*Anal.* Calcd. for [Pt enH$_2$O(OH)Cl$_2$]NO$_3$: Pt, 46.2. Found: Pt, 45.8.

An aqueous solution of [Pt enH$_2$O(OH)Cl$_2$]NO$_3$ at room temperature reacts with an excess of ethylenediamine to give an immediate precipitate of [Pt en(OH)$_2$Cl$_2$].

*Anal.* Found: Pt, 54.3.

**Tris-(ethylenediamine)-platinum(IV) Chloride.**—The method used by Smirnoff[25] to produce [Pt en$_3$]Cl$_4$ was applied in the preparation of this salt. Three grams (0.0058 mole) of H$_2$PtCl$_6$.6H$_2$O was dissolved in 65 cc. of absolute ethanol and 2.2 cc. of 95% (0.035 mole) ethylenediamine was added. This mixture was placed in a water bath at 80° and stirred constantly for one-half hour. During this time the original yellow precipitate of en H$_2$PtCl$_6$ gradually changed to the pale yellow [Pt en$_3$]Cl$_4$. This salt was collected on a filter and washed with absolute ethanol followed by ether. After drying at 75° the complex weighed 3 g. (theoretical yield) and a portion of this material was purified for analysis by recrystallization from a mixture of ethanol and water.

*Anal.* Found: Pt, 37.80; C, 13.61; H, 4.75.

**Decomposition of Tris-(ethylenediamine)-platinum(IV) Chloride.**—One half a gram of solid [Pt en$_3$]Cl$_4$ which contained a trace of ethylenediamine hydrochloride was placed in a large test-tube which was surrounded by an oil-bath and attached to a vacuum pump. At a pressure of 3 mm. there was no apparent change until a temperature of 175° had been reached at which time the salt became gray. The solid was then kept at 165° at this reduced pressure for ten hours during which time the ethylenediamine hydrochloride sublimed to the cooler portions of the test-tube. The gray residue which weighed 0.4 g. was then transferred to a beaker and 10 cc. of water was added. An appreciable amount of insoluble brown residue was removed on a filter and the tan filtrate was decolorized with a small amount of charcoal. This clear solution yielded 0.2 g. of [Pt en$_2$]Cl$_2$ when treated with a mixture of ethanol and ether.

*Anal.* Found: Pt, 50.58; C, 12.60; H, 4.18.

## Summary

Dichlorobis-(ethylenediamine)-platinum(IV) chloride has been prepared by (1) the chlorination of [Pt en$_2$]Cl$_2$, (2) the reaction of [Pt en$_2$(OH)$_2$]Cl$_2$ with hydrochloric acid and (3) the reaction of [Pt en$_2$(CO$_3$)$_2$] with hydrochloric acid.

The fact that in every case the [Pt en$_2$Cl$_2$]Cl$_2$ isolated had the same structure was established by their identical absorption spectrum. Evidence has likewise been cited which indicates that this cation has a *trans*-configuration.

It has been demonstrated that the coördinated chloro groups in this compound are extremely covalent compared to those of the corresponding cobalt(III) complex.

Attempts to prepare *cis*-[Pt en$_2$Cl$_2$]Cl$_2$ were not successful.

URBANA, ILLINOIS
EVANSTON, ILLINOIS

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(25) Smirnoff, *Helv. Chim. Acta*, **3**, 177 (1920).

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

# Carbon Dichloride as an Intermediate in the Basic Hydrolysis of Chloroform. A Mechanism for Substitution Reactions at a Saturated Carbon Atom[1]

BY JACK HINE[2]

In a literature survey on the effect of halogen atoms on the reactivity of other halogen atoms attached to the same carbon atom it was found that chloroform is much more reactive toward basic hydrolysis than methylene chloride or carbon tetrachloride (see Tables I and II). No clear explanation of this behavior was found by consideration of the two mechanisms (S$_N$1 and S$_N$2)[3] commonly accepted for substitution reactions at a saturated carbon atom. However, it seemed that mechanism I

$$\text{(I)}\qquad \mathrm{CHCl_3 + OH^-} \overset{\text{fast}}{\rightleftharpoons} \mathrm{CCl_3^- + H_2O}$$

$$\mathrm{CCl_3^-} \xrightarrow{\text{slow}} \mathrm{Cl^- + CCl_2}$$

$$\mathrm{CCl_2} \xrightarrow[\mathrm{H_2O}]{\mathrm{OH^-},\ \text{fast}} \mathrm{CO + HCO_2^-}$$

offered an adequate explanation of the behavior of chloroform.

The idea that carbon dichloride is an intermediate in the basic hydrolysis of chloroform is not new. Upon learning that chloroform and alkali yield carbon monoxide as well as formate, Geuther,[4] in 1862, suggested that chloroform is actually CCl$_2$·HCl and that the hydrogen chloride may be removed by alkali to give carbon dichloride, which is further hydrolyzed to carbon monoxide. A number of other workers have expressed similar views.[5] Most of them seem to utilize the fact that carbon monoxide is formed in the reaction as the sole evidence for the intermediacy of carbon dichloride, but Mossler also cites the reaction of chloroform vapor and air with solid potassium hydroxide to give phosgene. Since it was believed that neither of these facts is sufficient evidence to indicate that carbon dichloride is an intermediate in the basic hydrolysis of chloroform, a study of the subject was initiated.

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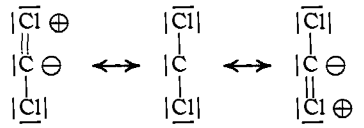
[2] du Pont postdoctoral fellow, 1948-1949. School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia.

[3] E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

[4] A. Geuther, *Ann.*, **123**, 121 (1862).

[5] J. U. Nef, *ibid.*, **298**, 367 (1897); J. Thiele and F. Dent, *ibid.*, **302**, 273 (1898); G. Mossler, *Monatsh.*, **29**, 573 (1903); G. Urbain, *Bull. soc. chim.*, [4] **51**, 853 (1932); **53**, 647 (1933); A. Tchakerian, *ibid.*, [4] **51**, 846 (1932); P. B. Sarkar, *Proc. Natl. Inst. Sci. India*, **2**, 63 (1936); *C. A.*, **32**, 2083$^2$ (1938); E. N. Allott, "Richter's Organic Chemistry," 3rd ed., Nordeman Publ. Co., New York, N. Y., 1934, Vol. I, p. 291.

The mechanism was first considered from a theoretical point of view. The concept of the reversible formation of the trichloromethyl anion from chloroform and alkali has a firm basis. The base-catalyzed addition of chloroform to carbonyl-containing compounds probably proceeds via this intermediate. The fact that Sakamoto has found the base-catalyzed deuterium exchange of chloroform to be rapid compared to the hydrolysis[6] is also evidential. The next step, the loss of chloride by the trichloromethyl anion by an $S_N1$ type mechanism, seems reasonable. There are several pieces of evidence which show that the accumulation of halogens on the same carbon atom causes increased $S_N1$ reactivity (probably by resonance stabilization of the carbonium ion). For example, Olivier and Weber[7] found that in hydrolysis by aqueous acetone, benzotrichloride is more reactive than benzal chloride which in turn is more reactive than benzyl chloride. Hughes[3] has stated that benzotrichloride hydrolyzes by an $S_N1$ mechanism under these conditions (the addition of hydroxyl ion has no effect on the rate). The negative charge of the trichloromethyl ion may very well influence its reactivity considerably. It must be much easier for the already negative trichloromethyl ion to lose a chloride ion than it would be for a neutral molecule to do so. It is to be noted that the carbon dichloride thus formed as a reactive intermediate should have considerable resonance stabilization. The principal contributing structures would be expected to be



**Kinetic Order of the Reaction.**—Saunders[8] found that the rate of hydrolysis of chloroform by alkali in 95% ethanol is first order with respect to both hydroxide and chloroform concentrations. Abel[9] obtained results in general agreement with Saunders when solutions of hydroxide concentrations up to 0.5 *N* were used, but states that in solutions which are from 1 to 4 *N* with respect to potassium hydroxide the reaction becomes higher order with respect to hydroxide. His data, however, merely show that the rate constant probably increases in solutions of this concentration. Since he runs the reaction with a very large excess of alkali, follows it only to a small percentage of completion, and takes only a few points per run, it is impossible to tell its order with respect to hydroxide. Exactly what is responsible for the increase in rate constants he observed is not known. It may well be called a medium effect, since 4 *N* ethanolic potassium hydroxide contains more than 20% potassium hydroxide.

In the current investigation it was found that the reaction in $66^2/_3\%$ aqueous dioxane is first order with respect to both chloroform and hydroxide ion concentrations. Inspection of Table I shows that a one hundred-fold change in the original concentration of chloroform caused the rate constant to change by less than 26%. It is also seen that runs with original hydroxide concentrations varying as much as twelve-fold all give rate constants in reasonable agreement when allowance is made for the salt effect.

TABLE I

RATES OF REACTION IN $66^2/_3\%$ AQUEOUS DIOXANE[a]

| Run | $[OH^-]_0$ | Added reagent | $k_2 \times 10^{2}$ [g] | % $HCO_2^-$ |
|---|---|---|---|---|
| 37[b] | 0.1272 | 0.103 $CCl_4$ | <0.0003 | |
| 38[b] | .1274 | .156 $CH_2Cl_2$ | <0.001 | |
| 42[c] | .02891 | | 2.04 | 51.2 |
| 43[d] | .02862 | | 1.52 | 3.0 |
| 31 | .02907 | | 1.91 | 9.4 |
| 39 | .02815[e] | | 2.04 | 9.3 |
| 34 | .00753 | | 1.98 | 17 |
| 44 | .08927 | .238 $NaClO_4$ | 1.22 | 7.3 |
| 35 | .00710 | .286 $NaClO_4$ | 1.35 | 4.0 |
| 36 | .00771 | .286 NaCl | 0.73 | [f] |
| 52 | .02755 | .095 $NaClO_4$ | 1.58 | 2.2 |
| 50 | .02885 | .095 NaCl | 1.35 | [f] |
| 49 | .02885[e] | .095 $KNO_3$ | 1.89 | 10.3 |
| 53 | .02909[e] | .095 KCl | 1.63 | [f] |
| 32 | .02876 | .286 $NaClO_4$ | 1.37 | 8.4 |
| 47 | .02897 | .286 $NaClO_4$ | 1.43 | 4.6 |
| 33 | .02870 | .286 NaCl | 0.74 | [f] |
| 40 | .02815[e] | .286 $KNO_3$ | 1.60 | 18 |
| 41 | .02791[e] | .286 KCl | 0.88 | [f] |
| 29 | | .310 $NaSC_6H_5$ | <0.001 | |
| 30 | | .0028 $NaSC_6H_5$ | <0.003 | |

[a] Concentration of chloroform about 0.128 *M* except where otherwise stated. [b] No chloroform. [c] Chloroform concentration 0.00381 *M*. [d] Chloroform concentration 0.3736 *M*. [e] Potassium hydroxide used in these cases; sodium hydroxide in all others. [f] Presence of excess chloride ion makes determination of % formate formed impossible. [g] $\text{Mole}^{-1}\cdot\text{liter}\cdot\text{min.}^{-1}$ (moles of chloroform).

**Alternate Mechanisms.**—After considering other possible mechanisms which fit the observed kinetics and which might be proposed for the basic hydrolysis of chloroform, it was decided that only the following are sufficiently probable to require comment

$$\text{(II)} \qquad CHCl_3 + OH^- \overset{\text{fast}}{\rightleftharpoons} CCl_3^- + H_2O$$

$$H_2O + CCl_3^- \xrightarrow{\text{slow}} \overset{\oplus}{H_2O}\text{-}\overset{\ominus}{C}Cl_2 + Cl^-$$

$$\overset{\oplus}{H_2O}\text{-}\overset{\ominus}{C}Cl_2 \xrightarrow[H_2O]{OH^-,\ \text{fast}} CO + HCO_2^-$$

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

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

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(6) Y. Sakamoto, *J. Chem. Soc. Japan*, **57**, 169 (1936); *Bull. Chem. Soc. Japan*, 11, 627 (1936); *C. A.*, **31**, $931^4$ (1937).

(7) S. C. J. Olivier and A. P. Weber, *Rec. trav. chim.*, **53**, 869 (1934).

(8) A. P. Saunders, *J. Phys. Chem.*, **4**, 660 (1900).

(9) E. Abel, *Z. Elektrochem.*, **29**, 391 (1923).

No consideration is given to mechanisms in which compounds containing a hydroxyl group and a chlorine atom attached to the same carbon atom, or compounds of divalent carbon (other than carbon monoxide), are postulated as reacting slowly. It is thought that such compounds would be very reactive.

**Salt Effect.**—The reaction was found to show a definite negative salt effect. However, even at ionic strengths of about 0.124, specific salt effects were quite apparent. It might be suspected that the diminution of rate caused by chlorides is a mass effect (which would be explainable by mechanism I but not by mechanisms II or III). However, the differences in rate between the sodium perchlorate and potassium nitrate runs could hardly be explained on this basis. When it is considered that the dielectric constant of $66^2/_3\%$ aqueous dioxane is about 20, it might be expected that the specific salt effects may become important at relatively low ionic strengths.

**Relative Reactivities of the Chlorides of Methane.**—As evidence for the improbability of mechanism III, the data which first suggested I may be mentioned. Petrenko-Kritschenko and Opotsky[10] found the per cent. of reaction shown in Table II to have occurred after having subjected the various chlorides of methane to the condition shown.

TABLE II

PERCENTAGE OF COMPLETION OF THE REACTION OF THE CHLORIDES OF METHANE WITH VARIOUS REAGENTS[a]

| Compound | NaOEt in 100% EtOH[b] | KOH in 95% EtOH[b] | $Me_4NOH$ in 95% EtOH[b] | 50% $H_2O$-EtOH[c] | Piperidine in 95% EtOH[d] |
|---|---|---|---|---|---|
| $CH_3Cl$ | 85 | 81 | 83 | 45 | 87 |
| $CH_2Cl_2$ | 8 | 7 | 8 | 2 | 4 |
| $CHCl_3$ | 84 | 78 | 85 | 0 | 1 |
| $CCl_4$ | 35 | 15 | 24 | .. | 10 |

[a] These figures are estimated from a graph given by Petrenko-Kritschenko and Opotsky[10] and the estimation is subject to an error of about 1%. [b] At 90° for thirty minutes. The concentration is stated to be 0.1 *N*. Presumably, this refers to both reactants, but this is not completely clear. However, the conclusions drawn are warranted if the halides are subjected to even approximately the same conditions. [c] At 90° for twelve hours; concentration, 0.1 *N*. [d] At 90° for five hours; concentration, 0.1 *N*.

It was thought desirable to check the relative reactivities of methylene chloride, chloroform and carbon tetrachloride under the conditions which were used for most of the reactions described in this paper. Therefore, the various halides were allowed to react at 36° with sodium hydroxide in $66^2/_3\%$ aqueous dioxane (two parts dioxane to one part water by volume). It is conservatively estimated that the second order rate constants for the reactions of methylene chloride and carbon tetrachloride with hydroxyl ion are more than one thousandth smaller than for chloroform under the same conditions (see Table I). It is noted that the reactivity of carbon tetrachloride under these conditions is considerably lower than it appears to be from the data of Petrenko-Kritschenko and Opotsky. This is probably because the reaction these workers were measuring was not a normal displacement reaction. This is shown by the fact that the reaction of sodium ethoxide with carbon tetrachloride is known to give neither ethyl orthocarbonate nor sodium carbonate, but does yield ethyl orthoformate, carbon monoxide, and sodium formate.[11] Therefore probably the first, and rate-controlling, step in the reaction of carbon tetrachloride under these conditions is reduction by the alcoholic alkali. In aqueous dioxane, where no such reducing agent is present, carbon tetrachloride would be expected to show diminished reactivity.

It appears that in general the replacement by halogen of a hydrogen attached to the α-carbon atom of an alkyl halide decreases $S_N2$ reactivity and increases $S_N1$ reactivity. This is shown in that the introduction of one chlorine atom into the $S_N2$ reactive methyl chloride produces the much less reactive methylene chloride. However, the introduction of another chlorine atom yields chloroform, which exhibits a greatly enhanced reactivity (compared to methylene chloride) toward the alkaline reagents.

Furthermore, according to the $S_N2$ mechanism there should be no particular reason to expect a relationship between relative rates of reaction of nucleophilic substituting reagents toward the chlorides of methane and the basicity of the reagents. However, according to mechanisms I and II, basic reagents should show a greatly increased reactivity toward chloroform. That this is the case is shown by comparison of the reactivities toward aqueous ethanol and piperidine with reactivities toward the strongly alkaline reagents. These data cannot be explained by the suggestion that for some unknown reason the presence of three chlorine atoms on the same carbon atom endows a compound with increased reactivity toward strongly basic reagents, since the rate of hydrolysis of benzotrichloride has been shown to be uninfluenced by the addition of hydroxide ion.[7]

Thus the relative reactivities of the chlorides of methane toward basic hydrolysis and reaction with less strongly alkaline reagents show that the former reaction of chloroform probably does not proceed by mechanism III.

**Reaction of Chloroform with Hydroxide and Thiophenolate Ions.**—It was believed that the most conclusive experiment which could be performed would be to trap the carbon dichloride intermediate. For this purpose, the thiophenolate anion was chosen. To show that the principal product of the reaction of chloroform with sodium hydroxide and sodium thiophenolate in homogeneous aqueous dioxane solution is

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[10] P. Petrenko-Kritschenko and V. Opotsky, *Ber.*, **59B**, 2131 (1926).

[11] J. U. Nef, *Ann.*, **308**, 329 (1899).

phenyl orthothioformate, the compound was isolated from the reaction in 85% yield.

If the basic hydrolysis of chloroform is a direct nucleophilic displacement (mechanism III), it might be expected that the highly nucleophilic thiophenolate ion would react even more rapidly than hydroxide (as it is known to in other $S_N2$ reactions). However, if the reaction proceeds by mechanism I or II, then thiophenolate should be much less reactive than hydroxide ion, since it is much less basic. The reaction of sodium thiophenolate with chloroform was found to be negligibly slow compared to the reaction with hydroxide ion (see Runs 29 and 30, Table I).

If the thiophenolate ion reacts with chloroform only by an $S_N2$ mechanism, the only effect which the addition of hydroxyl ion should have on the system would be to compete with the thiophenolate ion for the chloroform. However, if the basic hydrolysis of chloroform proceeds by mechanism I or II, and if thiophenolate ion is sufficiently reactive toward carbon dichloride or the trichloromethyl anion, the addition of hydroxide ion to a system containing chloroform and thiophenolate should cause a considerable increase in the rate of disappearance of thiophenolate ion to form phenyl orthothioformate compared to the rate in the absence of hydroxide ion.

This was found to be the case. In some instances the rate of thiophenolate disappearance increased more than one thousand-fold when hydroxide was added. Therefore, thiophenolate ion does not react with chloroform by an $S_N2$ attack under these conditions, and it does not seem likely that hydroxide ion does either.

In the formation of phenyl orthothioformate three thiophenolate ions become covalently attached to the carbon atom of chloroform. There is, at each step, the possibility of competing reactions in which a water molecule or hydroxyl ion becomes attached. It was found experimentally that the percentage of chloroform which is transformed to phenyl orthothioformate does not depend on the hydroxide ion concentration (see Table III). The only effective competitors, then, are thiophenolate ions and water molecules.

If the first order rate constant for the reaction of an intermediate with water is $k'_w$ and the rate constant for reaction with thiophenolate ion is $k'_t$, then the fraction of the intermediate to which thiophenolate becomes attached is

$$\frac{k'_t[C_6H_5S^-]}{k'_t[C_6H_5S^-] + k'_w}$$

Since only the molecules to which three thiophenolate ions have become attached yield phenyl orthothioformate, the fraction of chloroform which yields phenyl orthothioformate is

$$p = \left(\frac{k'_t[C_6H_5S^-]}{k'_t[C_6H_5S^-] + k'_w}\right)\left(\frac{k''_t[C_6H_5S^-]}{k''_t[C_6H_5S^-] + k''_w}\right)\left(\frac{k'''_t[C_6H_5S^-]}{k'''_t[C_6H_5S^-] + k'''_w}\right)$$

If at any step $k_t[C_6H_5S^-]$ is so large compared to $k_w$ that the latter may be ignored, the fraction for that step reduces to unity; that is, essentially all of the intermediate reacts with thiophenolate ions. That thiophenolate ions should be much more reactive than either water or hydroxide in at least some cases is not surprising when the great nucleophilicity of ions of this type is considered. It was found, for example, that while the reaction of 0.465 *N* sodium hydroxide and 0.465 *N* sodium bromoacetate in 66²/₃% aqueous dioxane at 36° was half complete in about ten hours, the corresponding reaction of sodium thiophenolate with sodium bromoacetate was 90% completed in about three minutes, and thus had a rate constant more than one thousand times as large. If it is assumed that in two of the steps thiophenolate ion is practically the exclusive competitor and the fractions for these two steps are equal to one, then the fraction of chloroform yielding phenyl orthothioformate is

$$p = \frac{k_t[C_6H_5S^-]}{k_t[C_6H_5S^-] + k_w} = \frac{k_t/k_w[C_6H_5S^-]}{k_t/k_w[C_6H_5S^-] + 1}$$

From this equation, and the values of $p$ and of $[C_6H_5S^-]$ experimentally determined in a given run, a value of $k_t/k_w$ may be calculated. If $k_t/k_w$ does not change with considerable changes in thiophenolate concentrations (at constant ionic strength), then the assumption that under the conditions tested effective competition of water molecules with thiophenolate ions occurs at only one of the three substitution steps is justified.

Inspection of the first eight runs listed in Table III shows that at constant ionic strength the value of $k_t/k_w$ does not change with changes in thiophenolate concentration. For the three runs made with thiophenolate concentrations of about

TABLE III

REACTION OF CHLOROFORM WITH SODIUM HYDROXIDE AND SODIUM THIOPHENOLATE[a]

| Run | $[NaOH]_0$ | $[NaOH]_{final}$ | $[NaSC_6H_5]_0$ | $\mu$ | % $CH(C_6H_5S)_3$ | $k_t/k_w$[b] |
|---|---|---|---|---|---|---|
| 78[c] | 0.0328 | 0.0090 | 0.0572 | 0.32 | 13.1 | 2.72 |
| 71[d] | .0306 | .0008 | .0600 | .32 | 12.6 | 2.50 |
| 74[e] | .1054 | .0114 | .0721 | .31 | 14.9 | 2.75 |
| 27 | .1374 | .0468 | .1718 | .31 | 29.6 | 2.74 |
| 75 | .1114 | .0220 | .1970 | .31 | 30.8 | 2.51 |
| 81 | .0688 | .0044 | .2386 | .31 | 34.7 | 2.40 |
| 80 | .0690 | .0514 | .2390 | .31 | 38.0 | 2.60 |
| 79 | .0684 | .0318 | .2406 | .31 | 36.0 | 2.44 |
| 26 | .0443 | .0124 | .2616 | .31 | 40.2 | 2.68 |
| 73 | .0412 | .0066 | .2642 | .31 | 37.8 | 2.39 |
| 77 | .0336 | .0034 | .0568 | .09 | 13.0 | 2.73 |
| 76 | .0320 | .0024 | .0577 | .09 | 11.9 | 2.43 |

[a] In all runs the original chloroform concentration was 0.122 *M*. [b] The value of $k_t/k_w$ was determined from the equation: $k_t/k_w = \Delta[C_6H_5S^-]/\Delta[OH^-][C_6H_5S^-]_{av.}$ Use of the average value of the thiophenolate concentration gives satisfactory results since the change in concentration during a run is usually less than 10% and never more than 23%. [c] 0.229 *N* sodium chloride added. [d] 0.229 *N* sodium perchlorate added. [e] 0.134 *N* sodium perchlorate added.

0.06 $N$, the average value of $k_t/k_w$ is 2.66; the two runs at concentrations around 0.18 $N$ had an average of $k_t/k_w$ equal to 2.62, while for the five runs with thiophenolate concentrations of about 0.25 $N$, $k_t/k_w$ averaged 2.50. In fact, the average deviation of all the values from 2.57, the mean, is 0.12, or less than 5%. These values agree within the experimental error (if the assumption were false, the second and third values should be higher than the first). Also it is seen that the value of $k_t/k_w$ is not significantly changed by specific salt effects. That is, the values are in satisfactory agreement whether the principal salt present is sodium perchlorate, sodium chloride, or sodium thiophenolate.

A comparison of Runs 79, 80 and 81 shows that the value of $k_t/k_w$ is not affected by the stage of the run at which the value is determined.

Therefore, it is believed that the assumption is justified, that at two of the three steps thiophenolate is almost the exclusive reactant, and that effective competiton occurs at only one of the steps. It is easily seen that if the reaction is proceeding by mechanism II, the step at which effective competition is occurring must be the one at which the first thiophenolate ion is introduced.

$$CCl_3^- + C_6H_5S^- \xrightarrow{k_t} C_6H_5SCCl_2^-$$

$$CCl_3^- \xrightarrow[H_2O]{k_w} H_2\overset{+}{O}\text{-}\overset{-}{C}Cl_2$$

This cannot be a step in which thiophenolate is almost the exclusive competitor ($k_w$ negligible compared to $k_t[C_6H_5S^-]$), because if it were, the addition of sodium thiophenolate to a system containing sodium hydroxide and chloroform should greatly increase the rate of disappearance of chloroform and, experimentally, this is not found to be the case. Therefore, if mechanism II is operative, the experimental value of $k_t/k_w$ must be the ratio of the rate of reaction of the trichloromethyl anion with thiophenolate ion to the rate of its reaction with water. Since the first reaction is between two negative ions, it should display a large positive salt effect, while the reaction between the trichloromethyl ion and a neutral water molecule should show a smaller salt effect. Hence it might be expected that $k_t/k_w$ should decrease with decreasing ionic strength. Yet inspection of Table III shows that in Runs 76 and 77 at ionic strength 0.09 instead of 0.31 the value of $k_t/k_w$ is not changed. It would not be expected that in a solvent of this dielectric constant, at the ionic strength used, the size of salt effects in reactions between ions should obey the Brønsted equation, but it seems likely that they will still be in the correct direction under these conditions. This was shown experimentally. The rate constant for the reaction of hydroxide ion with bromoacetate ion was increased from 0.0447 to 0.0645 when the ionic strength was increased from 0.093 to 0.29. The size of this salt effect is not sufficiently large to preclude the possibility that the salt effect on $k_w$ could also be this large, but it seems an unusual coincidence that this salt effect should be so nearly the size of the salt effect on $k_t$ that there should be no noticeable change in the value of $k_t/k_w$.

It may further be seen that mechanisms I and II differ in their prediction of the dependence of the rate of disappearance of chloroform on thiophenolate concentration. According to mechanism I, thiophenolate first enters the molecule by reaction with carbon dichloride, that is, after the rate-controlling step, and, therefore, sodium thiophenolate should have only a salt effect on the reaction rate. According to II, however, the rate should be

$$v = k_2[CHCl_3][OH^-](1 + [k_t/k_w][C_6H_5S^-]) \quad (1)$$

or, at constant value of $k_2$, the addition of sodium thiophenolate should increase the rate of disappearance of chloroform. Unfortunately though, there is no assurance that $k_2$ will remain constant when the concentration of sodium thiophenolate is changed even at constant total ionic strength. Equation (1) may be integrated with the help of several simplifying approximations which are permissible because the concentration of thiophenolate does not change greatly in the course of a given run. The value of $k_2$ is treated as a constant, and for the values of $p$ and the thiophenolate concentration, the average values present during the run are used. On this basis, equation (2) is obtained

$$v = k_2(a - x)(b - 3[1 - p]x)(1 + [k_t/k_w][C_6H_5S^-]_{av}) \quad (2)$$

This, upon integration, yields

$$k_2t(1 + [k_t/k_w][C_6H_5S^-]_{av}) = \frac{2.303}{3a[1 - p] - b}\log\frac{b(a - x)}{a(b - 3[1 - p]x)}$$

According to the carbon dichloride mechanism, however, the rate of disappearance of chloroform should be

$$v = k_2(a - x)(b - 3[1 - p]x)$$

which upon integration yields

$$k_2t = \frac{2.303}{3a[1 - p] - b}\log\frac{b(a - x)}{a(b - 3[1 - p]x)}$$

Thus, according to either mechanism, the value of $k_2$ may be obtained from the slope of the line through the values of

$$\frac{2.303}{3a[1 - p] - b}\log\frac{b(a - x)}{a(b - 3[1 - p]x)}$$

plotted against $t$. However, while according to mechanism I the size of the slope is $k_2$, according to mechanism II it is equal to

$$k_2(1 + [k_t/k_w][C_6H_5S^-]_{av}$$

For two kinetic runs the values of $k_2$ were determined in this manner. The lines obtained are shown in Fig. 1. According to the carbon dichloride mechanism the value of $k_2$ is 0.0116 in Run 26 and 0.0105 in Run 27. These values are in satisfactory agreement with the other values obtained for $k_2$ at the same ionic strength. According to mechanism II the value of $k_2$ is 0.0069 in Run 26 and 0.0073 in Run 27. While these values seem a little low, the possibility that sodium thiophenolate should have this large a specific salt effect on $k_2$ cannot be ruled out definitely. However, since $k_2$ equals $k_{eq}(k_w + k_t)$, and since $k_w$ must increase with increasing ionic strength (at the same rate that $k_t$ does), the specific salt effect of sodium thiophenolate would have to change $k_{eq}$ by approximately four-fold if mechanism II operates.

## Conclusions

While mechanism II cannot be ruled out absolutely on the basis of the present evidence, there are a number of reasons why mechanism I is definitely to be preferred. On the basis of the reasoning used by Hughes and Ingold in distinguishing between compounds reacting by the $S_N1$ and by the $S_N2$ mechanisms, mechanism II could be totally eliminated. Hughes[3] has stated "... first order reaction . . . due to bimolecular substitution with water molecules as reagent cannot be upheld . . . when the much more powerfully basic hydroxide ions are quite inactive." However, in at least one case, that of ethylene oxide, the $S_N2$ reactivity of hydroxide ion compared to that of water is relatively small.[12] Therefore, it seems a definite possibility that water, present in large excess as a constituent of the solvent, may be performing an $S_N2$ attack, although the much smaller quantities of hydroxide ion present are not doing so to an appreciable extent. Therefore, the criterion of Hughes and Ingold may be considered evidence, although not compelling evidence, against mechanism II.

A second weakness of mechanism II is the fact that it requires the trichloromethyl anion present in very small concentration to be very reactive toward $S_N2$ attack by water molecules and thiophenolate ions although the chloroform present in a much greater concentration is quite unreactive toward both reagents. It would appear that making negative the carbon atom which must be attacked by the negative end of the H–O dipoles in a water molecule or by the negative atom in a thiophenolate ion, would be more likely to cause a decrease in reactivity.

A third drawback to mechanism II is the fact that it requires water to display an unusually great activity (toward the trichloromethyl anion) compared to the usually highly reactive thiophenolate ion.

A fourth weakness of mechanism II concerning the effect of change of ionic strength on the value of $k_t/k_w$ has already been discussed.

With the carbon dichloride mechanism, the relative order of reactivity of various reagents is normal. For example, if carbon dichloride were a highly reactive intermediate, as it may well be expected to be, its great reactivity should tend to favor reaction with the reagent present in the greatest concentration, namely, water, so much that only a very highly nucleophilic ion such as thiophenolate could compete with any large degree of success. The work of Hughes, Ingold and co-workers[13] has shown that the ability of reactive intermediates (in their case, carbonium ions) to discriminate increases with increasing stability of the intermediate.

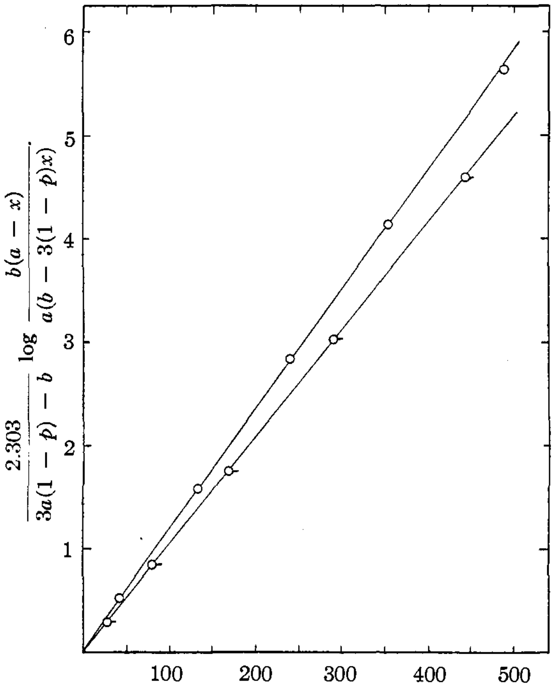

Fig. 1.—○, run 26, ○-, run 27.

## Related Topics

It is believed that this is the first good evidence for a methylene radical mechanism for nucleophilic substitution reactions at a saturated carbon atom occurring in solution, or what Ingold and Jessup[14] have referred to as 1:1 elimination. The reaction of trimethyl-9-fluorylammonium hydroxide to form dibiphenyleneëthylene, for which Ingold and Jessup have written a methylene radical mechanism, more probably proceeds by the type of mechanism suggested by Kharasch, Nudenberg and Fields[15] for the similar reaction of sodamide with allyl chlorides to form 1,3,5-hexatrienes.

While the methylene radical mechanism of the nucleophilic displacement reaction is not nearly as common as the $S_N1$ and $S_N2$ mechanisms, it seems probable that there are many compounds other than the haloforms which would react by this mechanism. Such compounds should have an active hydrogen on the alpha-carbon atom and

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[12] J. N. Brønsted, M. Kilpatrick and M. Kilpatrick, THIS JOURNAL, **51**, 428 (1929); H. J. Lichtenstein and G. H. Twigg, *Trans. Faraday Soc.*, **37**, 905 (1948).

[13] L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

[14] C. K. Ingold and J. A. Jessup, *ibid.*, 2357 (1929).

[15] M. S. Kharasch, W. Nudenberg and E. K. Fields, THIS JOURNAL, **66**, 1276 (1944).

enough $S_N1$ reactivity so that with the added advantage of a negative charge they can lose a halogen (or other) ion by this mechanism. Also, of course, the reactivity by other mechanisms must be sufficiently low to permit reaction by the methylene radical mechanism.

It seems likely that carbon dichloride is an intermediate in a number of the base-catalyzed reactions of chloroform beside the hydrolysis. Among these are: (1) the formation of orthoformate esters from alkali-metal alkoxides; (2) the Reimer and Tiemann reaction; (3) the formation of isocyanides from primary amines; (4) the formation of 3-chloropyridine from potassium pyrrole.

## Experimental

**Reagents.**—Dioxane, chloroform, and carbon tetrachloride were purified by the methods described by Fieser.[16] Eastman thiophenol was used.

**Kinetic Runs.**—The basic hydrolysis of chloroform under the conditions used yields a mixture of carbon monoxide and sodium formate. The percentage of each product formed can be determined by comparing the amount of chloride ion formed with the amount of hydroxide ion used up, since in the reaction to form carbon monoxide three chlorides are formed for each three hydroxides which react, while in the reaction to form formate, three chlorides are formed for every four hydroxide ions used up.

The rate of the reaction may be represented by the equation

$$v = k_2(a - x)(b - [3 + f]x) \qquad (4)$$

where $a = [\text{CHCl}_3]_0$, $b = [\text{OH}^-]_0$, $x = \Delta[\text{CHCl}_3]_t$, $t$ = time, $f$ = fraction of the chloroform going to formate, $k_2$ = rate constant (expressed in liters/mole of chloroform × minutes). Due to the fact that $f$ is experimentally determined by measuring a small difference between two large numbers, it cannot be determined with great accuracy, especially early in a kinetic run. The data indicate, however, that $f$ does not vary much throughout a given run. Because of this and the fact that it is usually found to be small (on the order of 0.1) compared to three, it is assumed to be constant and equation (4) integrated on this basis to give

$$k_2t = \frac{2.303}{a(3 + f) - b} \log \frac{b(a - x)}{a(b - [3 + f]x)}$$

The errors introduced by this procedure are quite small and in no way affect the conclusions drawn from the kinetic data. In the case of the runs made in the presence of a large excess of chloride ions, the accuracy in the determination of $f$ is so poor that $f$ has been assumed to be zero. If $f$ in these cases is actually 0.1, the values of $k_2$ obtained are 3% too large. This difference is in the vicinity of the probable error of $k_2$ and is not important. The values of $k_2$ were determined by plotting the quantity

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

against $t$ and determining the slope of the best line through the points. The reaction was followed by titration of hydroxide, $\Delta[\text{OH}^-] = (3 + f)x$. The value of $f$ was determined by titration for chloride relatively late in the reaction when greater accuracy was possible. As an example, the data from Run 39 are plotted in Fig. 2.

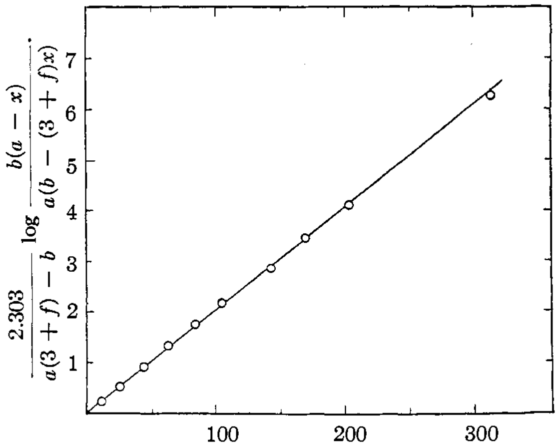

Fig. 2.—Basic hydrolysis of chloroform, run 39.

**Procedure.**—The reaction was followed by pipetting samples into cold water to stop the reaction and determining the hydroxide concentration by titration to the phenolphthalein end-point. Thiophenol was determined by a method based on that of Klason and Carlson.[17] Chloride was determined by pipetting samples into flasks containing an excess of nitric acid, followed by titration according to Volhard.

Run 27 is typical of the procedure used. Thirty-five ml. of 0.94 *N* carbonate-free aqueous sodium hydroxide, 70 ml. of dioxane and 2 ml. of thiophenol were pipetted into a flask and shaken to give a homogeneous solution, 100 ml. of which was pipetted into a 100-ml. volumetric flask which was submerged in an oil-bath maintained at 36 ± 0.01°, until the internal liquid level was at least a half inch below the oil level. At least thirty minutes was allowed for the contents of the flask to reach thermal equilibrium. Then two 5-ml. samples were pipetted from the flask, the first into about 1 ml. of glacial acetic acid in 20 ml. of methanol, and the second into about 10 ml. of ice-water. The second solution was immediately titrated with 0.1000 *N* hydrochloric acid. The first solution was titrated with 0.1001 *N* iodine solution until the yellow color of the iodine persisted. Methanol was added as necessary to keep the solution homogeneous. At zero time, 1 ml. of chloroform at 24° was pipetted into the reaction flask, which was then shaken vigorously. At

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[16] L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Inc., New York, N. Y., 1941, part II, chap. III.

[17] Klason and Carlson, *Ber.*, **39**, 738 (1906).

intervals, samples were taken in the manner previously described. Runs 71 through 81 were made under nitrogen to eliminate the possibility of oxidation of thiophenol.

**Preparation of Phenyl Orthothioformate.**—A solution of 48.8 millimoles of sodium thiophenolate and 24.8 millimoles of chloroform in 150 ml. of $66^2/_3\%$ aqueous dioxane was refluxed as 2.5 ml. of 13 *N* aqueous sodium hydroxide solution was added. At the end of the addition, the solution became hazy and the condenser was immediately reversed for distillation. When about two-thirds of the solvent was removed, the distillation was interrupted, an excess of dilute aqueous sodium hydroxide was added to the flask, and the phenyl orthothioformate was extracted with ether. Titration of the aqueous solutions revealed that 20.0 millimoles of the sodium thiophenolate had not reacted. The ether and other volatile material were removed from the organic layer by warming on a steam cone at a pressure of 2 mm. The crude oil thus obtained weighed 3.1 g. After six decolorizations with Norite, and crystallization from ethanol, 2.78 g. (85%) of light yellow crystals was obtained. These melted at 33–37°, and when mixed with pure authentic phenyl orthothioformate (m. p. 39°)[18] melted at 33.5–37.5°.

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## Summary

The kinetics of the basic hydrolysis of chloroform in $66^2/_3\%$ aqueous dioxane has been investigated. It is shown that the reaction probably proceeds by neither of the two mechanisms ($S_N1$ and $S_N2$) commonly accepted for substitution reactions at a saturated carbon atom.

The only three reasonable mechanisms which are in agreement with the experimental observation that the rate of the basic hydrolysis of chloroform is first order with respect to each of the two reactants, hydroxide ion and chloroform, are

$$\text{(I)}\qquad \mathrm{CHCl_3 + OH^-} \overset{\text{fast}}{\rightleftharpoons} \mathrm{CCl_3^- + H_2O}$$

$$\mathrm{CCl_3^-} \xrightarrow{\text{slow}} \mathrm{Cl^- + CCl_2}$$

$$\mathrm{CCl_2} \xrightarrow[\mathrm{H_2O}]{\mathrm{OH^-},\ \text{fast}} \mathrm{CO + HCO_2^-}$$

$$\text{(II)}\qquad \mathrm{CHCl_3 + OH^-} \overset{\text{fast}}{\rightleftharpoons} \mathrm{CCl_3^- + H_2O}$$

$$\mathrm{CCl_3^- + H_2O} \xrightarrow{\text{slow}} \mathrm{Cl^-} + \mathrm{H_2}\overset{+}{\mathrm{O}}\text{–}\overset{-}{\mathrm{C}}\mathrm{Cl_2}$$

$$\mathrm{H_2}\overset{+}{\mathrm{O}}\text{–}\overset{-}{\mathrm{C}}\mathrm{Cl_2} \xrightarrow[\mathrm{H_2O}]{\mathrm{OH^-},\ \text{fast}} \mathrm{CO + HCO_2^-}$$

$$\text{(III)}\qquad \mathrm{CHCl_3 + OH^-} \xrightarrow{\text{slow}} \mathrm{HOCHCl_2 + Cl^-}$$

$$\mathrm{HOCHCl_2} \xrightarrow[\mathrm{H_2O}]{\mathrm{OH^-},\ \text{fast}} \mathrm{CO + HCO_2^-}$$

When the relative reactivities of nucleophilic reagents toward the four chlorides of methane are compared, it is found that strongly basic reagents show a specifically enhanced reactivity toward chloroform as expected on the basis of a mechanism involving the trichloromethyl anion as an intermediate. It is found that although the reaction of sodium thiophenolate alone with chloroform is negligibly slow, it reacts rapidly in the presence of hydroxide ion to form phenyl orthothioformate. On the basis of these and other facts, mechanism III (the $S_N2$ reaction) is shown to be unlikely. It is shown that the carbon dichloride mechanism (I) is much more probable than mechanism II for a number of reasons: The percentage of chloroform which is transformed to phenyl orthothioformate is independent of the concentration of hydroxide, showing that the competition of hydroxide ions with thiophenolate ions is negligible under the conditions and that only water is competing. In the attack of three thiophenolate ions to form phenyl orthothioformate, it is found that at only one of the three steps is competition of water with the thiophenolate noticeable. The percentage of chloroform yielding phenyl orthothioformate is independent of the ionic strength between 0.09 and 0.31.

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[18] S. Gabriel, *Ber.*, **10**, 185 (1877).