APPLICATION OF ION CHROMATOGRAPHY TO THE STUDY OF HYDROLYSIS OF SOME HALOGENATED HYDROCARBONS AT AMBIENT TEMPERATURES

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APPLICATION OF ION CHROMATOGRAPHY TO THE STUDY OF
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By Dumas A. Otterson

SUMMARY

Ion chromatography with eluent suppression and conductometric
detection enables the evaluation of very slow rates of hydro-
lysis of halogenated compounds. Data has been obtained for the
room temperature hydrolysis in two mixtures. They contain a
dilute carbonate buffer (pH ~ 10.3) and either chloroform (CHCl₃)
or fluorotrichloromethane (CFC₁₃). The chloride ion (Cl⁻) con-
centration in the aqueous phase increased by about 1500 ppb per
day in the CHCl₃ mixture but less than 1 ppb per day in the CFC₁₃
mixture. The faster rate is due to the hydrolysis of CHCl₃. The
slower rate has not been definitely attributed to the hydrolysis
of CFC₁₃. The errors were too great to demonstrate that hydro-
lysis actually occurred in the CFC₁₃ samples. However, the data
for these samples and the control samples were different enough
to suggest that hydrolysis did occur. These data could be used
as an example of how the identification of the hydrolyzing sub-
stance could be expedited by this technique. The data for CFC₁₃
mixtures and the detection of formate ions in the CHCl₃ mixtures
indicates that this technique can expedite investigations of the
hydrolysis mechanisms. This technique may even have the sensi-
tivity required to evaluate rates of hydrolysis of halogenated
hydrocarbons in water at temperatures and pH values observed in
nature.
The slow hydrolysis of many halogenated hydrocarbons at ambient temperature does not appear to have been investigated. Apparently, the analytical methods that were available could not measure the changes in concentration for such slow rates of hydrolysis in a reasonable amount of time. A more sensitive method would overcome this difficulty and expedite these investigations. Ion chromatography is a very sensitive technique for the determination of the concentration of many anions in aqueous solution in the microgram per liter (ppb) range. A number of the anions can be determined using the data from a single twenty minute run (refs. 1 and 2). The extreme sensitivity, thoroughness, and speed of the analyses indicate that this technique would expedite the study of reactions which produce anions such as fluoride (F\textsuperscript{-}), chloride (Cl\textsuperscript{-}), sulfate (SO\textsubscript{4}\textsuperscript{2-}), and nitrate (NO\textsubscript{3}\textsuperscript{-}). Hydrolysis of halogenated hydrocarbons generally produces halide ions; so investigations of this class of reactions should be improved by the use of this technique.

Ion chromatography is the form of ion exchange chromatography which utilizes eluent suppression and conductometric detection. Eluent suppression is the process by which the eluent with high conductivity is converted to a form with low conductivity. The
eluent generally used in ion chromatography for the determination of a large number of anions is a dilute buffer which contains sodium carbonate (Na$_2$CO$_3$) and sodium bicarbonate (NaHCO$_3$). These sodium salts are converted to carbonic acid (H$_2$CO$_3$) when the eluent passes through the acid form of a cation exchange resin. This slightly ionized weak acid has a much lower conductivity than the highly ionized carbonate salts. This conversion allows accurate measurement of small increases in conductivity due to the anions of the sample. The limits of detection have been found to be in the ppb range (ref. 2).

These limits of detection are much smaller than those of the methods used in earlier studies of halogenated hydrocarbons. The earlier investigations generally involved hydrolysis at higher pH values or above room temperature. Either the pH of the aqueous phase was greater than 11.9 (refs. 3, 4, 5 and 6) or the temperature (often as high as 100$^\circ$ C) was higher than room temperature (refs. 7, 8 and 9). The rate of hydrolysis of chloroform (CHCl$_3$) was evaluated in solutions with pH = 12.2 at 35$^\circ$ C (ref. 4). The analytical techniques were sensitive in the milligrams per liter (ppm) range. Thus, one can note that the greater sensitivity of ion chromatography should enable investigations of the hydrolysis of this class of compound at other conditions that would lead to even slower rates of hydrolysis.
The need to investigate hydrolysis at ambient temperature appears to be increasing as the result of modern requirements. For example, hydrolysis could be a reaction that limits the shelf life of ultra-pure reagents. This would occur if the hydrolysis products were more harmful than the reactants. In some cases, the hydrolysis products are less harmful. For example, halogenated hydrocarbons have been found in sources of drinking water. Some of these compounds have been classified as carcinogens. Most of the hydrolysis products are not. Often they are halide ions and halogen-free carbon compounds. Thus, hydrolysis could be a mechanism by which this type of carcinogen is destroyed in nature. Very slow rates of hydrolysis must be measured in order to evaluate these possibilities. Such measurements would be expedited by the use of ion chromatography for the determination of the halide ions. The present investigation was prompted by unexplained increases in the Cl\(^-\) concentration of a standard nitrate (NO\(_3\)) solution which were detected by ion chromatography. This solution contained a dilute carbonate buffer (pH = 10.3) and CHCl\(_3\). CHCl\(_3\) had been added to prevent loss of NO\(^-\). The possibility that the Cl\(^-\) was due to hydrolysis of CHCl\(_3\) is suggested by Hine's report that Cl\(^-\) is produced by the hydrolysis of CHCl\(_3\) at 35\(°\)C and pH = 12.2 (ref. 4). The purposes of the present investigation were to learn if room temperature (approximately 22\(°\)C) hydrolysis of CHCl\(_3\) at pH = 10.3 could have produced the Cl\(^-\) in the standard NO\(_3\) solution and to learn if ion chromatography could be used to study hydrolysis at slower rates.
The experimental work involved the determination of the anion concentrations in the aqueous phase of three types of solution after various aging periods at room temperature (~22°C). The three samples were the carbonate buffer (pH = 10.3) and mixtures of this buffer and either chloroform or fluorotrichloromethane (CFC13). The mixtures will be referred to as the control samples, the CHCl3 samples and the CFC13 samples, respectively. The control samples were included to provide data to evaluate the errors due to contamination. CFC13 samples were included for two reasons. One, data from these samples could reveal the value of ion chromatography for the investigation of the hydrolysis of halo-carbons which contain more than one kind of halogen. Two, the rate of hydrolysis of CFC13 is expected to be slower than that of CHCl3 under the same conditions. Thus, experimental work which differed only in the type of halocarbon present could yield information on two rates of hydrolysis.

EXPERIMENTAL
Apparatus and Conditions

*Dionex Model 10 Ion Chromatograph

Eluent - Dilute carbonate buffer (pH = 10.3) containing 0.003 M NaHCO3 and 0.0024 M Na CO3

Pumping speed - 110 ml per hour

Sample loop - 500 microliter (μl)

Anion precolumn (3x150 mm) - separator column (3x500 mm) filled with low capacity anion exchange resin

*Mention of a specific product or company does not constitute endorsement by the National Aeronautics and Space Administration.
Anion suppressor column (6x250 mm) - filled with high capacity strong acid cation exchange resin

Conductance cell - 6 μl

Bottles - 125 ml borosilicate, glass stoppered - unused prior to this work

Syringe - 5 ml glass syringe, equipped with a syringe filter holder (13 mm diam) containing a 0.3 μm glass fiber filter and a blunt end hypodermic needle.

Reagents

Reagent grade chemicals were used when available. Reagent grade chloroform (CHCl₃) contains a preservative (0.75% ethanol). The purity of fluorotrichloromethane (CFCl₃) must be inferred from the manufacturer's specification. The boiling point varied less than 0.3° F (0.2° C) from 74.7° F (23.7° C) during the evaporation of 85% of the material. The high boiling impurities are less than 0.01%; water, less than 0.001%; and Cl⁻ is specified as "none."

Before use each halocarbon was washed three times with water. About 20 ml of a halocarbon was vigorously shaken with about the same volume of deionized water. The aqueous layer was decanted before each subsequent washing.

Deionized water was used to prepare reagents and to rinse equipment. The deionizing system included an activated charcoal column and two mixed-bed deionizer columns. The specific resistance of the water entering the last mixed-bed deionizer column is rarely less than 1 megohm per centimeter. Hence, the
resistance of the water produced by the system is probably somewhat closer to the value 18 megohms per centimeter which is claimed by the manufacturer.

PROCEDURE

Six 125 ml borosilicate bottles were washed several times with eluent before 100 ml of eluent were added to each of them. The anion content of the eluent in each bottle was determined by ion chromatography. To do so, about 3 ml of a sample are drawn into a clean and dry 5 ml glass syringe. This portion of the solution is used to rinse the entire sample inlet including the 0.5 ml sample loop of the ion chromatograph and to fill the loop. The details of this procedure as well as cleaning and drying the syringe are discussed elsewhere (ref. 2). Only after the anion concentrations were found to be close to background levels, was one of the halocarbons added. One milliliter of either washed CHCl₃ or washed CFC₁₃ were added to the eluent to prepare the hydrolysis samples. The contents of these bottles will be referred to as the CHCl₃ samples and the CFC₁₃ samples, respectively. The control samples contain 100 ml of the eluent with no additive. Two samples of each mixture were prepared and used for this investigation. The anion concentrations that are reported are those of the aqueous phase of each sample.

The anion concentrations of each solution were determined by ion chromatography after each aging period. The resulting chromatograms contained peaks which were attributed to F⁻, Cl⁻, NO₃⁻ and SO₄²⁻ or to interfering ions.
The instrument was calibrated by making ion chromatograms with aqueous solutions containing known concentrations of the four named ions at each attenuation setting of the instrument that was used. The sensitivity of the instrument is quite stable. It changed less than 2% over a 5 month period. The limits of detection were calculated using the sensitivity of the most sensitive attenuation setting and twice the noise level. In this case, the thickness of the base line is greater than the noise level and is used in these calculations. The sensitivities are about 0.3 ppb for $F^-$, 1 ppb for $Cl^-$, and not over 5 ppb for $NO_3^-$ and $SO_4^{2-}$. The aging periods ranged from 1 minute to 44 days. All samples were analyzed within 25 minutes after being prepared and after aging 60 to 90 minutes as well as 2, 9, 20, 29 and 44 days. In addition the CHCl$_3$ samples were also analyzed after aging 1, 25, 70 and 90 minutes.

RESULTS

The concentrations of $F^-$, $Cl^-$, and $SO_4^{2-}$ in the aqueous phase of each sample and their duration of aging are tabulated in Table I. The $NO_3^-$ data are not included because none exceeded the limit of detection. The possibility that some of the tabulated results could be due to interfering ions will be discussed later. The $Cl^-$ concentration of the aqueous phase of these samples changed more than the concentrations of the other ions. During the first ninety minutes of aging, the $Cl^-$ concentration of the two CHCl$_3$ samples increased from about 44 ppb (micrograms per liter) to 129 ppb while that of the two control samples decreased...
from about 40 ppb to less than 20 ppb. The Cl⁻ content then increased with longer aging periods. The initial decrease was probably due to adsorption on the container walls and the increases to contamination. The Cl⁻ content of the CHCl₃ samples increased from about 44 ppb to more than 60,000 ppb during the 44 day test period but was never greater than 70 ppb for the other 4 samples. The Cl⁻ content of the aqueous phase are plotted as a function of the age of the CHCl₃ samples in figures 1A and 1B. The data are indicated by circles for one CHCl₃ sample and by squares for the other. Figure 1A presents the data for the entire test period and figure 1B for the first 90 minutes of aging. The data indicate that Cl⁻ has been formed in the CHCl₃ samples during the entire test period but that the rate of Cl⁻ formation decreased as the samples aged.

The Cl⁻ concentrations of both CFCl₃ samples generally increased with age. The rate of increase was slow (about 0.6 ppb per day). However, the Cl⁻ data for the control samples showed no obvious trends with increasing age. The differences in Cl⁻ results for the control samples after 2 days aging were as much as 20 ppb in several instances. The differences for the CFCl₃ samples generally were less than 4 ppb or less although in one instance the difference was 9 ppb. Obviously better control of contamination is required to establish that the Cl⁻ concentration was actually increasing in the CFCl₃ samples. Improvements in the technique for transferring an aliquot of the sample to the ion chromatograph might permit study of such slow rates. It might also be accomplished by means of a statistical treatment of the data.
The apparent F⁻ concentration of the CHCl₃ and the CFCl₃ samples increased more slowly than the Cl⁻ concentrations of the same sample. Possible causes for the apparent production of F⁻ will be considered later. The apparent F⁻ concentrations of the CHCl₃ samples increased from about 6 ppb to about 33 ppb. Those of the CFCl₃ samples increased from 2 ppb to 10 or 12 ppb while those of the control samples did not consistently increase or decrease. The F⁻ concentrations of the control samples were below 5 ppb except the concentration increased from about 2 ppb to about 8 ppb in one sample during the last aging period. This single large increase suggests a random error in the analysis or an unusually large contamination. The differences in the F⁻ results for the CFCl₃ samples and the control samples are too small to warrant any conclusion about the formation of F⁻ in the CFCl₃ samples. A statistical treatment of the data might provide a better indication of the changes in concentration.

The statistics of a straight line provide a technique to average data which change at a constant rate. Least squares formulae are available to fit a straight line to a series of data points. Formulae are also available that can be used to calculate the slope and intercept of such lines and standard deviations of each (ref. 10). This treatment of the data would result in larger standard deviations if the relationship between concentration and aging period were not linear. Such enhancements of error would merely weaken support for inferences based on comparison of the several sets of data. This type of averaging of
the data in which the linearity is not known would tend to prevent unwarranted inferences. The data for CFC13 samples are too inaccurate to establish the linearity of the relationship between the halide concentration and the length of aging. Thus it appears that the only practicable means to average these data appears to be by use of these formulae.

Table II presents the average slope (and its standard deviation) of the root mean square line that best fits the data for F⁻ and Cl⁻ of each sample. These slopes are the average rate of increase in halide concentration (ppb per day). No background corrections were made. These corrections would merely have changed the intercepts of these lines but would not have affected the slope. The slopes can be used to differentiate between random contamination and regular increases in the concentration of the substances being considered. Such increases in the control samples could only be due to increasing contamination. On the other hand, they could also be the result of hydrolysis reactions in the CHCl3 or CFC13 samples. The rates of Cl⁻ formation are greatest for the CHCl3 samples; considerably less for the CFC13 samples; and least for the control samples. These three types of sample show a similar relationship for F⁻ formation except for one CFC13 sample and one control sample. For these two samples the rate is greater for the control. An examination of the data indicates that the large rate for one control sample is due to one F⁻ result which indicated that the F⁻ concentration increased from 3 to 8 ppb during the last test.
period. If this result is omitted from the statistical treatment, the rate of $F^-$ formation would be $0.005 \pm 0.08$ ppb per day instead of $0.15 \pm 0.04$ ppb per day given in the table. With this change it appears that $F^-$ was formed in the CFC13 samples. This shows the need for better control of contamination.

An additional advantage of using ion chromatography for this type of investigation is revealed by the $SO_4^{2-}$ data. They indicate the presence of unsuspected impurities. These data are consistent with the view that an impurity in the CFC13 samples had reacted to produce $SO_4^{2-}$ ion. The $SO_4^{2-}$ concentration of these samples increased slowly to about 80 ppb or more. In contrast, the $SO_4^{2-}$ concentrations found in the CHCl3 and the control samples were all less than 35 ppb except for one result which was 83 ppb. These data suggest that either an impurity in the CFC13 had hydrolyzed to form $SO_4^{2-}$ or an unknown interfering substance had been introduced at the same time as the $Cl^-$ and $F^-$.  

DISCUSSION

The most probable cause of slow continuous increases in halide concentration in the CHCl3 and the CFC13 samples is the hydrolysis of a halogen-containing organic compound. Such reactions can be very slow. Other possible causes of these increases do not appear to be consistent with the experimental conditions. The other causes include extraction of an inorganic halide-containing impurity from the halocarbon; halide ion contamination during the investigation; hydrolysis of a halogenated
hydrocarbon other than the one being investigated; and interference due to a hydrolysis product. Extraction of inorganic halides should be complete in a few hours; so increases in halide concentration that occur after a day or two cannot be due to inorganic halide impurities. Furthermore, the amount of halide ion that could be added as an inorganic impurity in one milliliter of the types of CHCl₃ or CFCI₃ that were used is too small to be detected in 100 mL of eluent. Other possible causes for the increases in anion concentration will be considered in the particular discussions of the hydrolysis of CHCl₃ or CFCI₃.

The increase in Cl⁻ concentration of more than 60,000 ppb is too large to be ascribed to any cause other than room temperature hydrolysis of CHCl₃. The amount of Cl⁻ contamination that can occur while the samples are aged and during the transfer of aliquots to the ion chromatograph can be estimated using the Cl⁻ results of the control samples. They never exceeded 52 ppb. Moreover the Cl⁻ results for the CFCI₃ never exceeded 70 ppb. Obviously, the probability that contamination can account for the Cl⁻ results of the CHCl₃ samples is virtually nil. The amount of Cl⁻ formed is too large to be due to the hydrolysis of chlorinated hydrocarbon impurity in the CHCl₃. The formation of this amount of Cl⁻ would require the hydrolysis of an amount equivalent to about 0.5% of the added CHCl₃ or more depending on the stoichiometry of the hydrolysis. Hine has shown that all three Cl⁻ ions are liberated when each CHCl₃
hydrolyzes at higher temperature (35°C) and higher pH (i.e., 12.6) (ref. 3 and 4). He also indicates that the net hydrolysis reactions are:

\[
\begin{align*}
\text{CHCl}_3 + 4\text{OH}^- & \rightarrow 3\text{Cl}^- + \text{HCOO}^- + 2\text{H}_2\text{O} \\
\text{CHCl}_3 + 3\text{OH}^- & \rightarrow 3\text{Cl}^- + \text{CO} + 2\text{H}_2\text{O}
\end{align*}
\]

The only substances that are present in reagent grade CHCl₃ in excess of 0.5% are CHCl₃ and ethanol. Preliminary tests indicate that Cl⁻ and ethoxide ions (C₂H₅O⁻) could have about the same elution time. However, the amount of ethanol in about 1 ml of stabilized CHCl₃ could have caused an increase in apparent Cl⁻ of less than 10 ppb. Cl⁻ contamination in the ethanol used to test the ethanol sensitivity could also have contributed to this result. So interference due to ethoxide can not account for the amount of Cl⁻ formed in the CHCl₃ samples. If the hydrolysis reactions reported by Hine occur under the conditions of this work, formate ion (HCOO⁻) is the only hydrolysis product that could interfere. However, this ion does not have the same elution time as Cl⁻, so the measured rate of Cl⁻ formation is due to the hydrolysis of CHCl₃ at pH = 10.3 and at room temperature.

The rate of hydrolysis of CHCl₃ found in this work is expected to be less than that found by Hine at 35°C and at pH = 12.6. The data reported for these conditions indicate that hydrolysis of CHCl₃ could cause the Cl⁻ concentration to increase by about 15 or more ppm per day. In the present work the Cl⁻ content increased about 1.6 ppm per day when averaged over the entire 46
day test period or about 1.8 ppm per day during the first two days.

The increase in the apparent $F^-$ concentration of the CHCl$_3$ samples could be due to an interfering substance or to the hydrolysis of an $F^-$ containing impurity. Formate ion is a hydrolysis product of CHCl$_3$ that has approximately the same elution time as $F^-$ when this eluent is used. More definitive work should be carried out. The use of an eluent such as 0.005 M sodium tetraborate would separate the $F^-$ from formate ion responses. Hence, it would be possible to show whether formate was formed in this hydrolysis or an $F^-$ containing impurity in the CHCl$_3$ had hydrolyzed. Apparently, ion chromatography could expedite an investigation of the factors that influence the relative amounts of HCOO$^- +$ CO formed by hydrolysis of CHCl$_3$.

The investigation of reactions involving compounds that contain more than one kind of halide can be expedited by the use of ion chromatography. A good example is the data obtained for the CFCl$_3$ samples even though the errors are too large to demonstrate that hydrolysis had actually occurred in them. However, these data can be used to demonstrate how improved data from more precise work can be used in this type of investigation.

First, the possibility that formate ion could be responsible for the peak attributed to $F^-$ must be considered. This does not appear to be the case for the CFCl$_3$ samples. If the hydrolysis in these samples produced $Cl^-$ and HCOO$^-$ in the same proportion as in the CHCl$_3$ samples, the interference would be less
than one thousandth of the Cl\(^-\) formed. This would amount to less than 0.07 ppb for the CFC\(_{13}\) samples. The ratio would have to be considerably larger for these samples than the one found with the CHCl\(_3\) samples before HCOO\(^-\) interference could account for all F\(^-\) indicated for the CFC\(_{13}\) samples.

The data of Table I suggests that both Cl\(^-\) + F\(^-\) may have been formed in the CFC\(_{13}\) samples. However, the uncertainty indicated by the F\(^-\) data for the CFC\(_{13}\) samples and the control samples is too great for it to demonstrate that F\(^-\) was actually produced. In spite of this, these data will be used to show how data from more accurate work can yield important information. This can be done by comparing the ratio of the amounts of Cl\(^-\) + F\(^-\) formed with the stoichiometric ratio of these halides in CFC\(_{13}\). The rates of F\(^-\) + Cl\(^-\) formation found in Table II are used for this comparison because they are averages of the data. The stoichiometric ratio in CFC\(_{13}\) is 5.6 g of Cl\(^-\) per g of F\(^-\). The ratios of the rates of formation are 3±1g Cl\(^-\) per g F\(^-\) and 5±2 g Cl\(^-\) per g F\(^-\). The differences are too great to prove that CFC\(_{13}\) is the substance which hydrolyzed but improved data could yield valuable information. No corrections were in the data for the initial halide concentrations in each sample. If this is done, the ratios of Cl\(^-\) to F\(^-\) formed become 5.6±1 and 4.0±1.6. If this data were sufficiently reliable, they would show that CFC\(_{13}\) did hydrolyze and that all of the halide ions are removed from each molecule during the reaction. This discussion shows how ion chromatography might expedite studies of the hydrolysis of halocarbons which contain more than one kind of halogen.
CONCLUDING REMARKS

Ion chromatography has been shown to be a valuable analytical technique for the study of reactions that produce anions. Room temperature hydrolysis of mixtures of a carbonate buffer (pH = 10.3) and either CHCl₃ or CFCl₃ were evaluated. The rate increase in Cl⁻ concentration was found to be about 1500 ppb per day in the aqueous phase of the CHCl₃ samples and about 0.6 ppb per day in that of the CFCl₃ samples. Thus hydrolysis of CHCl₃ can readily account for the Cl⁻ that was found in the aged standard NO₃⁻ solutions which contained CHCl₃ to prevent loss of NO₃⁻. Room temperature hydrolysis of CHCl₃ was definitely indicated by the data. The amount of Cl⁻ produced in the CFCl₃ samples was not sufficient to prove that CFCl₃ had hydrolyzed. This is consistent with the known stability of CFCl₃. Although the CFCl₃ data is marginal, it does show the ability of ion chromatography to identify and to determine very low concentrations of ionic reaction products. This is essential for the investigation of reaction mechanisms. The wide range of rates that have been measured indicates that room temperature hydrolysis of CHCl₃ can be investigated at even lower pH values than 10.3. Indeed, ion chromatography may even be capable of measuring hydrolysis at conditions that predominate in water supplies.
REFERENCES


7. Hine, J.; and Langford, P. B.: Methylene Derivatives as Inter-
mediates in Polar Reactions. XIV. The Effect of pH on the
Rate of Hydrolysis of Chloroform. J. Am. Chem. Soc., vol. 80,
pp. 6010-6013.

8. Fells, I.; and Moelwyn-Hughes, E. A.: The Kinetics of the
1326-1333.

9. Fells, I.; and Moelwyn-Hughes, E. A.: The Kinetics of the
Hydrolysis of the Chlorinated Methanes. J. Chem. Soc., 1959,
pp. 398-409.

# TABLE I.  - EFFECT OF AGING THE SAMPLES ON THE ANION CONTENT OF THE AQUEOUS PHASE

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before adding halocarbon</th>
<th>Age after adding halocarbon</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>≤25 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F⁻ concentration (ppb)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Control</td>
<td>39</td>
<td>9</td>
</tr>
<tr>
<td>4. Control</td>
<td>31</td>
<td>12</td>
</tr>
<tr>
<td>3. CFC₁₃</td>
<td>32</td>
<td>35</td>
</tr>
<tr>
<td>6. CFC₁₃</td>
<td>27</td>
<td>21</td>
</tr>
<tr>
<td>2. CHCl₃</td>
<td>42</td>
<td>59 (25 min)</td>
</tr>
<tr>
<td>5. CHCl₃</td>
<td>42</td>
<td>59 (25 min)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F⁻ concentration (ppb)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Control</td>
<td>2.7</td>
<td>3.1</td>
</tr>
<tr>
<td>4. Control</td>
<td>2.5</td>
<td>4.1</td>
</tr>
<tr>
<td>3. CFC₁₃</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>6. CFC₁₃</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>2. CHCl₃</td>
<td>1.2</td>
<td>8.9 (1 min)</td>
</tr>
<tr>
<td>5. CHCl₃</td>
<td>2.0</td>
<td>9.2 (25 min)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F⁻ concentration (ppb)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Control</td>
<td>1.1</td>
<td>2.0</td>
</tr>
<tr>
<td>4. Control</td>
<td>2.2</td>
<td>4.1</td>
</tr>
<tr>
<td>3. CFC₁₃</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>6. CFC₁₃</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>2. CHCl₃</td>
<td>6.6</td>
<td>35 (1 min)</td>
</tr>
<tr>
<td>5. CHCl₃</td>
<td>4.4</td>
<td>11 (25 min)</td>
</tr>
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</table>
TABLE II. - AVERAGE RATES OF HALIDE FORMATION

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate of increase</th>
<th>Apparent $F^-$, ppb/day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Cl^-$, ppb/day</td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>0.26±0.24</td>
<td>0.15±0.04</td>
</tr>
<tr>
<td>Control</td>
<td>-0.21±0.19</td>
<td>-0.08±0.05</td>
</tr>
<tr>
<td>CFC13</td>
<td>0.61±0.25</td>
<td>0.12±0.04</td>
</tr>
<tr>
<td>CFC13</td>
<td>0.62±0.24</td>
<td>0.22±0.02</td>
</tr>
<tr>
<td>CHC13</td>
<td>1480±170</td>
<td>0.70±0.20</td>
</tr>
<tr>
<td>CHC13</td>
<td>1660±180</td>
<td>0.60±0.11</td>
</tr>
</tbody>
</table>
Figure 1. Chloride ion formation due to room temperature hydrolysis of chloroform.
The application of ion chromatography to the study of very slow rates of hydrolysis of some halogenated hydrocarbons has been investigated. The halide concentrations in the aqueous phase of mixtures of a carbonate buffer (pH = 10.3) and either chloroform (CHCl₃) or fluorotrichloromethane (CFCl₃) after aging for various lengths of time at room temperature, were determined by ion chromatography. Hydrolysis of CHCl₃ caused the Cl⁻ concentration to increase by about 1500 ppb per day. On the other hand, neither the F⁻ or Cl⁻ concentration in the CFCl₃ mixture increased by as much as 1 ppb per day. The magnitude of errors in the determination of halides prevented any firm conclusions regarding hydrolysis in this mixture. However, these results were used to show how ion chromatography could expedite identification of the hydrolyzing substance as well as investigations of hydrolysis mechanisms. This technique may even have sufficient sensitivity to evaluate rates of hydrolysis of CHCl₃ in water at temperatures and pH values observed in nature.