[Contribution from the Department of Chemical Research of Parke, Davis and Company]

THE AUTO-OXIDATION OF CHLOROFORM

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Pure chloroform is known to be decomposed by the air with the formation of hydrochloric acid, phosgene and carbon dioxide.[1] The development of an oxidizing substance has also been noted and this has been referred to previously as chlorine. The literature on the subject has been brought together by Baskerville.[2]

As no proof exists that the oxidizing substance is chlorine, and further, as the formation of phosgene and carbon dioxide leaves no doubt that the reaction is one of oxidation, the writer was led to a study of the question, suspecting that we have here an example of peroxidation similar to that which occurs with benzaldehyde and with ethers.[3]

When pure[4] chloroform is exposed in such a manner that it comes in contact with a sufficient supply of air, it is decomposed at a remarkable rate, a fairly good idea of which may be obtained by following the development of acidity and also of the oxidizing substance which has previously been called chlorine. A maximum rate of oxidation is obtained by filling glass-stoppered bottles to one-third of their volume and allowing them to stand in diffused light. For reasons which will become obvious later, no experiments were made in sunlight. The reaction proceeds slowly at first and the rate gradually increases from day to day. At the end of a period varying from 3 to 4 weeks the development of oxidizing substance reaches a maximum at which time the solution has frequently become hazy and green. Soon afterward nearly all of the oxidizing substance disappears. When at its maximum the solution is usually close to 0.2 N in oxidizing strength, which may be measured by its action upon acidified potassium iodide solution. During the first two weeks of the oxidation the acidity developed was about twice that of the oxidizing value. After this time the acidity showed a relative increase in value. It was measured by dissolving 1 cc. of the chloroform in 400 cc. of water and titrating with standard sodium hydroxide solution, until a permanent color was produced with phenolphthalein. Of course, this method caused the hydrolysis of phosgene or any other substance capable of hydrolysis.

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[1] Schoorl and van den Berg, *Chem. Centr.*, **1905**, II, 1623.

[2] Baskerville, *J. Ind. Eng. Chem.*, **4**, 281 (1912).

[3] Clover, This Journal, **44**, 1107 (1922).

[4] All chloroform used in this work was purified by shaking the commercial product thoroughly with an equal volume of water thrice, drying it twice with calcium chloride in a filled bottle of amber glass and then distilling. A product so purified was usually free from oxidizing substance and contained only a slight trace of free acid; when this was not the case it was discarded.

Although the accumulation of oxidizing substance ceased after a few weeks, there was no decrease in the rate of decomposition of the chloroform, for the acidity continued to increase rapidly. One sample which was not exceptional became more than *N* in acidity in six weeks.

When the pure chloroform was saturated with water the decomposition was found to take place more rapidly, as indicated by the acidity which in one experiment became 1.7 *N* after an exposure of six weeks. At no time during this period was there present more than a very small amount of oxidizing substance.

It has already been observed in the case of ethers[3] that a relatively small amount of auto-oxidation takes place in amber glass when compared with flint glass. With chloroform the rate in amber is nearly one-half that in the flint. However, the accumulation of oxidizing substance goes much further in the amber and in one experiment reached a strength of 0.6 *N* in about two months. At this point the strength began to fall off rapidly. Undoubtedly, light is a factor in both the formation and decomposition of the oxidizing substance.

Some experiments were carried out in an atmosphere of dry air but the results did not differ much from those previously obtained without this precaution.

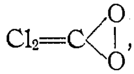
Nature of the Oxidizing Substance

After it was learned that the oxidizing substance accumulates only for a limited time and then disappears, it was possible to select solutions of considerable strength at the proper time. When such a solution was added to water the latter showed a decided test for *hydrogen peroxide* by means of chromic acid. By comparing the strengths of colors obtained in such experiments with those obtained with very dilute solutions of hydrogen peroxide of known strength, it was possible to learn approximately the amount of this substance obtained from the oxidized chloroform. In this way, it was determined that the amount of hydrogen peroxide which resulted from the treatment with water depended largely upon the amount of water used. When the latter was in sufficient quantity to yield a solution of about 1 part in 100,000 the yield obtained was close to 80% of the oxidizing substance contained in the chloroform. When a limited amount of water was used the yield was only a small fraction of this.

The fact noted in the preceding paragraph suggests that the hydrogen peroxide does not exist in the chloroform as such, but that it is formed by reaction with the oxidizing substance upon water. This view is confirmed by the fact that hydrogen peroxide is only very slightly soluble in chloroform. An aqueous solution of the peroxide containing about 38% of the latter was shaken thoroughly with an equal volume of chloroform. The latter was 0.008 *N* in active oxygen, which is only a very small fraction of the oxidizing strength of the chloroform solutions under consideration.

Furthermore, the behavior of the oxidizing substance toward a solution of potassium iodide leaves no doubt that the hydrogen peroxide was formed through reaction with water. When the oxidized chloroform is added directly to a dilute acidified solution of potassium iodide the liberation of iodine is rapid and complete within the least time possible to make a titration. When the experiment is repeated with all factors unchanged except that the chloroform solution is first added to the water and shaken, the addition of acidified potassium iodide then results in a very slow liberation of iodine in a manner characteristic of hydrogen peroxide. The direct action of the oxidizing substance is that of a much more powerful agent, being similar to that of chlorine or hypochlorous acid.

It may be concluded that the oxidizing substance is a *peroxide* which is formed directly by the peroxidation of the chloroform. The fact that a good yield of hydrogen peroxide is obtained through hydrolysis only in very dilute solution makes it impracticable to isolate a considerable quantity of this substance. There is evidence of a small amount of free chlorine in the hydrolyzed product as shown by the immediate action upon potassium iodide in dilute solution. Perhaps this chlorine existed along with the peroxide in the chloroform, having been formed from it as a decomposition product. The stronger solutions of peroxide which were obtained in amber bottles always had a green color. This color disappeared on partial evaporation of the solvent as did also the characteristic action upon potassium iodide. The large loss of active oxygen which occurs when the peroxide is treated with a limited amount of water can be explained only by assuming the escape of this oxygen as gas. Chlorine is found in such a solution only to a very small extent.

It was anticipated that the peroxide could be isolated by evaporation of the unchanged chloroform. Although the strength of the peroxide solution is increased by this process, still there is much loss of peroxide and all of the latter disappears soon after removal of the solvent. The amount of residue is almost negligible. Several ether peroxides have been obtained as approximately pure residues upon evaporation of the unchanged ethers, but as the experience with chloroform is so decidedly different it seems likely that in the latter case peroxide formation does not consist in the simple addition of oxygen alone but also in the separation of hydrochloric acid as follows: $CHCl_3 + O_2 = CO_2Cl_2 + HCl$. It would be very difficult to prove that hydrochloric acid is formed in the primary action of peroxidation, but there can be no doubt about the presence of a monocarbon peroxide derivative which can be explained satisfactorily only by the formula, , dichloro-carbon-peroxide.

Preservatives or Anticatalysts

It has been the general custom for many years to preserve chloroform by the addition of 0.5 to 1% of *alcohol*, and this method seems to have given perfect satisfaction so far as the development of objectionable decomposition products is concerned. It has not been shown whether the alcohol acts as an anticatalyst, preventing the oxidation of the chloroform, or whether it destroys the objectionable products by entering into reaction with them. This question has been discussed by Baskerville[5] who has collected the literature on the subject.

In studying the action of alcohol the writer has been especially impressed by the small amount of this substance necessary to prevent the formation of even a trace of peroxide, phosgene or acid. It has been found repeatedly that pure chloroform containing 0.25% of alcohol after standing for three months in diffused light under conditions most favorable to oxidation, shows no trace of the above mentioned impurities. Starch solution was employed in testing for peroxide. The acidity was determined by the use of 0.01 N alkali. The initial acidity of the purified chloroform was usually such that 4 or 5 drops of 0.01 N sodium hydroxide were required to produce a permanent color with phenolphthalein when 1 cc. of the chloroform was dissolved in water which had been previously brought to a definite color with alkali. It will be recalled that without the addition of alcohol to the chloroform a very high acidity would have been shown by the latter at the end of six weeks. It is difficult to understand how the presence of so small an amount of alcohol could prevent, by ordinary reaction, the formation of a trace of acid. However, alcohol in sufficient quantity does destroy peroxide which has developed in pure chloroform, but a high degree of acidity remains. A sample in which the oxidation had proceeded for less than two weeks and in which the acid value was, according to previous experience, not much more than twice the oxidizing value, was treated with about 2% of alcohol. After about one-half hour the solution became turbid. In two hours practically all peroxide had disappeared but the acidity was nearly as great as it was before the alcohol was added. This experiment also confirms the conclusion previously reached, that no hydrogen peroxide is present for this would not have been destroyed.

When alcohol was used as a preservative in the proportion of 1 to 1000, a trace of peroxide was first noticeable at the end of 6 weeks when there was also found to be a small increase in the acidity of the chloroform. At 1 to 2000 the alcohol was less effective as a preservative, for the same result was obtained after about one week.

Other Preservatives.—Some other substances besides alcohol are known to have a preservative action upon chloroform. The writer se-

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[5] Baskerville, *J. Ind. Eng. Chem.*, **4**, 364 (1912).

lected for study several common organic substances of different types with the hope of throwing additional light upon the question of the role of the preservative.

Phenol, benzyl alcohol, petroleum ether, purified liquid petrolatum and methyl alcohol have been found to be very effective. Different samples of chloroform containing 1% of these substances were exposed in the usual manner for a period of five months. At no time was it possible to obtain even a slight coloration by means of potassium iodide and starch; also, not even a slight increase in the acidity could be detected in any case. It is thought that all of these substances would be perfectly effective at a greater dilution, but this has not been carefully tested except in the case of the petroleum oils.

The phenol solution was finally evaporated in a current of air. The residue was not colored and it dissolved completely in water. It was converted into 2,4,6-tribromophenol, which was found to be pure after recrystallization from dil. acetic acid; m. p., 93°.

The petrolatum solution was finally evaporated and all chloroform was removed from the residue by repeatedly adding alcohol to it and distilling off the alcohol. Finally, the residue was tested for chlorine by means of copper oxide, with negative results.

These effective preservatives represent greatly different types of substances, and it is apparent that chemical structure is not an important factor in the preserving action. As to the question of a chemical change in the preservative, the results here are in agreement with the experience with alcohol. It has not been possible to show the presence of any substance which might be expected to be formed by the oxidation or chlorination of the preservatives.

Further experiments with the petroleum oils have shown that these are considerably more effective than alcohol and this is especially significant because the former are so resistant to chemical change. Pure chloroform containing 1 part of petroleum ether in 1000 was under observation for three and a half months, during which no trace of peroxide could be detected. The same result was obtained with liquid petrolatum. At a dilution of 1 part in 2000 a trace of peroxide first appeared with liquid petrolatum after five weeks. With petroleum ether, the result was not quite so good.

Benzene, benzoic acid, ether and acetone were found to have a decided anticatalytic action but are not as effective as the substances previously mentioned. Acetic acid and carbon tetrachloride are almost without action, which proves that the preservative action is not due merely to the presence of a foreign substance.

Observations were made on the auto-oxidation of two other substances closely related to chloroform, namely, bromoform and methylene chloride.

The latter developed a decided, although very small amount of oxidizing substance after 10 weeks' standing. With bromoform the development of oxidizing substance and acid was rapid at first but it soon reached a maximum which was not large.

Summary

Chloroform undergoes auto-oxidation in diffused light with the formation of a peroxide, which is very probably dichloro-carbon-peroxide. This substance is formed at a gradually increasing rate and its accumulation proceeds up to a certain point, where rapid decomposition sets in. Beyond this point the oxidation of the chloroform continues, although very little peroxide is found in the solution.

The phosgene, carbon dioxide, chlorine and hydrochloric acid present in the oxidized product result from decomposition and hydrolysis of the peroxide.

The preservative plays the role of an anticatalyst.

DETROIT, MICHIGAN

NOTES

The Molecular Conductivity of Potassium Iodide in Epichlorohydrin.—Epichlorohydrin[1] was treated with anhydrous copper sulfate for a few days and the product distilled. It had a constant boiling point of 115°. After a second distillation the distillate was colorless and had a constant conductance of 0.2×10^{-7}. This could not be changed after repeated treatment and distillation. The potassium iodide used was known to have been of very high purity.

The solubility of potassium iodide in this solvent was first found by a preliminary experiment. It was found that a gram molecule in 60 liters would give just the convenient solution. Therefore, 0.0277 g. of potassium iodide was dissolved in 10 cc. of epichlorohydrin and the conductance was found by the well-known Kohlrausch method. Every necessary precaution was taken and the conductivity cell was kept in a thermostat at a constant temperature of 18.00°. The value of the cell constant at that temperature was found to be 0.260.

Mol. vol. Liters	Spec. cond. $\times 10^4$ mhos	Mol. cond. Mhos
60	2.3	13.8
120	1.3	15.6
240	0.8	19.2
480	0.53	25.4

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[1] A commercial product.