

[5] There is a dependence on the nature of the cation at these concentrations, however, the reaction proceeding more rapidly in the presence of potassium salts. This might reasonably be expected to result from the lessened tendency of the potassium ion to form ion-pairs with the trichloromethyl anion.

pieces of evidence in addition to the observed decreases in reaction rate.

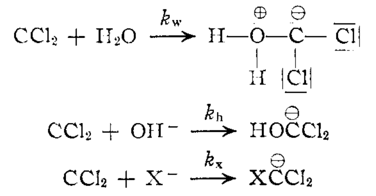
1. While the rate constants obtained in the presence of perchlorate, nitrate, fluoride and chloride ions show no definite trend, those found with added sodium bromide and iodide climb considerably as the reaction progresses (see Fig. 2). This is the expected result of the combination of bromide and iodide ions with carbon dichloride since dichlorobromomethane and dichloroiodomethane have been found to hydrolyze considerably faster than chloroform.[6]

2. Dichloroiodomethane has been isolated from a solution of chloroform undergoing basic hydrolysis in the presence of 0.20 *N* sodium iodide. This demonstrates that iodide does enter the haloform molecule as required by the interpretation given.

3. Horiuti and Tanabe have shown that the exchange of Cl^{36} anions with chloroform is strongly base catalyzed.[7] While this fact makes mechanism III improbable, it does not in itself distinguish between I and II. It is, however, required by I in the present interpretation of the decrease in hydrolysis rate by chloride ion as a mass law effect.

4. The application of the "swamping salt" principle[8] does not eliminate or diminish the effect of chloride ions, as it should a specific salt effect due to ionic size, ion-pair forming ability or some related attribute. Instead, chloride ions slow the basic hydrolysis of chloroform as effectively in the presence of 1.5 *N* sodium perchlorate as in its absence.

Relative Efficiency of Halide Ions in Combining with Carbon Dichloride.—Additional strong support for mechanism I is provided by the success of the following quantitative treatment of the extent of the decrease in rate produced by added halide ions. From mechanism I, carbon dichloride molecules may react with any of the following three reagents



$$CCl_2 + H_2O \xrightarrow{k_w} H-\overset{\oplus}{\underset{H}{O}}-\overset{\ominus}{\underset{|\underline{Cl}|}{C}}-\overline{\underline{Cl}}|$$

$$CCl_2 + OH^- \xrightarrow{k_h} HO\overset{\ominus}{C}Cl_2$$

$$CCl_2 + X^- \xrightarrow{k_x} X\overset{\ominus}{C}Cl_2$$

In terms of the rate constants for these three modes of reaction, we may express the fraction, *F*, of the carbon dichloride formed which escapes reconversion to haloform thus

$$F = \frac{[H_2O] + \frac{k_h}{k_w}[OH^-]}{[H_2O] + \frac{k_h}{k_w}[OH^-] + \frac{k_x}{k_w}[X^-]} \quad (1)$$

Hence *F* is the fraction which is found, by the acidimetric method used in following the kinetics, to undergo hydrolysis. Therefore, at the beginning of the reaction before any haloform other than chloroform has been formed, the reaction rate in the presence of a given concentration of halide ion will be equal to *F* multiplied by the rate in the absence of halide but in the presence of the same concentration of a salt with the same cation and an anion which does not appreciably combine with carbon dichloride, provided that the salt concentrations used are low enough that the rate in the presence of a non-intervening anion is independent of its exact nature. For this reason and the fact that the concentrations of the various reagents are best known at the beginning of a reaction, we shall use initial rate constants in our discussion. These are sensibly equal to the average rate constants[9] in all cases except those runs in the presence of bromide and iodide ions, where extrapolation is necessary.

If *k* represents the initial rate constant in the presence of a given concentration of a salt whose anion does not significantly combine with carbon dichloride and *k*′ represents that found in the presence of the same concentration of chloride, bromide or iodide ions, then from equation 1 and the second sentence following it

$$\frac{k'}{k} = \frac{[H_2O] + \frac{k_h}{k_w}[OH^-]}{[H_2O] + \frac{k_h}{k_w}[OH^-] + \frac{k_x}{k_w}[X^-]} \quad (2)$$

where $[H_2O]$, $[OH^-]$ and $[X^-]$ are initial concentrations in the run for which *k*′ is the initial rate constant. Solution of (2) for the *competition factor*, k_x/k_w, yields

$$\frac{k_x}{k_w} = \frac{\left([H_2O] + \frac{k_h}{k_w}[OH^-]\right)\left(\frac{k}{k'} - 1\right)}{[X^-]} \quad (3)$$

Values of k_x/k_w obtained for the three different halide ions from equation 3 will be measures of the relative ability of these ions to combine, as nucleophilic reagents, with the electrophilic carbon dichloride molecule. It would therefore be expected that this ability should run parallel to the quantitative measures of the nucleophilicity of these ions reported by Swain and Scott.[10] These workers have defined nucleophilic constants, *n*, for various nucleophilic reagents in terms of the rate constant for a reaction of this nucleophilic reagent with a given substrate in aqueous solution, the rate constant for the reaction of the nucleophilic reagent water with the same substrate under the same conditions and a constant *s* dependent on the nature of the substrate. In terms of our rate constants, the equation of Swain and Scott may be given the form

$$\log \frac{k_x}{k_w} = sn_x \quad (4)$$

While we have not made kinetic studies in the presence of enough different hydroxide ion concentrations to permit a determination of k_h/k_w, the competition factor for hydroxide ion, it may be seen from equation 3 that the value of k_h/k_w chosen will affect the absolute values but not the relative values of the k_x/k_w constants. Thus, since the value of

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[6] J. E. Singley, M.S. Thesis, Georgia Institute of Technology, 1952; A. M. Dowell, Jr., Ph.D. Thesis, Georgia Institute of Technology, 1954.

[7] J. Horiuti and K. Tanabe, *Proc. Japan Acad.*, **27**, 404 (1951); **28**, 127 (1952).

[8] For a discussion of the theory of this principle see L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 94.

[9] The amount of decrease in rate constants due to the action of a "mass-law effect" of the chloride ions resulting from hydrolysis may be calculated to be considerably smaller than our experimental error.

[10] C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953).

k_h/k_w will not affect the extent to which our data fit the equation of Swain and Scott, but only the magnitude of the proportionality constant *s*, we may choose a value of k_h/k_w in accord with the nucleophilic constant of the hydroxide ion and still use equation 4 as a test for our mechanistic interpretation. This procedure will yield the most probable absolute values of the competition factors.[11] Values of k_h/k_w were therefore calculated from the values of k/k' found at a concentration of 0.08 *N* (see Table II) by use of (3) and (4) as simultaneous equations. The average value thus obtained was 229. From this value and equation 3 the competition factors listed in Table II were calculated.

TABLE II

COMPETITION FACTORS TOWARD CARBON DICHLORIDE

Ion	Concn.	k/k'^a	k_x/k_w	$n_x{}^b$
Chloride	0.08	0.929[c]	56.8	3.04
Chloride	.16	.866[d]	61.1	
Chloride	.20	.778	79.1	
Bromide	.08	.819	164	3.89
Bromide	.20	.571	158	
Iodide	.08	.608	480	5.04
Iodide	.16	.426[e]	532	
Hydroxide			229	4.20

[a] All k/k' values were calculated from data run in the same bath at the same time, except for 0.16 *N* iodide. [b] From ref. 10. [c] Average of values from runs 1 and 2. [d] Average of values from runs 5 and 6. [e] From run 7 and an average value of *k* from run 6.

A plot of log k_x/k_w against n_x is shown in Fig. 1. The data lie near a straight line whose slope (*s* in equation 4) is 0.54. The linear relationship between the data for the various halide ions shows that the relative amounts by which these ions decrease the rate of the basic hydrolysis of chloroform is just that which would be predicted from their relative nucleophilicities. Since a small change in ionic strength should have very little effect on the competition factors,[10] the fact that about the same values are obtained at a concentration of 0.16 *N* as at 0.08 *N* shows that the diminution of reaction rate increases with increasing halide ion concentration in just the way expected from the carbon dichloride mechanism. The fact that the point for water falls on the same straight line shows that the combination of water molecules with carbon dichloride is very probably a nucleophilic attack to form $\overset{\oplus}{H_2O}-\overset{\ominus}{C}Cl_2$ as shown, rather than some other type of reaction such as a proton donation to form the $CHCl_2$ carbonium ion. The similar values for the competition factors found in the presence of 1.5 *N* sodium perchlorate strengthen the validity of the interpretation based on mechanism I.

The ability of an electrophilic reagent such as carbon dichloride to discriminate in its reactions with various nucleophilic reagents would be expected to be related to its stability, since a very highly reactive intermediate might be expected to react at every collision and hence to react largely with water. In this connection the increasing ability of halide ions to compete with water for carbonium ions has been shown to increase with the stability of the carbonium ions.[4,12] The competition factors reported herein for carbon dichloride are almost as large as those found for the benzhydryl carbonium ion.

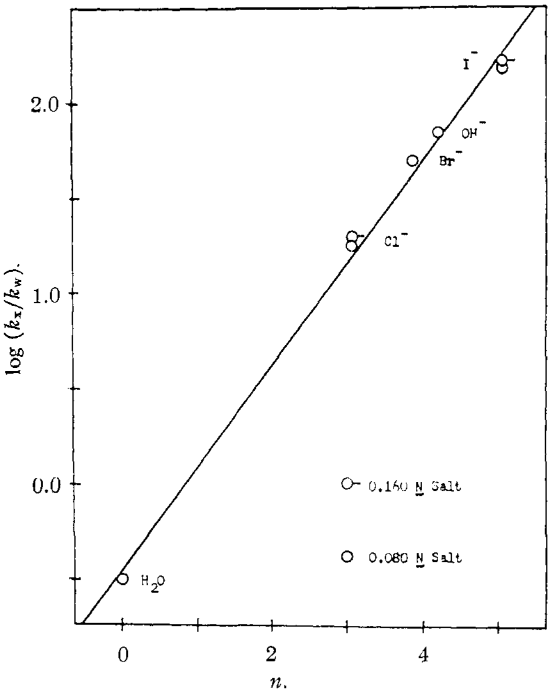

Fig. 1.—Plot of the log of the competition factors (k_x/k_w) *vs.* the nucleophilic constants (*n*) for water and halide and hydroxide ions.

Experimental

Reagents.—Chloroform was purified as described by Fieser,[13] and stored in brown bottles under nitrogen. Nitrogen was bubbled through it immediately before every use in order to remove phosgene and hydrogen chloride. The salts used were the C.P. anhydrous materials except for sodium perchlorate in which case the C.P. hydrate was dried under vacuum at 155°. Carbonate-free sodium hydroxide solutions were used. All solutions were made in distilled water which had been boiled and cooled under nitrogen.

Formation of Dichloroiodomethane from Chloroform and Sodium Iodide in Alkaline Solution.—When aqueous solutions of chloroform, sodium iodide and sodium hydroxide were allowed to stand for several hours under nitrogen at 35°, and then extracted with carbon tetrachloride, the carbon tetrachloride solution developed a purple "iodine" color which could be removed by shaking with aqueous sodium thiosulfate solution, but which was re-formed when the carbon tetrachloride solution alone was again shaken with air. This behavior was found to be identical to that occurring with carbon tetrachloride solutions of dichloroiodomethane (prepared by the method of Auger).[14] The same procedure carried out in the absence of sodium hydroxide produced no color at all.

Dichloroiodomethane was isolated from the reaction mixture in the following similar experiment on a somewhat larger scale. Two liters of an aqueous solution containing 10 ml. (14.8 g.) of chloroform, 60 g. of sodium iodide and 0.138 *N* in carbonate-free sodium hydroxide was kept at 35° for 16 hours and then extracted with methylene chloride. The combined water-washed methylene chloride extracts were

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(11) This correction for the competition of hydroxide ions is not a large one, the values of k_x/k_w resulting being less than 8% larger than if the effect of hydroxide ions had been ignored completely.

(12) C. G. Swain, C. B. Scott and K. H. Lohmann, THIS JOURNAL, **75**, 136 (1953).

(13) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., Inc., Boston, Mass., 1941, part II, p. 365.

(14) M. V. Auger, *Compt. rend.*, **146**, 1037 (1908).

dried over Drierite and fractionated through a column 10 in. long, 1/4 in. in diameter and packed with a tantalum spiral. The fraction boiling at 42.2° at 38 mm. weighed 1.12 g., n^{25}_D 1.5774, d^{25}_4 2.3853; molar refractivity calcd. 29.35, found 29.31. Auger reported b.p. 131° at 760 mm., d^{0}_4 2.41.[14]

Kinetic Runs.—All runs were made in 100-ml. volumetric flasks in a constant temperature bath maintained at 35.0 ± 0.1°. Chloroform was introduced into the reaction vessels by the use of a 0.25-ml. "tuberculin" syringe graduated in 0.01 ml. and found to deliver 0.250 ml. with an average deviation of 0.002 ml. The runs were carried out by dissolving 0.250 ml. of chloroform (at a known temperature) in 80 ml. of the aqueous salt solution under nitrogen in each of several reaction vessels. After the material had reached thermal equilibrium in the bath, 20 ml. of similarly equilibrated standard sodium hydroxide solution was added. "Points" were taken by quantitatively transferring the contents of a reaction flask into a titration flask containing a known amount (an excess) of acid. The contents were then titrated with standard sodium hydroxide solution to the phenolphthalein end-point. In most runs, a point was taken within one or two minutes, the hydroxide ion concentration determined used as the "initial concentration" and its difference from that originally added used in correcting the original concentration of chloroform to get its "initial concentration." This procedure eliminated several possible sources of error, such as that due to phosgene present as an impurity in the chloroform, but the resultant changes in the rate constants were usually negligible.

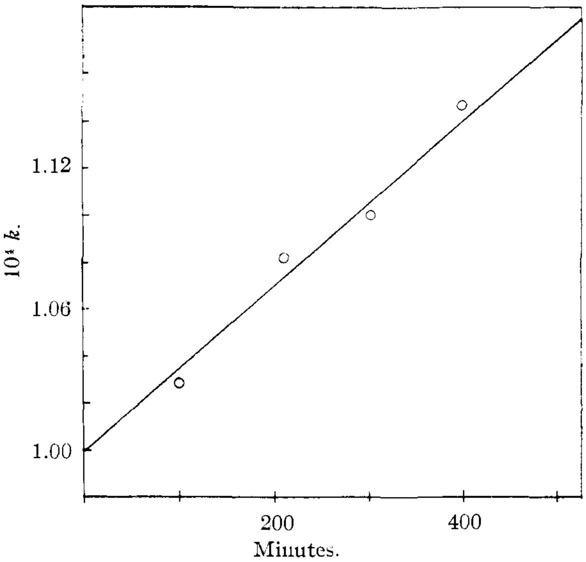

Fig. 2.—Integrated rate constants for the basic hydrolysis of chloroform in the presence of 0.160 N NaI (run 7) plotted against time.

Calculation of Rate Constants.—Rate constants were calculated from each point by use of the integrated rate equation[2]

$$k = \frac{2.303}{t(a[3+f] - b)} \log \frac{b(a - x)}{a(b - [3+f]x)}$$

where $a = [\mathrm{CHCl_3}]_0$, $b = [\mathrm{OH^-}]_0$, $x = \Delta[\mathrm{CHCl_3}]_t$, t = time (in seconds), k = rate constant (expressed in liters/mole of chloroform × seconds), and f = fraction of the chloroform hydrolyzed which gives formate. For f, a value of 0.15 was used in all cases, since the preliminary results of an investigation into the effect of reaction conditions on the value of f show that this value should not be far wrong in any of the present runs. It should also be noted that the value of k is rather insensitive to changes in f, particularly when chloroform is used in considerable excess as it was in all of the present cases. Data for a typical run are shown in Table III. A plot of the integrated rate constant *versus* time and the extrapolation to zero time for a run using sodium iodide are shown in Fig. 2.

TABLE III

KINETICS OF THE BASIC HYDROLYSIS OF CHLOROFORM IN THE PRESENCE OF 0.160 N NaCl AT 35.0°

$[\mathrm{CHCl_3}]_0$ = 0.03095, $[\mathrm{OH^-}]_0$ = 0.03528, 0.1776 N NaOH used for back titration

Time, sec.	Change in alkali titer, ml.	$k \times 10^4$, sec.$^{-1}$ mole^{-1} l.
5,940	2.10	1.95
10,800	3.56	1.93
17,040	5.37	2.02
24,600	7.18	2.02
28,320	7.93	2.00
	Av.	1.98 ± 0.04

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ATLANTA, GEORGIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

Vapor Phase Nitration of Aliphatic Ethers, Alcohols, Ketones and Carboxylic Acids[1,2]

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The vapor phase nitration technique has been extended to include aliphatic ethers, alcohols, ketones and acids. Nitration of aliphatic ethers produced nitro ethers and nitro alkanes. The alcohols gave nitro alkanes, and in one case a nitro alcohol. Ketones yielded nitro ketones and nitro alkanes. Propionic acid, on nitration, produced β-nitropropionic acid.

The vapor phase nitration of alkanes, cycloalkanes, aromatics and haloalkanes has been studied in our laboratories. We have now extended this type of nitration to include aliphatic ethers, alcohols, ketones and carboxylic acids. Many nitro derivatives of ethers,[4-6] alcohols,[7] ketones,[8-10] and

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(3) (a) Sugar Research Foundation, 52 Wall St., New York 5, N. Y.; (b) Mallinckrodt Chemical Works, St. Louis, Missouri.

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