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THE MECHANISM OF THE HYDROLYSIS
OF BROMOCHLOROIODOMETHANE

A THESIS

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Master of Science in Chemistry

By

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THE MECHANISM OF THE HYDROLYSIS
OF BROMOCHLOROIODOMETHANE

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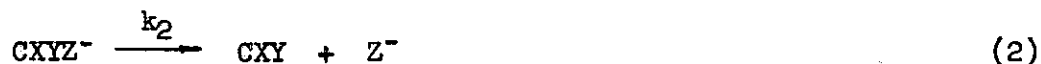
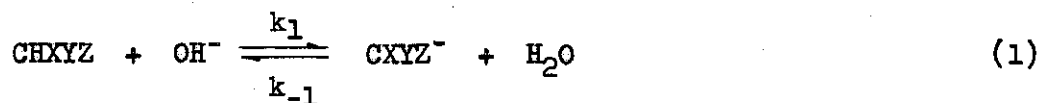
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CHAPTER I

INTRODUCTION

The alkaline hydrolysis of most haloforms has been shown (1) to occur by the mechanism



followed by rapid reaction of CXY with water. On the basis of this mechanism, Hine and Ehrenson (2) proposed a semi-empirical equation to correlate the rates of haloform hydrolysis. This equation uses the known rate constants for carbanion formation, and contains parameters for the relative abilities of the halogens to stabilize dihalomethylenes, the relative ease with which halogens are separated as anions from the trihalomethyl anion, and the carbanion character of the transition state for dihalomethylene formation.

For the above reactions the overall hydrolysis rate constant may be expressed

$$k_h = \frac{k_1 (k_2/k_{-1})}{1 + (k_2/k_{-1})}$$

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

(2) J. Hine and S. J. Ehrenson, unpublished manuscript, Georgia Institute of Technology.

and since k_1 is known (or may be closely approximated), a correlation of k_2/k_1 values is equivalent to a correlation of k_2 values. Hine and Ehrenson's correlation equation takes the form

$$\log \frac{\left(\frac{k_2}{k_1}\right)_{\text{CHXYZ}}}{\left(\frac{k_2}{k_1}\right)_{\text{CHCl}_3}} = M_X + M_Y + N_Z + \log \frac{n_Z}{3} + q \log \frac{(k_1)_{\text{CHXYZ}}}{(k_1)_{\text{CHCl}_3}} \quad (3)$$

where chloroform is used as the reference compound. M_X and M_Y are the methylene stabilization factors for the two halogens that become a part of the dihalomethylene; N_Z is the constant for that halogen which is lost as an anion; $\log n_Z/3$ is a statistical factor in which n_Z is the number of halogens of the type being lost as an anion, and the "3" refers to the fact that there are three of these in chloroform; q is a proportionality constant. The use of chloroform as a reference compound defines M_{Cl} and N_{Cl} as zero.

Values of the rate constants at 50°C. used in evaluating the parameters are listed in Table 1. From the values of the parameters obtained, halogens appeared to facilitate dihalomethylene formation in the order $\text{F} \gg \text{Cl} > \text{Br} > \text{I}$. The ability of the halogens to separate as anions showed the order $\text{Br} > \text{I} > \text{Cl}$. In haloforms containing chlorine and bromine and/or iodine, the loss of chlorine as an anion was found to be an insignificant part of the reaction. However, in compounds containing both bromine and iodine, the loss of each of these halogens would be expected to contribute substantially to the reaction as a whole. It was

felt that a study of the mechanism of the hydrolysis of bromochloriodomethane would shed more light on the quantitative values of the bromine and iodine parameters.

Table 1. Rate Constants for Carbanion Formation and Hydrolysis of Haloforms at 50°C. (2).

Haloform	k_1 (1./m.s.)	$k_h \times 10^4$ (1./m.s.)
CHClI ₂	103.9	9.2
CHCl ₃	6.57	18.8
CHBr ₃	327.4	84
CHCl ₂ I	25.04	95
CHBr ₂ Cl	103.9	220
CHCl ₂ F	0.2117	300
CHBrCl ₂	25.04	354
CHFI ₂	40.41	4900
CHBrClF	4.014	18000
CHBr ₂ F	21.26	50000

In bromochloriodomethane, both CBrCl and ClCl should be formed at appreciable rates during the hydrolysis. This results in two separate paths the reaction might take. In the correlation treatment, these two paths are treated as two separate reactions. One of the sources of error in the calculated values of the parameters is that for many of the haloforms k_1 , the rate constant for carbanion formation, was estimated by extrapolating data from lower temperatures. The two paths of the

bromochloriodomethane hydrolysis both involve the same carbanion. Thus the ratio of the rate of formation of CBrCl to the rate of formation of ClCl is essentially independent of the value of k_1 for bromochloriodomethane.

An assumption inherent in the correlation equation is that k_{-1} is inversely proportional to k_1 for the haloforms correlated. For the hydrolysis of bromochloriodomethane, it is seen that the ratio of the rate of formation of CBrCl to the rate of formation of ClCl is independent of the magnitude of k_{-1} .

In this thesis, the rate of formation of each of the intermediates will be determined, and the effect of applying these results to the correlation equation will be indicated.

CHAPTER II

PROCEDURE

Kinetic Procedure

Two procedures were commonly used to perform the kinetic runs. The hydrolysis of chlorodiodomethane was studied using a single-flask technique. A one-liter Erlenmeyer flask was covered with masking tape, and the tape was painted black to exclude light. The flask was capped with a polyethylene stopper. In a typical run, 990 ml. of a solution of salt(s) in boiled distilled water was placed under nitrogen in a two-liter volumetric flask. About 0.2 ml. of chlorodiodomethane was added to this solution using a calibrated syringe. The flask was shaken vigorously until the haloform was completely dissolved, then the solution was placed in the black reaction flask and allowed to attain temperature equilibrium in the constant temperature bath. Ten milliliters of approximately 0.3 N sodium hydroxide was added, and the flask was shaken vigorously. This was considered the zero time of the reaction. Five or six 50 ml. samples were withdrawn at intervals of about one and one-half minutes and titrated with standard hydrochloric acid to the phenolphthalein end point. These acid titers were extrapolated to zero time (if they decreased materially with time) or averaged (if they did not decrease materially) to obtain the effective initial base concentration. This method has the advantage of reducing errors in the initial base concentration arising from the presence of very reactive impurities which consume

base. The initial haloform concentration was calculated from the weight of haloform introduced and the volume of solution. Fifty-milliliter samples were periodically removed and titrated with hydrochloric acid. All samples were removed by forcing the liquid into a 50 ml. pipet under a slight nitrogen pressure.

The hydrolysis of bromochloriodomethane and of bromodichloromethane were studied using a multiple-flask technique. In a typical run, about 0.2 ml. of bromochloriodomethane measured from a calibrated syringe was dissolved by vigorous shaking in 490 ml. of boiled distilled water under nitrogen. This solution was placed in an opaque separatory funnel under nitrogen. Forty-nine-milliliter portions of the solution were placed in ten 50 ml. low-actinic volumetric flasks previously flushed with nitrogen, the 49 ml. mark being determined by previous calibration. The reaction vessels were sealed with ground glass stoppers coated with Dow-Corning silicone high-vacuum grease. The flasks were placed in the constant temperature bath and allowed to equilibrate. Then 1.00 ml. of standard sodium hydroxide was added to each flask and the flask shaken vigorously and replaced in the bath. Zero time was taken as the time when each flask was shaken. The initial base concentration was calculated from the amount of standard base added and the volume of the samples. An alternative method of determining the initial base concentration was to titrate several additional 50 ml. samples with hydrochloric acid effectively at zero time (accomplished by allowing these samples to remain at room temperature where the reaction rate is sufficiently slow to preclude any detectable amount of reaction). Another method was to determine the acid titer of a number of 50 ml. samples which contained base but no haloform.

One-hundred-milliliter low-actinic volumetric flasks were used in several runs, the amounts of materials used being twice as large as previously described. In runs where the samples were extracted with carbon disulfide and analyzed on the infrared spectrophotometer, no stopcock grease was used on any piece of equipment involved in the kinetic run, since this stopcock grease absorbs strongly in the infrared. The reaction flasks in these cases were capped with small rubber nipples.

For those reactions of bromochloriodomethane in the presence of iodide ion that were to be used for determining f_I (do not confuse with f , the fraction of haloform hydrolyzed which gives formate), a point was placed in an ice bath when it was removed from the constant temperature bath. This time was taken as the end time for the point. After the solution had cooled to approximately 0°C. it was titrated with hydrochloric acid to the phenolphthalein end point, then extracted once with about ten milliliters of carbon disulfide. The extract was dried with about one gram of silica gel, diluted to an appropriate approximate concentration of haloform, then analyzed for bromochloriodomethane and chlorodiodomethane on a Perkin Elmer Model 21 double-beam recording infrared spectrophotometer. The absorption of the sample was measured against a reference cell filled with the solvent, carbon disulfide. This procedure tends to cancel any variations in solvent purity which might occur from time to time.

Titration for Halide Ion

For points from which both base and halide ion were to be determined (i.e. in the determination of f), hydrochloric acid is unsuitable for the

base titration. In these cases standard perchloric acid was used to determine the base concentration, and then the halide ion concentration was determined by titrating with standard silver nitrate using the adsorption indicator dichlorofluorescein. The procedure is described by Kolthoff and Sandell (3), and was used as described except that a few milliliters of a two per cent dextrin solution was added to prevent flocculation of the silver halide sol. The titration is sensitive to light, particularly to fluorescent light, so all halide titrations were carried out with the lights off and out of direct sunlight.

Preparation of Salt Solutions

Stock solutions of sodium iodide and of an equimolar mixture of sodium nitrate and sodium perchlorate were diluted with boiled distilled water to form the salt solutions used in the hydrolysis of chlorodiodomethane in these salts at 64.5°C. Weighed samples of sodium iodide were dissolved in boiled distilled water to form the salt solution used in the hydrolysis of bromochloriodomethane in iodide ion at 50°C. In either case, nitrogen was bubbled through the solutions for about fifteen minutes prior to adding the haloform.

Free Radical Inhibitors

In the mixed solvent 66 2/3 per cent aqueous dioxane, free radical reactions assume a much greater importance than in the solvent water. To suppress these free radical reactions, diphenylamine was added in small amounts to the reaction mixture. Hine and coworkers (2) found that 0.26

(3) I. M. Kolthoff and E. B. Sandell, Textbook of Quantitative Inorganic Analysis, 3rd ed., MacMillan Company, New York, N. Y., 1952, p. 543.

per cent diphenylamine was sufficient to inhibit completely the free radical reactions in the reactions of bromoform with sodium methoxide in methanol, and iodoform with sodium hydroxide in 66 2/3 per cent aqueous dioxane. The tendency for free radical reactions to intervene appears to increase with increasing molecular weight of the haloform, and appears to be greater in methanol than in dioxane-water mixtures. Therefore 0.4 per cent diphenylamine was added to the 66 2/3 per cent aqueous dioxane reaction solutions.

The low solubility of diphenylamine in water (0.03 grams per 100 grams of water at 20°C.) prevented its use in the solvent water. p-Phenylenediamine is another efficient radical inhibitor which is both soluble in water (3.8 grams per 100 grams of water at 24°C.) and is a weak enough base ($pK_1 = 7.96$) so that it consumes no appreciable amount of acid during the titration of the kinetic points. This amine was tried in several runs in the hydrolysis of bromochloriodomethane in water at 50°C. The material produced a reddish color in the reaction mixture which obscured the phenolphthalein end point. Recrystallization of the diamine failed to remedy this situation. However, a run containing 0.4 per cent p-phenylenediamine was made using a Beckman pH meter to determine the end points of the titrations. The rate constants calculated from this run were within the experimental error of rate constants from runs which contained no inhibitor. Subsequently no free radical inhibitor was used in the solvent water.

Extinction Coefficient Measurements

Extinction coefficients for bromochloriodomethane and chlorodiiodomethane at four wavelengths in the infrared region were determined

over a wide range of concentrations in carbon disulfide and found to be constant within the experimental error. Since iodine does not absorb in the infrared, its presence as an impurity (up to 0.5 per cent of the haloform) was ignored. At those wavelengths where the compounds absorb strongly, a 0.10 mm. sodium chloride cell was used. From data obtained with this cell, the length of a longer sodium chloride cell was determined and found to be 3.08 ± 0.08 mm. The 3.08 mm. cell was used to find extinction coefficients for the haloforms at wavelengths where they do not absorb strongly. All measurements were made on a Perkin Elmer Model 21 double-beam recording infrared spectrophotometer using the following program: slit width control 965; response 2:2; gain 5.2; automatic suppression 0; speed 0. A sodium chloride prism was used.

Miscellaneous Techniques

The thermostatic device used to maintain the temperature in the kinetic runs consisted of a five gallon glass jar, a Sargent Heater and Circulator, and a Sargent Thermonitor. Except on rare occasions this apparatus held a temperature constant to within 0.02°C . both at 50°C . and at 64.5°C . The bath thermometer was calibrated against Bureau of Standards thermometers.

A spring-wound clock was used to time all kinetic runs except those involving bromodichloromethane; for these runs a stopwatch was used.

In general, glassware was cleaned as soon as possible after use. The method of cleaning of the reaction vessels consisted of allowing them to stand filled with sulfuric acid-sodium dichromate cleaning solution for an hour or so, rinsing with tap water five or six times, rinsing once with

distilled water, and allowing them to drip dry. Occasionally the flasks were dried by shaking with a small amount of acetone and flushing dry with nitrogen.

The titration of all kinetic points except those involving the use of a pH meter was effected in 200 ml. Erlenmeyer flasks. In later runs, a magnetic stirrer was used to stir the solution as it was titrated. In the case of the single-flask method, the 50 ml. pipet was allowed to drain for ten seconds after the steady flow had ceased. In multiple-flask techniques, the contents of the reaction flask were emptied into an Erlenmeyer flask. The reaction flask was rinsed twice with distilled water, and the rinsings were added to the solution to be titrated.

Preparation and Purification of Reagents

Water.--Distilled water was boiled and stored under nitrogen.

Dioxane.--Commercial dioxane was purified by the method of Fieser (4), distilled under nitrogen, and stored under nitrogen in a brown bottle over sodium wire.

Methanol.--Commercial absolute methanol was boiled under nitrogen, and stored under nitrogen in brown bottles.

Sodium Methoxide.--Freshly-cut sodium washed in methanol was added to absolute methanol under nitrogen. The sodium methoxide was standardized by titrating samples in aqueous solution with hydrochloric acid using phenolphthalein as an indicator.

Sodium Hydroxide.--Approximately one N carbonate-free sodium hydroxide was prepared by diluting a filtered 50 per cent aqueous solution of C.P.

(4) L. F. Fieser, Experiments in Organic Chemistry, Part II, 3rd ed., D. C. Heath and Co., New York, N. Y., 1955, p. 284.

NaOH pellets. Approximately 0.3 N sodium hydroxide was prepared by dilution of a portion of the one N solution. The solutions were standardized against potassium biphthalate samples using phenolphthalein as an indicator. The sodium hydroxide solutions were stored under nitrogen in polyethylene bottles.

Standard Hydrochloric and Perchloric Acids.--These acids were prepared by dilution of commercial concentrated reagents and standardized against sodium hydroxide using phenolphthalein as an indicator.

Standard Silver Nitrate.--Solid silver nitrate was dissolved in distilled water and stored in a brown bottle. The solution was standardized against known weights of dried sodium chloride using dichlorofluorescein as an indicator. The titration procedure has been described previously.

Carbon Disulfide.--Commercial carbon disulfide was stored over silica gel. This removed a slight brownish tinge which the liquid possessed when initially obtained.

Diphenylamine.--Eastman White Label diphenylamine was used without further purification.

p-Phenylenediamine.--Eastman White Label p-phenylenediamine was used both in its original form and also after recrystallization from benzene or toluene. The amine, grayish or reddish-gray as initially obtained, is light sensitive. It was not possible to obtain a pure white product through recrystallization. A small quantity of white crystalline p-phenylenediamine was prepared by sublimation, but this was not used in the research.

Bromodichloromethane.--Dow bromodichloromethane was distilled once and used without further purification.

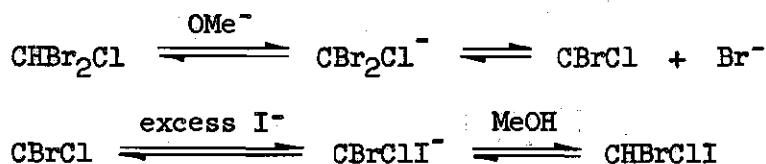
Dibromochloromethane.--Dow dibromochloromethane was used without further purification.

Chlorodiiodomethane.--Chlorodiiodomethane was prepared by the method of Auger (5). Four hundred grams of iodoform was intimately mixed with 130 grams of mercuric chloride, and the mixture heated under a partial vacuum of 33 mm. of mercury. About 70 ml. of deep red liquid was obtained. The distillation head temperature was 85 to 120°C. The product was fractionated under nitrogen on a Todd column in the dark. The first fraction (boiled up to 100°C. at 32 mm.) was discarded. The second fraction (boiled 100 to 103°C. at 32 mm.) was washed once with approximately one N sodium thiosulfate solution, then with distilled water, then refracted. Approximately 40 ml. boiling at 102 to 103°C. at 32 mm. was collected and stored under nitrogen with a few crystals of silica gel in a low-actinic volumetric flask. The flask was kept in the dark when not in use. The liquid had a slight reddish tinge that darkened over a period of weeks. Therefore the liquid was periodically washed with sodium thiosulfate and water to remove iodine. The chlorodiiodomethane decomposed very rapidly in the presence of air and was somewhat sensitive to light.

Bromochloriodomethane.--Bromochloriodomethane was prepared by a method developed in this laboratory. The method was analogous to that used by Dowell (6) to obtain dichloriodomethane from chloroform. Dibromochloromethane was treated with sodium methoxide and excess sodium iodide in methanol. The proposed mechanism for this reaction is as follows:

(5) V. Auger, Compt. rend., 146, 1037 (1908).

(6) A. M. Dowell, Jr., Ph.D. Thesis, Georgia Institute of Technology, 1954.



Nine hundred grams (six moles) of sodium iodide and 255 ml. (three moles) of dibromochloromethane were dissolved in 1750 ml. of absolute methanol at reflux under nitrogen in the dark. Four hundred seventy ml. of 4.80 N sodium methoxide (2.3 moles) was added dropwise from a separatory funnel over a period of four hours. The mixture was stirred by an air-tight motor-driven stirrer. After refluxing, the flask and its contents were allowed to cool under nitrogen and were kept at room temperature in the dark for two days.

The following separation and purification was carried out under nitrogen in indirect yellow light. Water was added to the mixture until a heavy organic layer settled out. The organic layer was washed once with water. The methanol-water layer was extracted twice with n-pentane. The pentane extractions were evaporated to a volume of about 200 ml. on a water aspirator. The remaining liquid was added to the original organic layer, and the liquid was fractionated on a Todd column under a partial vacuum. Three fractions were collected, about 105 ml. of the desired product being obtained over the range 61 to 71°C. at 24 mm. pressure. The product was stored in a low-actinic volumetric flask under nitrogen and was kept in the dark when not in use.

Two other portions of bromochloriodomethane were prepared at later dates, the procedure being substantially the same except that in the second run methylene chloride was used to extract the methanol-water

mixture, and in the third run n-hexane was used for the extraction. The yield of bromochloriodomethane based on dibromochloromethane was 39 per cent in the original run, 57 per cent in the second run, and about 20 per cent in the third run. The haloform is somewhat sensitive to light and very sensitive toward oxygen. The liquid assumed a red color due to iodine (never more than 0.5 per cent) over a period of weeks, so it was periodically washed with sodium thiosulfate solution, then water, and stored with a few crystals of silica gel. Prior to use, the yields from the first two runs were combined and refractionated. About 200 ml. of material boiling at 68 to 69°C. at 30 mm. was obtained. The yield from the third run was refractionated at the time of preparation, and again about a month later.

The density of the bromochloriodomethane was determined to be 2.808 g./cc. at 24.0°C. The refractive index was found to be 1.6310 at 24.0°C. Using these data the molecular refractivity of bromochloriodomethane was calculated from the Lorentz-Lorenz equation and was found to be 32.391. The molecular refractivity calculated from atomic refractive constants (7) was found to be 32.250.

The freezing point of bromochloriodomethane was found to be -24.5°C.

The only references to bromochloriodomethane in the literature are by Garino and Muzio (8) and Garino and Teofili (9). The density of

(7) N. A. Lange, Handbook of Chemistry, 8th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1952, p. 1421.

(8) M. Garino and I. Muzio, Gazz. chim. ital., 52, II, 226 (1922).

(9) M. Garino and E. Teofili, ibid., 56, 847 (1926).

bromochloriodomethane was reported to be between 2.931 and 3.120 g./cc., and the compound was reported to boil with decomposition at 180 to 190°C. at atmospheric pressure. The freezing point was reported as about 5°C. (9).

CHAPTER III

RESULTS AND DISCUSSION

Rate Equation and Determination of f

Among the end products of the hydrolysis of most haloforms under basic conditions are carbon monoxide and/or formate ion. Four moles of base are consumed in producing one mole of formate, while three moles of base are required to give one mole of carbon monoxide. In order to relate the amount of base consumed to the amount of haloform used, it is necessary to determine the fraction of haloform hydrolyzed which gives either carbon monoxide or formate. This can be determined from a knowledge of the total halide ion produced by the consumption of a certain amount of base; the following expression can be used:

$$f = 3 \left(\frac{\Delta[\text{OH}^-]}{[\text{X}^-]} - 1 \right)$$

where f is the fraction of haloform hydrolyzed which gives formate (the rest gives carbon monoxide); $\Delta[\text{OH}^-]$ is the moles per liter of base consumed; and $[\text{X}^-]$ is the moles per liter of halide ion generated (10).

For the haloforms studied, the rate constants were calculated from the integrated rate equation¹

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

¹For the derivation of this expression, see reference 10.

$$k = \frac{2.303}{t[(3 + f) H_0 - B_0]} \log \frac{B_0}{(3 + f) H_0} \cdot \frac{B + [(3 + f) H_0 - B_0]}{B}$$

Here H_0 is the initial haloform concentration; B_0 is the initial base concentration; B is the base concentration at time t ; $(3 + f)$ is the number of moles of base that react per mole of haloform; the meaning and means of determination of f have been discussed previously. Although f appears to be not very dependent on temperature or the presence of dioxane for haloforms studied in this laboratory, the value of f as determined by the technique described is extremely sensitive to impurities and side reactions (6, 11). Fortunately, however, the rate expression is not very sensitive to the value of f .

Ehrenson (12) chose a value of f of zero for chlorodiodomethane, since his determinations of f were widely scattered about zero (even negative), and since it had been noted that f was lower for haloforms containing the heavier halogens than for other haloforms. For bromochloriodomethane, f was determined by the author to be 0.10 ± 0.04^1 . In the hydrolysis of bromochloriodomethane in the presence of excess iodide ion, where chlorodiodomethane is generated and is available for hydrolysis, no measurements of f were made. However, since only a very small percentage of the total hydrolysis is due to chlorodiodomethane, the value of f

(11) J. E. Singley, Jr., M.S. Thesis, Georgia Institute of Technology, 1952.

(12) S. J. Ehrenson, Ph.D. Thesis, Georgia Institute of Technology, 1957.

¹The deviation given is the average deviation, as are all deviations listed herein.

of 0.10 was retained. The actual value of f , while possibly somewhat lower, is surely within the experimental error of 0.04. Since chloroform and bromodichloromethane give the same dihalide intermediate, the f value of 0.15 for bromodichloromethane was chosen from Dowell's (6) data on chloroform.

Results of Rate Determinations

Table 2 summarizes the rate data obtained.

Table 2. Rate Constants for Basic Haloform Hydrolysis Reactions.

Hydrolysis Reaction	Temperature, °C.	$k \times 10^4$ (l./m.s.)
CHCl ₂ Br in water	50	356.5 ± 7.0
CHBrClI in 66 2/3 per cent aqueous dioxane	50	104.5 ± 2.9
CHBrClI in water	50	55.3 ± 2.8
CHBrClI in water	30	2.66 ± 0.14
CHClI ₂ in water with 0.30 M NaI	64.5	15.56 ± 0.50
CHClI ₂ in water with 0.30 M salts (0.15 M NaNO ₃ , 0.15 M NaClO ₄)	64.5	59.2 ± 1.7

The value of k for bromodichloromethane was obtained for use in the correlation equation 3, since an accurate value of k was not available previously. From the data on bromochloriodomethane in water at 50°C. and 30°C., it was found that the heat of activation ΔH^\ddagger is 28.9 kcal./mole for this reaction; ΔS^\ddagger was found to be 20.5 entropy units. The

heat and entropy of activation were calculated from the equation¹

$$k_{\text{reaction}} = \frac{kT}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}$$

Determination of f_I

As was stated previously, the purpose of this research was to determine the value of the rate constant for the formation of CBrCl relative to that for the formation of ClCl in the hydrolysis of bromochloriodomethane. In order to determine the extent to which the reaction proceeds through CBrCl or ClCl, it would be desirable to capture the intermediates and measure the amount of the captured material which originated from each intermediate.

Several capturing agents were considered. Capture by olefins has the disadvantage that a three-membered ring must be formed, at least temporarily; and this ring might be difficult to form. Furthermore, olefins would probably not be sufficiently nucleophilic to compete effectively with the large amount of water in the reaction mixture.

Another possible nucleophilic capturing agent is a sulfinic acid, RSO_2H , or its sodium salt. This possibility was tested experimentally using sodium benzenesulfinate. Capture by this compound should result in a solid derivative of the form $\text{C}_6\text{H}_5\text{SO}_2\text{CHX}_2$, X representing halogen. Dibromochloromethane was allowed to react with sodium methoxide in the presence of sodium benzenesulfinate in methanol at reflux. A variety of

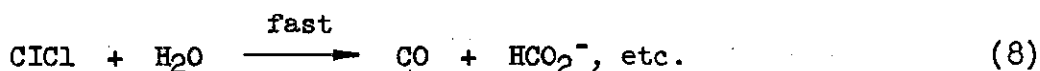
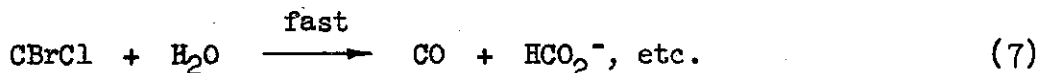
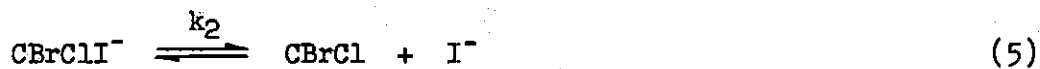
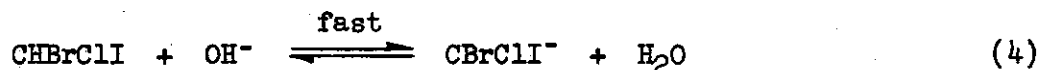
¹For the significance of this equation, see reference 13.

(13) A. I. Frost and R. G. Pearson, Kinetics and Mechanism, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 96.

concentrations of the reagents was tried, but no solid organic derivative (other than starting materials) was isolated. Therefore, this method was abandoned.

Sodium halides were considered as agents to capture the CX_2 intermediates. Data on dibromochloromethane indicate that the ability of the sodium halides to capture the intermediates follows the order $NaF \ll NaCl < NaBr < NaI$ (14). Apparently the greater nucleophilicity of iodide ion renders it most effective as a capturing agent for the species in question. The successful use of sodium iodide as an agent to capture the intermediates $CBrCl$ and $ClCl$ (formed in the reaction of $CHBrClI$ with $NaOH$) is described on the following pages.

The hydrolysis of bromochloriodomethane is represented by the following equations:



The ratio of k_2 to k_3 or a related number was sought. By means of a suitable derivation¹ it was possible to express the fraction of the

(14) J. Hine and A. M. Dowell, Jr., *J. Am. Chem. Soc.*, **76**, 2688 (1954).

¹See Appendix I.

reaction proceeding through the intermediate CICI as a function of a number of experimentally accessible terms. The result of this derivation is given by the following expressions:

$$Q = \frac{r_3[I^-] (1 + r_2[I^-])}{\left(\frac{1}{f_1} + r_2[I^-]\right) (1 + r_3[I^-])} \quad (9)$$

$$Q_1 = Q = \frac{(A + 1) (H_0 - x)^A y}{(H_0)^{A + 1} - (H_0 - x)^{A + 1}} \quad (10)$$

where A is a constant whose value is

$$A = \frac{-k_h^I (1 + r_2[I^-])}{k_h^{Br} [1 + r_3[I^-] + f_1 r_2[I^-] (1 + r_3[I^-])]} \quad (11)$$

and f_1 is defined as $k_3/(k_2 + k_3)$; $[I^-]$ is the iodide ion concentration; H_0 is the initial bromochloriodomethane concentration; $(H_0 - x)$ is the concentration of bromochloriodomethane at a time t , when y is the chlorodiodomethane concentration. k_h^I and k_h^{Br} are the rate constants for the basic hydrolysis of chlorodiodomethane and bromochloriodomethane, respectively, in water, or more accurately in a concentration of inert salts equal to $[I^-]$. The values of the constants r_2 and r_3 are determined by the effectiveness of iodide ion at capturing the intermediates CBrCl and CICI, respectively.¹ $[I^-]$ and H_0 were the values used in a study of the

¹See page 26 ff.

hydrolysis of bromochloriodomethane in water with excess iodide ion, and $(H_0 - x)$ and y were obtained from this study.

The constant Q was represented by two expressions, 9 and 10, which contained only known values except for f_I . Clearly the solution of these equations for f_I was theoretically possible. The algebraic solution would be extremely tedious, if possible at all. The solution for f_I could be obtained by plotting on the same graph the right-hand sides of equations 9 and 10 for various values of f_I between zero and one; the intersection of the two curves would indicate the value of f_I that satisfied both equations. This method, however, would entail considerable exhaustive calculation, requiring a separate set of computations for each set of $x-y$ values obtained in the kinetic runs.

A better method consists of allowing an electronic computer to compare the values of equations 9 and 10 for various values of f_I . To accomplish this, use was made of the IBM Model 650 Magnetic Drum Electronic Data Processing Machine. The method of solution consisted of allowing the computer to perform the following operations. Beginning with $f_I = 0$, f_I was increased by a suitable increment, and the difference between equations 9 and 10 was calculated. f_I was increased in this manner until the difference $(Q - Q_1)$ changed sign. The value of f_I for which this function changed sign was recorded as the solution sought.

Two programs were used, both employing the Bell General Purpose System designed by R. W. Hamming and Miss R. A. Weiss of the Bell Telephone Laboratories¹. The first program provided for calculation of all

¹Information concerning the use of this system can be obtained from the Rich Electronic Computer Center, Georgia Institute of Technology.

values of f_I between zero and one accurate to 0.002. Examination of early results indicated that only one solution was found in this range, so a second program, designed to conserve machine time, was prepared which provided for the calculation of only one value of f_I . This second program was further designed to start the search for f_I at a point well above zero but below the expected value of f_I . Values obtained from this program were also correct to 0.002.

As a matter of interest, about five seconds of machine time was required to perform an evaluation of $(Q - Q_1)$ for each value of f_I .

Interpretation of f_I

Results of the study of the hydrolysis of bromochloriodomethane at 50°C. in iodide ion indicate that f_I has the value 0.732 ± 0.019 . This means that at 50°C. the reaction proceeds about 73 per cent through the intermediate $CICl$ and about 27 per cent through $CBrCl$.

The overall hydrolysis rate constant for bromochloriodomethane in water is 55.3×10^{-4} l./m.s. at 50°C. The rate constant for that part of the reaction proceeding through $CICl$ is therefore $0.732 \times 55.3 \times 10^{-4}$ or 40.5×10^{-4} l./m.s., and the rate constant for that part of the reaction proceeding through $CBrCl$ is $(1 - 0.732) \times 55.3 \times 10^{-4}$ or 14.8×10^{-4} l./m.s. The hydrolysis of bromochloriodomethane was treated as two reactions; the above rate constants were combined with data for other haloform hydrolyses at 50°C. in water, and the parameters in Hine and Ehrenson's correlation equation were recalculated. A value of 103.9 l./m.s. was chosen for bromochloriodomethane because data of Hine and

coworkers (15) on bromodichloromethane, dichloriodomethane, bromoform, and iodoform showed that replacement of bromine by iodine did not materially change the values of k_1 , and k_1 for dibromochloromethane was found to be 103.9 l./m.s. at 50°C. The values of the parameters are listed in Table 3. The old parameter values had been calculated without data on bromochloriodomethane.

Table 3. Values of Parameters of Equation 3 at 50°C.

Parameter	Old Value	New Value
M_{Br}	-1.131	-1.164
M_I	-2.039	-1.696
M_F	3.193	3.071
N_{Br}	0.936	1.090
N_I	0.486	0.327
q	0.196	0.114

It is seen that iodine appears to be considerably poorer at escaping as an anion from the trihalocarbanion than previously thought, and is somewhat better at stabilizing the dihalomethylene intermediate.

The new parameter values allow the prediction of the haloform hydrolysis rate constants with an average deviation of 0.086 in the term $\log \frac{k_2}{k_{-1}}$. A comparison of the actual and calculated values of this log term is given by Table 4.

(15) J. Hine, N. W. Burske, M. Hine, and P. B. Langford, J. Am. Chem. Soc., 79, 1406 (1957).

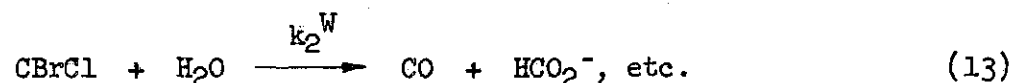
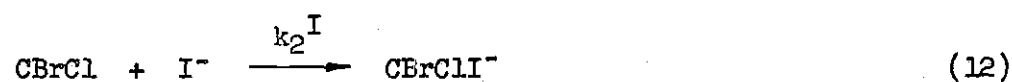
Table 4. Actual and Calculated Values of $\log k_2/k_{-1}$

Haloform	$-(\log k_2/k_{-1})$ actual	$-(\log k_2/k_{-1})$ calculated
CHCl ₃	3.544	3.544
CHClI ₂	5.053	4.953
CHBr ₃	4.591	4.588
CHCl ₂ I	3.421	3.628
CHBr ₂ Cl	3.675	3.658
CHCl ₂ F	0.782	0.819
CHBrCl ₂	2.850	2.865
CHI ₂	1.911	1.928
CHBrClF	0.090	-0.116
CHBr ₂ F	0.512	0.655
CHBrClI ^a	4.409	4.491
CHBrClI ^b	4.847	4.722

^aThrough CCl₃. ^bThrough CBrCl.

Evaluation of r_2 and r_3

In the hydrolysis of bromochloriodomethane in excess aqueous iodide ion, the intermediate CBrCl disappears in two ways:



We may define F_2 as the fraction of CBrCl that disappears by hydrolysis.

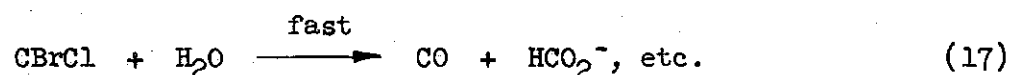
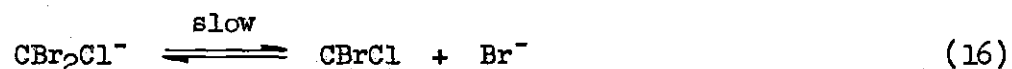
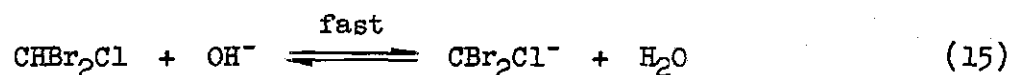
Then

$$F_2 = \frac{k_2^W [\text{CBrCl}]}{k_2^W [\text{CBrCl}] + k_2^I [\text{CBrCl}] [\text{I}^-]}$$

Defining k_2^I/k_2^W as r_2 , we have

$$F_2 = \frac{1}{1 + r_2 [\text{I}^-]} \quad (14)$$

The experimental value of r_2 may be obtained through a study of the hydrolysis of dibromochloromethane (equations 15, 16, and 17), in which the only carbon dihalide intermediate formed in significant quantities is CBrCl.



If a large quantity of iodide ion were present in the solution, it would compete with the water for the CBrCl intermediate. Attack by water results in hydrolysis, while attack by iodide ion results in the formation of a different haloform, bromochloroiodomethane. The result of the competition between the water and the iodide would be measured by F_2 , the fraction of CBrCl that is consumed by hydrolysis. The concentrations of hydroxide, bromide, chloride, iodide generated by hydrolysis, etc. are very low compared to the concentration of sodium iodide to be used. Also, hydroxide, bromide, and chloride are

usually poorer nucleophilic agents than iodide (16). Therefore, the presence of all such species other than iodide and water were ignored for purposes of the following calculation. If no iodide were present, F_2 would equal one. With iodide present, F_2 would assume some value between zero and one. In order to reduce salt effects, it would appear desirable to carry out the hydrolysis reactions (with and without iodide ion) at the same ionic strength.

The apparent rate constants for the hydrolysis of dibromochloromethane in iodide ion would drop as the reaction proceeded due to the formation of the less reactive bromochloriodomethane. Therefore the observed rate "constants" must be extrapolated to zero time, when there is no bromochloriodomethane present. Denoting this extrapolated rate constant for the hydrolysis of dibromochloromethane in a quantity of iodide ion by $(k_h^*)_{\text{CHBr}_2\text{Cl}}$ and the rate constant for the hydrolysis in the same concentration of inert salt by $(k_h)_{\text{CHBr}_2\text{Cl}}$, then it is seen that

$$(k_h^*)_{\text{CHBr}_2\text{Cl}} = F_2 (k_h)_{\text{CHBr}_2\text{Cl}}$$

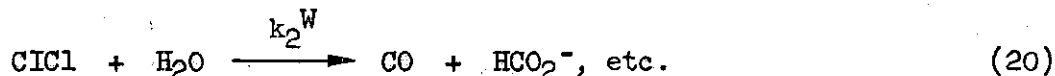
Substituting for F_2 from equation 14, we have

$$\frac{(k_h^*)_{\text{CHBr}_2\text{Cl}}}{(k_h)_{\text{CHBr}_2\text{Cl}}} = \frac{1}{1 + r_2 [\text{I}^-]} \quad (18)$$

The value of the constant r_2 can thus be determined using equation 18.

(16) C. G. Swain and C. B. Scott, J. Am. Chem. Soc., 75, 141 (1953).

By an entirely analogous treatment, a relationship similar to equation 14 is found for F_3 , the fraction of the intermediate CICl that disappears by hydrolysis in the reactions



We write for F_3

$$F_3 = \frac{1}{1 + r_3[\text{I}^-]} \quad (21)$$

When the compound chlorodiiodomethane is hydrolyzed in the presence of a large quantity of iodide ion, the observed hydrolysis rate constant should be truly constant, since capture of CICl by iodide ion regenerates the starting haloform. Denoting the rate constant for the hydrolysis of chlorodiiodomethane in a quantity of iodide ion by $(k_h^*)_{\text{CHClI}_2}$ and the rate constant for the hydrolysis in the same concentration of inert salt by $(k_h)_{\text{CHClI}_2}$, we have, analogous to equation 18,

$$\frac{(k_h^*)_{\text{CHClI}_2}}{(k_h)_{\text{CHClI}_2}} = \frac{1}{1 + r_3[\text{I}^-]} \quad (22)$$

Hine and coworkers (17) have demonstrated that the r values are not very temperature dependent; therefore some data obtained at 40°C . on the hydrolysis reactions of dibromochloromethane were used to calculate

(17) J. Hine, R. Butterworth, and P. B. Langford, unpublished manuscript, Georgia Institute of Technology.

r_2 . Hine found that at 40°C. the ratio $(k_h^*)_{\text{CHBr}_2\text{Cl}} / (k_h)_{\text{CHBr}_2\text{Cl}}$ was 0.606 for salt concentrations of 0.089 M. Inserting these data in equation 18, a value of r_2 of 7.31 l./m. was obtained.

From the data in Table 2 for chlorodiiodomethane at 64.5°C., r_3 was calculated and found to have a value of 9.34 l./m. From the average deviations in the rate constants, a range of values for r_3 was established as 8.62 to 10.19. In the inert salt runs, two salts, sodium nitrate and sodium perchlorate, were used in the same solution in an attempt to reduce errors in $(k_h)_{\text{CHClI}_2}$ due to any specific salt effects of the anions.

Dependence of f_I on the Values of the Constants

Table 5 lists the values of some of the constants encountered in the evaluation of f_I at 50°C. from equations 9 and 10.

Table 5. Values of Constants

Constant	Value
k_h^I	$(9.21 \pm 0.29) \times 10^{-4}$ l./m.s.
k_h^{Br}	$(55.3 \pm 2.8) \times 10^{-4}$ l./m.s.
r_2	7.31 l./m.
r_3	9.34 l./m.

The value for k_h^I was taken from data obtained by Ehrenson (9) on the reaction of chlorodiiodomethane plus sodium hydroxide in water at 50°C. The value for k_h^{Br} was obtained by the author. The determination of r_2 and r_3 has been discussed previously.

The role of the constant \underline{A} in equation 10 is that of a correction term. This is most easily seen by comparing equations 39, 42, and 43 in Appendix 1. The negative term in the right side of equation 39 arises from the fact that some of the chlorodiodomethane that is formed hydrolyzes and is lost. The studies on the bromochloriodomethane hydrolysis in iodide ion were conducted before as much as 30 per cent of the bromochloriodomethane was hydrolyzed. Within this period, the extent of the hydrolysis of chlorodiodomethane is small compared to the amount of chlorodiodomethane formed by capture of CBrCl by iodide ion. Thus, the negative term in equation 39 is small compared to the positive term, even when considerable chlorodiodomethane has been generated. The negative part of equation 42 is likewise small compared to the rest of the expression. Note that \underline{A} in equation 43 is the constant part of the negative term in equation 42. Thus \underline{A} arises from an attempt to correct $\underline{dy/dt}$ for the slow hydrolysis of chlorodiodomethane.

The role of \underline{A} as a correction term was demonstrated by varying the value of $\underline{k}_h^{\text{Br}}$ and observing the effect of this variation on the calculated values of \underline{f}_I . It was found that inserting the value of 52.5×10^{-4} for $\underline{k}_h^{\text{Br}}$ (a decrease in $\underline{k}_h^{\text{Br}}$ of five per cent) caused a change in \underline{f}_I of only about 0.2 per cent.

It was stated previously that the symbols $\underline{k}_h^{\text{Br}}$ and $\underline{k}_h^{\text{I}}$ should represent the rate constants for the reactions of bromochloriodomethane and chlorodiodomethane, respectively, with sodium hydroxide in a solution of inert salts of concentration equal to the iodide concentration in the runs from which values of \underline{H}_0 , \underline{x} , and \underline{y} were obtained. Since several such runs were made at different iodide ion concentrations, the evaluation of

the proper numbers for k_h^{Br} and k_h^{I} in each case would entail considerable experimental work. However, providing that the ionic strength is not too large, it is reasonable to assume that for any given ionic strength of inert salts, the ratio of k_h^{I} to k_h^{Br} will be approximately the same as for another ionic strength. In the final equations, k_h^{I} and k_h^{Br} occur only as a ratio in the constant A , and A is itself only a correction term. Therefore, it was felt justified to use the values of k_h^{I} and k_h^{Br} in water with no added inert salts.

The effect on f_{I} of varying r_2 or r_3 is considerably greater than the effect of varying k_h^{Br} or k_h^{I} . When r_3 was changed from 9.34 to 8.64 (the lower average value; an eight per cent change), f_{I} was raised by about six per cent. When the upper average limit of r_3 (10.19, a nine per cent change) was used, f_{I} was lowered by about five per cent. Thus the values calculated for f_{I} appear to be affected somewhat proportionately to the value selected for r_3 (and r_2). The uncertainty in the values of r_2 and r_3 probably constitutes the major source of error in the determination of f_{I} .

Determination of Haloform Concentrations

Chlorodiiodomethane and bromochloriodomethane have pairs of absorption maxima in the infrared whose wavelengths lie close together and whose origin appears to be similar or identical. One pair occurs at 8.505μ for bromochloriodomethane and 8.615μ for chlorodiiodomethane; another pair occurs at 9.057μ for bromochloriodomethane and 9.357μ for chlorodiiodomethane. These pairs of absorption maxima were chosen for the analysis of kinetic points for haloform content. Therefore,

the extinction coefficients for both haloforms at all four wavelengths were determined using the equation

$$D = \log \frac{I_0}{I} = \epsilon c l \quad (23)$$

where D is the optical density; I_0 is the intensity of light after passing through a cell of length l cm. filled with solvent; I is the intensity of light after passing through an identical cell filled with sample; c is the concentration of dissolved material in m./l. for which ϵ is the extinction coefficient. The results are summarized in Table 6.

Table 6. Extinction Coefficients for Haloforms.

Wavelength (μ)	$\epsilon_{\text{CHBrClI}}$ (1./m.cm.)	$\epsilon_{\text{CHClI}_2}$ (1./m.cm.)
8.505	59.7 \pm 1.4	7.69 \pm 0.16
8.615	5.97 \pm 0.10	59.1 \pm 1.2
9.057	173.8 \pm 3.9	10.83 \pm 0.37
9.357	1.75 \pm 0.03	171.3 \pm 3.2

Since the extinction coefficients for the absorption maxima at 8.505 μ and 8.615 μ are the same within the experimental error, and likewise the extinction coefficients for the maxima at 9.057 μ and 9.357 μ , the value 59.4 l./m.cm. was chosen as the extinction coefficient for bromochloriodomethane at 8.505 μ and chlorodiiodomethane at 8.615 μ , and 173 l./m.cm. was chosen as the value for bromochloriodomethane at 9.057 μ and chlorodiiodomethane at 9.357 μ .

In order to determine the concentration of a haloform from the optical density at one of its maxima, it was necessary to correct this optical density for the presence of the other haloform. This was most easily accomplished by solving simultaneously two equations such as the following;

$$\frac{D_a}{l} = 59.4 H_1 + 7.69 H_2 \quad (24)$$

$$\frac{D_b}{l} = 5.97 H_1 + 59.4 H_2 \quad (25)$$

where D_a is the optical density at 8.505μ ; D_b is the optical density at 8.615μ ; H_1 is the concentration of bromochloriodomethane in the carbon disulfide extract; H_2 is the chlorodiodomethane concentration in the extract; and l is the cell length in cm. For the 0.308 cm. cell, the following expressions for H_1 and H_2 were obtained by solving simultaneously equations 24 and 25:

$$H_1 = 0.05538 D_a - 0.00717 D_b \quad (26)$$

$$H_2 = 0.05466 D_b - 0.1005 H_1. \quad (27)$$

At the other pair of wavelengths, the equations took the form

$$\frac{D_c}{l} = 173 H_1 + 10.83 H_2$$

$$\frac{D_d}{l} = 1.75 H_1 + 173 H_2$$

where \underline{D}_c refers to 9.057μ , and \underline{D}_d refers to 9.357μ . Solving these expressions with \underline{l} as 0.308 cm., equations 28 and 29 were obtained.

$$H_1 = 0.01878 D_c - 0.00118 D_d. \quad (28)$$

$$H_2 = 0.01877 D_d - 0.01012 H_1. \quad (29)$$

This method gave rise to two sets of haloform concentrations which could serve as mutual checks on each other. Of principal interest, however, were not the concentrations of the haloforms in the carbon disulfide extract, but the actual concentrations in the reaction solution. These were most easily obtained from a knowledge of the total haloform concentration in the reaction solution and the ratio of the concentrations of the two haloforms present. The ratio of the haloform concentrations was obtained from the infrared analysis and was calculated as $\underline{H}_1/\underline{H}_2$. The total haloform concentration in the reaction solution was equal to the initial bromochloriodomethane concentration (initial chlorodiodomethane concentration was of course zero) less the amount of haloform consumed by hydrolysis. The amount of haloform consumed by hydrolysis was equal to the decrease in base concentration at a particular time, divided by $(3 + \underline{f})$, since $(3 + \underline{f})$ moles of base are required to hydrolyze one mole of haloform. The chlorodiodomethane concentration was then equal to the total haloform concentration multiplied by the fraction

$$\frac{1}{1 + \frac{H_1}{H_2}}.$$

The bromochloriodomethane concentration was the difference between the total haloform concentration and the chlorodiodomethane concentration.

In this manner, data was obtained for the calculation of f_I from a study of the reaction of bromochloriodomethane plus sodium hydroxide in water with iodide ion added.

Investigation of Possible Sources of Error in the Infrared Analysis

Various substances are produced by the hydrolysis of haloforms, and other products might be generated in small quantities by side reactions. Therefore the possibility existed that some substance which could simulate bromochloriodomethane or chlorodiodomethane in the infrared might be extracted from the reaction solution by carbon disulfide. The chlorodiodomethane concentration at early points in the reaction is considerably lower than the concentration of bromochloriodomethane. The presence of any "pseudo-chlorodiodomethane" other than bromochloriodomethane in the extract might introduce a considerable error in the ratio of the haloforms. This possibility was investigated by making several blank determinations. In each run from which haloform concentrations were obtained, two or three points taken at zero time were analyzed to determine if any pseudo-chlorodiodomethane (other than bromochloriodomethane) were present at the beginning of the reaction. Although accurate detection of quantities present in very small amounts (less than one per cent of the bromochloriodomethane) is not feasible with the methods used, it was determined that essentially no impurity of the sort described was present initially in the reaction solutions.

Analysis of some carbon disulfide extracts obtained from aqueous sodium hydroxide-sodium iodide solutions indicated that these solutions contained no extractable material which could simulate either of the haloforms in the infrared.

The possibility was investigated of some impurity being formed as the reactions proceeded which could simulate chlorodiiodomethane. Bromochloroiodomethane was allowed to hydrolyze in aqueous base with no iodide ion present. Points were extracted with carbon disulfide and analyzed for bromochloroiodomethane and chlorodiiodomethane. The points were taken within the time required for an amount of hydrolysis of bromochloroiodomethane comparable to that occurring in the reactions with iodide ion present. A simple calculation shows that under these conditions, no more than 0.1 per cent chlorodiiodomethane could be formed. The results of the analysis fixed the level of pseudo-chlorodiiodomethane (other than bromochloroiodomethane) at about 0.5 to 1 per cent throughout the reaction, including the zero points. This was taken as evidence that no pseudo-chlorodiiodomethane impurity was built up during the reaction. Since the zero points of the iodide runs showed the absence of such an impurity, it was concluded that impurities never reached a detectable level during the time in which points were taken.

Several measurements were made to determine the completeness of the carbon disulfide extraction of haloform. It was found that the technique used resulted in essentially complete extraction of haloforms by carbon disulfide. Therefore, any differences in the distribution coefficients between water and carbon disulfide for bromochloroiodomethane and chlorodiiodomethane could be ignored without introducing any appreciable error.

Correlation of Haloform Hydrolysis Rates in Dioxane-water

Rate data are available for the basic hydrolysis of eight haloforms in 66 2/3 per cent aqueous dioxane at 50°C. The rate constants are listed in Table 7.

Table 7. Rate Constants for Hydrolysis of Haloforms
in 66 2/3 Per Cent Aqueous Dioxane at 50°C.

Haloform	$k \times 10^4$ (1./m.s.)
CHCl_3^{a}	20.8
$\text{CHCl}_2\text{Br}^{\text{b}}$	502
$\text{CHClBr}_2^{\text{b}}$	251
CHBr_3^{c}	87.0
$\text{CHCl}_2\text{I}^{\text{d}}$	293
$\text{CHClI}_2^{\text{d}}$	17.7
CHI_3^{d}	1.55
$\text{CHBrClI}^{\text{e}}$	104.5

^aAt 49.9°C. Reference 1. ^bRate constants extrapolated from data at lower temperatures. See reference 1 for data at 0°C., 25.3°C., and 35.7°C. ^cReference 1. ^dReference 2. ^eFrom Table 2.

Values of k_1 , the rate constant for carbanion formation, have not been determined in this solvent. Therefore, Hine and Ehrenson's correlation equation 3 was modified to give an expression which did not contain k_1^1 . For the chlorine-bromine containing haloforms, the modified expression is

¹See references 2 and 12 for the assumptions involved in this modification.

$$\log \frac{(k_h)_{\text{CHBr}_n\text{Cl}_3 - n}}{(k_h)_{\text{CHCl}_3}} = \log \frac{n}{3} + n(A_{\text{Br}} + M_{\text{Br}}) + (N_{\text{Br}} - M_{\text{Br}}) \quad (30)$$

where A_{Br} is a constant for the haloforms containing bromine and chlorine. The meaning of the other symbols is the same as in equation 3. For the chlorine-iodine containing haloforms, the expression (call it number 30') is given by equation 30 with "I" replacing "Br." Denote $(A_{\text{Br}} + M_{\text{Br}})$ by S_{Br} , $(A_{\text{I}} + M_{\text{I}})$ by S_{I} , $(N_{\text{Br}} - M_{\text{Br}})$ by T_{Br} , and $(N_{\text{I}} - M_{\text{I}})$ by T_{I} . Then for bromochloriodomethane, where the hydrolysis can occur by two major paths, the correlation expression is given by

$$\log \frac{(k_h)_{\text{CHBrClI}}}{(k_h)_{\text{CHCl}_3}} = \log \left[\frac{10^{(S_{\text{Br}} + S_{\text{I}} + T_{\text{Br}})}}{3} + \frac{10^{(S_{\text{Br}} + S_{\text{I}} + T_{\text{I}})}}{3} \right] \quad (31)$$

Using these equations, the hydrolysis rates can be correlated in terms of four parameters: S_{Br} , S_{I} , T_{Br} , and T_{I} . The optimum values of the parameters, obtained by a least-squares approximation, are given in Table 8. Using these values of the parameters, the hydrolysis rates are correlated with an average deviation of 0.05 log units in the log function

$$\log \frac{(k_h)_{\text{haloform}}}{(k_h)_{\text{CHCl}_3}}$$

Table 8. Values of Parameters of Equations 30, 30',
and 31 at 50°C.

Parameter	Value
S_{Br}	-0.607
S_I	-1.38
T_{Br}	2.47
T_I	2.98

CHAPTER IV

CONCLUSIONS

Bromochloriodomethane was prepared by a new technique which consisted of treating dibromochloromethane with sodium methoxide in methanolic sodium iodide.

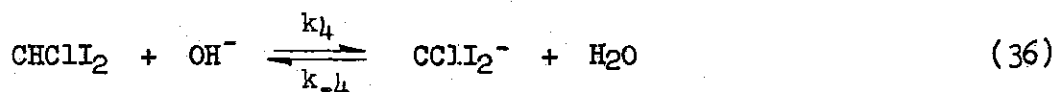
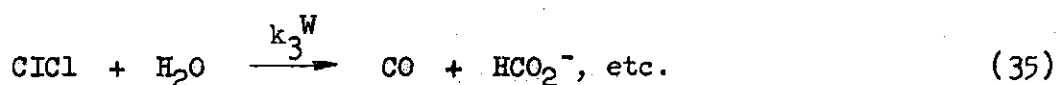
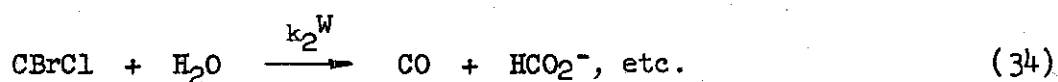
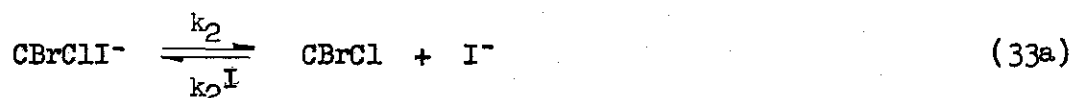
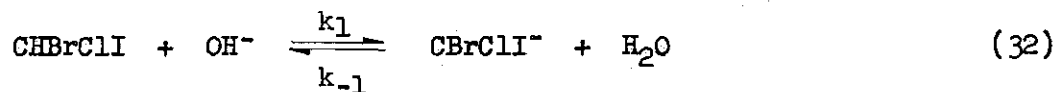
In the reaction of bromochloriodomethane with sodium hydroxide in water at 50°C., the fraction f_I of the reaction proceeding through the intermediate $CI\dot{C}l$ was found to be 0.732; the fraction proceeding through $CBr\dot{C}l$ is 0.268. The largest source of error in the determination of f_I was in the values found for r_2 and r_3 .

As a result of applying the data on bromochloriodomethane to Hine and Ehrenson's correlation equation, it was found that iodine was considerably poorer at escaping as an anion from the trihalocarbanion than previously predicted, and iodine is somewhat better at stabilizing the dihalomethylene intermediate. The new parameters predict eleven rates of hydrolysis with an average deviation of 0.086 in the term $\log k_2/k_{-1}$.

APPENDIX I

DERIVATION OF AN EXPRESSION FOR f_I

In order to derive a soluble expression for f_I , consider the following reactions with their associated rate constants.



The rate-controlling steps in the hydrolysis of bromochloriodomethane are given by equations 33a and 33b; 32 is a rapid reversible equilibrium; 34 and 35 are fast and irreversible steps. We wish to determine the relative magnitudes of k_2 and k_3 . Consider the state of the CHBrClI-NaOH system in the presence of a large excess of iodide ion. Let x be the amount of CHBrClI which has disappeared at time t ; H_0 , the initial CHBrClI concentration; y the amount of CHClI₂ formed at time t ; B , the base concentration at time t . CHBrClI effectively disappears by two routes, 33b and 34; it is regenerated in the presence of a large quantity

of iodide ion by the reverse reaction 33a, i.e. by capture of the CBrCl intermediate by iodide. Another way of stating this is that all of the CHBrClI which forms ClCl is lost; and of the amount which forms CBrCl, that fraction which hydrolyzes is lost. Denote the fraction of CBrCl which disappears by hydrolysis by F_2 . We may write

$$\frac{dx}{dt} = \frac{k_1}{k_{-1}} k_2 F_2 [H_0 - x] [B] + \frac{k_1}{k_{-1}} k_3 [H_0 - x] [B],$$

or, combining terms,

$$\frac{dx}{dt} = \frac{k_1}{k_{-1}} [H_0 - x] [B] (k_2 F_2 + k_3). \quad (38)$$

Chlorodiiodomethane is formed from that fraction of the intermediate ClCl (generated initially from CHBrClI) that is captured by iodide ion; chlorodiiodomethane disappears effectively by the reaction 35.

Denoting the fraction of ClCl that disappears by hydrolysis by F_3 , then the fraction that is captured by iodide ion is $(1 - F_3)$. We may now write

$$\frac{dy}{dt} = \frac{k_1}{k_{-1}} k_3 (1 - F_3) [H_0 - x] [B] - \frac{k_4}{k_{-4}} k_5 F_3 [B] y. \quad (39)$$

Dividing equation 39 by equation 38,

$$\frac{dy}{dx} = \frac{k_3 (1 - F_3)}{k_2 F_2 + k_3} - \frac{\frac{k_4}{k_{-4}} k_5 F_3 y}{\frac{k_1}{k_{-1}} [H_0 - x] (k_2 F_2 + k_3)}. \quad (40)$$

It was noted in the text that F_2 can be expressed as $1/(1 + r_2[I^-])$, and F_3 can likewise be expressed as $1/(1 + r_3[I^-])$, where $[I^-]$ is the iodide ion concentration, and r_2 and r_3 are determined experimentally from studies of dibromochloromethane and chlorodiiodomethane respectively. Inserting these expressions for F_2 and F_3 in equation 40 and rearranging terms, we have

$$\frac{dy}{dx} = \frac{k_3 r_3 [I^-] (1 + r_2 [I^-])}{[k_2 + k_3 (1 + r_2 [I^-])] (1 + r_3 [I^-])} \quad (41)$$

$$= \frac{\frac{k_4}{k_{-4}} k_5 (1 + r_2 [I^-])}{\left[\frac{k_1}{k_{-1}} (k_2 + k_3) + \frac{k_1}{k_{-1}} k_3 r_2 [I^-] \right] (1 + r_3 [I^-])} \left(\frac{y}{H_0 - x} \right).$$

Notice that $k_4 k_5 / k_{-4}$ is simply the rate constant for the hydrolysis of chlorodiiodomethane; denote this rate constant by k_h^I . Also notice that $k_1 (k_2 + k_3) / k_{-1}$ is the rate constant for the hydrolysis of bromochloroiodomethane; denote this rate constant by k_h^{Br} . Let us further express the fraction $k_3 / (k_2 + k_3)$ by f_I . Introducing these notations and rearranging terms, equation 41 becomes

$$\frac{dy}{dx} = \frac{r_3 [I^-] (1 + r_2 [I^-])}{\left(\frac{1}{f_I} + r_2 [I^-] \right) (1 + r_3 [I^-])} \quad (42)$$

$$= \frac{k_h^I (1 + r_2 [I^-])}{k_h^{Br} \left[1 + r_3 [I^-] + f_I r_2 [I^-] (1 + r_3 [I^-]) \right]} \left(\frac{y}{H_0 - x} \right).$$

In equation 42, all the terms on the right-hand side are constant except $y/(H_0 - x)$. For simplicity the equation may be written

$$\frac{dy}{dx} = \frac{Ay}{H_0 - x} + Q \quad (43)$$

$$\text{where } A = \frac{-k_h^I (1 + r_2[I^-])}{k_h^{Br} [1 + r_3[I^-] + f_I r_2[I^-] (1 + r_3[I^-])]} \quad (44)$$

$$\text{and } Q = \frac{r_3[I^-] (1 + r_2[I^-])}{\left(\frac{1}{f_I} + r_2[I^-]\right) (1 + r_3[I^-])} \quad (45)$$

Expression 43 is a linear differential equation in y , easily soluble by standard methods¹. Applying an integrating factor

$$e^{\int \frac{A dx}{x - H_0}} = (x - H_0)^A$$

to the terms of equation 43, it is seen that the solution is

$$y (x - H_0)^A = \int Q (x - H_0)^A dx + C$$

$$\text{or } y (x - H_0)^A = \frac{Q (x - H_0)^{A+1}}{A+1} + C$$

where C is the constant of integration. Its value can be determined by imposing the initial condition $x = 0$ when $y = 0$. The value of C is

¹See for instance reference 18.

(18) A. L. Nelson, K. W. Folley, and M. Coral, Differential Equations, D. C. Heath and Company, New York, N. Y., 1952, p. 40.

$$- \frac{Q (-H_0)^{A+1}}{A+1}.$$

The solution now takes the form

$$y = \frac{Q (x - H_0)}{A+1} - \frac{Q (-H_0)^{A+1}}{(A+1) (x - H_0)^A},$$

or, rearranging terms to avoid the possibility of being forced to raise a negative number to a fractional power,

$$y = \frac{Q (x - H_0)}{A+1} + \frac{Q H_0}{A+1} \left(\frac{H_0}{H_0 - x} \right)^A. \quad (46)$$

Solving for Q , and designating this expression for Q by Q_1 , the final result is

$$Q = Q_1 = \frac{(A+1) (H_0 - x)^A y}{(H_0)^{A+1} - (H_0 - x)^{A+1}} \quad (47)$$

where the meanings of the symbols has been stated previously.

APPENDIX II

TABLES

Table 9. $\text{CHCl}_2\text{Br} + \text{NaOH}$ in Water at 50°C .

CHCl_2Br	0.01208 <u>M</u>	$f = 0.15$
NaOH	0.006255 <u>M</u>	50 ml. samples
HCl	0.02502 <u>M</u>	

Time in Seconds	ml. of HCl	$\underline{k} \times 10^4$ (l./m.s.)
0	12.50	---
230	9.12	351.0
230	9.10	353.5
235	9.10	346.0
325	8.10	349.2
335	7.80	370.3
360	7.85	339.6
425	7.20	344.7
445	7.00	347.1
465	6.75	354.3
510	6.24	366.9
560	5.96	357.7
635	5.38	361.9
655	5.40	349.2
665	5.30	352.1
780	4.52	359.7
805	4.26	370.1
855	4.20	353.3
875	4.02	360.0
875	3.90	370.3
915	3.90	354.1
945	3.63	365.3
1015	3.44	355.9
1070	3.13	363.9
1085	3.12	359.8

$$\underline{k} = (356.5 \pm 7.0) \times 10^{-4} \text{ l./m.s.}$$

Table 10. CHBrClI + NaOH in 66 2/3 Per Cent Aqueous Dioxane at 50°C.

Determination of \underline{f} .

HClO ₄	(a)	0.02518 $\underline{\underline{M}}$	AgNO ₃	0.05064 $\underline{\underline{M}}$
	(b)	0.02600 $\underline{\underline{M}}$		
	(c)	0.02600 $\underline{\underline{M}}$		50 ml. samples

ml. of HClO ₄	ml. of AgNO ₃	\underline{f}
(a) 12.40	----	---
(b) 9.86	----	---
(c) 12.25	----	---
(b) 5.89	2.00	0.055
(b) 5.31	2.31	0.031
(b) 4.96	2.52	0.000
(c) 6.98	2.60	0.119
(b) 4.45	2.70	0.084
(a) 6.71	2.72	0.121
(b) 4.02	2.97	0.026
(c) 6.19	3.00	0.109
(a) 5.75	3.17	0.130
(b) 3.05	3.32	0.157
(c) 5.45	3.37	0.105
(b) 2.80	3.50	0.104
(a) 5.09	3.58	0.047
(c) 4.76	3.71	0.107
(c) 4.08	3.93	0.199
(a) 4.00	4.01	0.125
(c) 3.70	4.25	0.096

$$\underline{f} = 0.10 \pm 0.04$$

Table 11. CHBrClI + NaOH in 66 2/3 Per Cent

Aqueous Dioxane at 50°C.

CHBrClI	0.008798 <u>M</u>	HClO ₄ (a)	0.02518 <u>M</u>
		(b)	0.02600 <u>M</u>
NaOH (a)	0.006245 <u>M</u>	(c)	0.02600 <u>M</u>
(b)	0.006188 <u>M</u>		
(c)	0.006370 <u>M</u>		

$$\underline{f} = 0.10$$

50 ml. samples

Time in Seconds	ml. of HClO ₄	$\underline{k} \times 10^4$ (l./m.s.)
(a) 0	12.40	---
(b) 0	11.90	---
(c) 0	12.25	---
(a) 940	9.20	114.1
(b) 990	9.11	112.7
(b) 1385	8.28	107.5
(a) 1405	8.30	105.0
(a) 1655	7.83	103.1
(c) 1685	7.85	101.5
(b) 1835	7.50	102.7
(c) 2025	6.98	107.9
(a) 2210	6.71	105.3
(b) 2235	6.70	104.7
(c) 2495	6.19	107.4
(a) 2870	5.75	103.2
(b) 2990	5.70	100.6
(c) 3060	5.45	104.9
(b) 3495	5.19	97.3
(a) 3520	5.09	98.6
(c) 3650	4.76	103.7
(b) 4120	4.28	102.5
(c) 4185	4.08	106.4
(a) 4375	4.00	102.8
(c) 4750	3.70	102.7

$$\underline{k} = (104.5 \pm 2.9) \times 10^{-4} \text{ l./m.s.}$$

Table 12. CHBrClI + NaOH in Water at 50°C.

CHBrClI	(a) 0.004429 <u>M</u>	HCl	0.02519 <u>M</u>
	(b) 0.003285 <u>M</u>		$\underline{f} = 0.10$
NaOH	0.006282 <u>M</u>		50 ml. samples

Time in Seconds	ml. of HCl	$\underline{k} \times 10^4$ (1./m.s.)
(a) 0	12.47	---
(b) 0	12.47	---
(a) 2745	10.20	55.90
(b) 4200	9.70	63.53
(a) 4290	9.10	57.40
(b) 4395	9.97	53.48
(a) 6210	8.19	54.04
(b) 6300	8.75	61.40
(b) 7605	8.52	55.12
(a) 8210	7.30	53.23
(b) 9075	7.90	56.56
(b) 9120	7.87	56.81
(b) 10020	7.51	57.72
(a) 10230	6.53	52.69
(b) 11430	6.87	60.96
(a) 12540	6.08	48.35
(b) 13185	6.50	58.63
(b) 14040	6.61	53.40
(b) 14910	6.10	57.87
(b) 15915	6.14	53.62
(a) 15995	4.99	49.99
(b) 17055	5.80	54.88
(b) 17580	5.74	54.11
(b) 19605	5.40	53.17
(b) 22650	4.79	54.20
(b) 25820	4.58	50.34

$$\underline{k} = (55.3 \pm 2.8) \times 10^{-4} \text{ 1./m.s.}$$

Table 13. CHBrClI + NaOH in Water at 30°C.

CHBrClI	0.003285 <u>M</u>	HCl	0.02534 <u>M</u>
NaOH	0.006203 <u>M</u>	<u>f</u>	= 0.10
			50 ml. samples

Time in Seconds	ml. of HCl	<u>k</u> x 10 ⁴ (1./m.s.)
0	12.24	----
54000	10.55	2.83
72000	10.00	2.93
89640	9.71	2.72
152600	8.31	2.79
219300	7.46	2.56
274700	6.62	2.62
310300	6.42	2.46
341900	6.00	2.51
345200	5.90	2.55

$$\underline{k} = (2.66 \pm 0.14) \times 10^{-4} \text{ 1./m.s.}$$

Table 14. $\text{CHCl}_2 + \text{NaOH}$ in Water at 64.5°C .with 0.30 M NaI .

CHCl_2	0.002121 $\underline{\text{M}}$	HCl (a, b)	0.00995 $\underline{\text{M}}$
		(c, d)	0.01121 $\underline{\text{M}}$
NaOH (a)	0.003039 $\underline{\text{M}}$	$\underline{f} = 0.00$	
(b)	0.003021 $\underline{\text{M}}$		
(c)	0.002942 $\underline{\text{M}}$		
(d)	0.002939 $\underline{\text{M}}$		
		50 ml. samples	

Time in Seconds	ml. of HCl	$k \times 10^4$ (l./m.s.)
(a) 0	15.27	---
(b) 0	15.18	---
(c) 0	13.12	---
(d) 0	13.11	---
(c) 21600	10.70	15.53
(c) 21900	10.68	15.47
(d) 21900	10.70	15.26
(c) 23700	10.48	15.67
(d) 25800	10.12	16.71
(b) 25800	11.73	16.65
(c) 27120	10.30	14.80
(c) 27900	10.25	14.70
(a) 30000	11.62	15.24
(d) 30060	9.81	16.16
(c) 30600	10.00	14.82
(d) 34500	9.31	16.81
(b) 35400	10.98	15.47
(a) 36900	10.80	15.96
(d) 39780	9.16	15.32
(c) 40200	9.20	15.00
(b) 41100	10.51	15.27
(d) 43560	9.00	14.73
(c) 44100	8.90	15.06
(a) 45000	10.21	15.39
(b) 46500	9.89	15.93
(c) 48000	8.44	15.89
(d) 49380	8.47	15.28
(a) 51300	9.73	15.27
(c) 51360	8.38	15.12
(b) 52200	9.58	15.36
(c) 54000	8.21	15.09
(c) 57480	7.81	15.85
(a) 58200	9.35	14.77
(b) 58500	9.00	15.75

Table 14, cont.

Time in Seconds	ml. of HCl	$\underline{k} \times 10^4$ (1./m.s.)
(c) 61200	7.40	16.60
(c) 61500	7.40	16.52
(a) 64200	8.98	14.61
(b) 64500	8.43	16.28
(a) 68100	8.52	15.30
(a) 70800	8.32	15.39
(b) 72300	7.83	16.59
(a) 75300	7.88	15.93
(a) 75600	8.00	15.46

$$\underline{k} = (15.56 \pm 0.50) \times 10^{-4} \text{ 1./m.s.}$$

Table 15. $\text{CHCl}_2 + \text{NaOH}$ in Water at 64.5°C .With 0.30 M Salts (0.15 M NaNO_3 and 0.15 M NaClO_4)

CHCl_2	0.002121 <u>M</u>	HCl (a) 0.00995 <u>M</u>
		(b) 0.01121 <u>M</u>
NaOH (a)	0.002993 <u>M</u>	(c) 0.01121 <u>M</u>
(b)	0.002843 <u>M</u>	
(c)	0.002847 <u>M</u>	

$$\underline{f} = 0.00$$

50 ml. samples

Time in Seconds	ml. of HCl	$\underline{k} \times 10^4$ (l./m.s.)
(a) 0	15.04	---
(b) 0	12.68	---
(c) 0	12.70	---
(c) 4500	10.80	58.64
(b) 5760	10.18	62.85
(c) 6780	10.12	55.27
(b) 7560	9.59	61.66
(a) 7800	11.34	63.07
(c) 8820	9.50	55.04
(a) 9300	10.92	60.08
(b) 10020	8.86	60.65
(c) 10740	8.83	57.43
(a) 11100	10.30	58.35
(a) 12900	9.73	58.41
(c) 13260	8.25	55.95
(b) 13680	7.89	60.15
(c) 14940	7.85	55.92
(b) 15660	7.50	58.71
(a) 15900	8.89	58.27
(c) 17700	7.23	56.13
(a) 18000	8.37	58.05
(b) 18540	6.87	58.82
(c) 19080	6.90	56.87
(b) 19620	6.60	59.64
(a) 19800	7.90	58.62
(b) 21180	6.35	58.92
(a) 21900	7.42	58.85
(b) 22500	6.06	59.69
(c) 22500	6.20	57.77
(a) 23100	7.20	58.49
(b) 23580	5.90	59.30
(a) 24480	6.87	59.22

Table 15, cont.

Time in Seconds	ml. of HCl	$\underline{k} \times 10^4$ (l./m.s.)
(b) 24720	5.62	60.65
(b) 25920	5.36	61.68
(a) 26280	6.40	60.91
(b) 26400	5.25	62.24
(b) 26520	5.22	62.41
(a) 27300	6.20	61.15
(c) 28200	5.12	60.29
(c) 28380	5.08	60.51
(c) 28680	5.06	60.17
(a) 28800	5.90	61.73

$$\underline{k} = (59.2 \pm 1.7) \times 10^{-4} \text{ l./m.s.}$$

Table 16. CHBrClI + NaOH in Water at 50°C. with Added NaI.

Determination of f_I .

NaOH (a) 0.01420 M
 (b) 0.01402 \overline{M}
 (c) 0.01417 \overline{M}

NaI (a) 0.388 M
 (b) 0.614 \overline{M}
 (c) 0.646 \overline{M}

HCl 0.05000 \overline{M}

$f = 0.10$

50 ml. samples

ml. of HCl	Optical Density at		CHBrClI m./l. x 10 ³	CHClI ₂ m./l. x 10 ³	f_I
	8.505 μ 9.057 μ	8.615 μ 9.357 μ			
(a) 14.20	---	---	6.509	0.000	---
(b) 14.02	---	---	6.385	0.000	---
(c) 14.17	---	---	6.385	0.000	---
(c) 13.50	0.185 0.512	0.047 0.086	5.324 5.320	0.845 0.849	0.704 0.706
(b) 13.49	0.235 0.675	0.059 0.113	5.377 5.361	0.837 0.853	0.884 ¹ 0.904 ¹
(b) 13.30	0.237 0.675	0.070 0.147	5.116 5.083	1.037 1.070	0.826 ¹ 0.848 ¹
(c) 13.27	0.163 0.438	0.052 0.111	4.963 4.887	1.132 1.208	0.706 0.748
(c) 13.02	0.166 0.468	0.069 0.162	4.511 4.476	1.503 1.538	0.734 0.750
(a) 12.84	0.234 0.644	0.074 0.157	4.956 4.906	1.114 1.164	0.754 0.784
(b) 12.76	0.220 0.615	0.101 0.246	4.328 4.270	1.650 1.708	0.770 0.794

Table 16, cont.

ml. of HCl	Optical Density at		CHBrClI	CHClI ₂	f_I
	8.505 μ	8.615 μ	m./l. x 10 ³	m./l. x 10 ³	
	9.057 μ	9.357 μ			
(c) 12.71	0.209	0.108	4.089	1.825	0.712
	0.573	0.259	4.065	1.849	0.720
(b) 12.57	0.232	0.121	4.076	1.841	0.754
	0.641	0.293	4.052	1.865	0.762
(c) 12.54	0.221	0.137	3.745	2.114	0.740
	0.600	0.338	3.723	2.136	0.746
(b) 12.40	0.243	0.147	3.788	2.074	0.762
	0.661	0.360	3.773	2.089	0.768
(a) 12.36	0.199	0.081	4.469	1.446	0.732
	0.553	0.184	4.451	1.464	0.740
(c) 12.32	0.206	0.145	3.478	2.310	0.720
	0.556	0.363	3.464	2.324	0.724
(c) 12.24	0.206	0.162	3.267	2.495	0.744
	0.547	0.409	3.247	2.515	0.750
(b) 12.15	0.199	0.140	3.476	2.306	0.744
	0.554	0.353	3.497	2.285	0.738
(c) 12.06	0.190	0.166	3.047	2.657	0.732
	0.510	0.444	2.985	2.719	0.748
(a) 11.91	0.208	0.105	4.028	1.742	0.718
	0.573	0.247	4.028	1.742	0.718
(c) 11.84	0.218	0.210	2.836	2.797	0.706
	0.578	0.568	2.766	2.867	0.724
(b) 11.80	0.215	0.189	3.018	2.651	0.732
	0.591	0.515	2.966	2.703	0.746
(c) 11.79	0.160	0.172	2.634	2.983	0.738
	0.403	0.463	2.522	3.095	0.764

Table 16, cont.

ml. of HCl	Optical Density at		CHBrClI	CHClI ₂	\bar{f}_I
	8.505 μ	8.615 μ	m./l. x 10 ³	m./l. x 10 ³	
	9.057 μ	9.357 μ			
(b) 11.67	0.221	0.215	2.815	2.812	0.738
	0.589	0.587	2.742	2.885	0.756
(a) 11.61	0.232	0.134	3.743	1.930	0.708
	0.637	0.332	3.712	1.961	0.720
(b) 11.46	0.215	0.237	2.564	2.995	0.728
	0.559	0.646	2.481	3.078	0.748
(a) 11.34	0.221	0.149	3.430	2.156	0.720
	0.611	0.379	3.417	2.169	0.724
(b) 11.28	0.186	0.231	2.331	3.170	0.726
	0.483	0.642	2.256	3.245	0.744
(a) 11.10	0.248	0.184	3.223	2.286	0.710
	0.665	0.470	3.186	2.323	0.722
(a) 10.81	0.216	0.177	3.000	2.415	0.694
	0.570	0.460	2.943	2.472	0.708
(a) 10.60	0.257	0.230	2.816	2.532	0.690
	0.679	0.610	2.754	2.594	0.706
(a) 10.50	0.232	0.225	2.666	2.649	0.704
	0.627	0.617	2.608	2.707	0.718
(a) 10.20	0.234	0.262	2.382	2.837	0.704
	0.621	0.730	2.312	2.907	0.722

¹not averaged

$$\bar{f}_I = 0.732 \pm 0.019$$

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