[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF AMHERST COLLEGE.]

HYDROLYSIS OF ORGANIC HALIDES AND THE CORROSION OF METALS.

[PRELIMINARY CONTRIBUTION.]

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During the past year my attention has been directed to the influence of certain metals upon the hydrolysis of aliphatic halides and also the influence which certain aliphatic halides have upon the corrosion of these metals. The work was hardly more than begun when this country declared war, and very little progress has been made since. Work on this line has now stopped altogether, and as it is possible that the interruption may be of indefinite duration, it seems advisable to give a brief statement of the qualitative results so far obtained, hoping to take up the subject in detail at the earliest opportunity.

The observation that led to this work is the fact that while dry carbon tetrachloride can be kept indefinitely in metal containers (tin cans) moist carbon tetrachloride has a very marked corrosive effect. The question arose as to whether carbon tetrachloride and concentrated ammonia water could be kept together for long periods in a metal container without destructive corrosion of the container, and specifically, it was desirable to use tin cans for this purpose.

The opinion prevalent among those who have had to deal with the action of moist carbon tetrachloride on iron or tin-plate containers appears to be that the action is due to the hydrolysis of the organic halide and subsequent action of the hydrochloric acid thus formed upon the metal. If this explanation is correct, the addition of concentrated ammonia water should effectually prevent corrosion, as it would keep the liquid alkaline. This hypothesis has not been borne out by the results of experiments.

In the following experiments bright iron wire nails were placed in the test liquids in tightly stoppered bottles. In each case the nail extended above the liquid into the air space in the upper part of the bottle. The tests were made at room temperature.

1. An iron nail in water and carbon tetrachloride rusted rapidly. The effect was noticeable after 12 hours.
2. An iron nail in concentrated ammonia water showed no sign of rusting in ten months.
3. An iron nail in concentrated ammonia water in which ammonium chloride was dissolved showed no sign of rusting in ten months.
4. An iron nail in concentrated ammonia water and carbon tetrachloride rusted very much more rapidly than in water and carbon tetrachloride without the ammonia.

5. An iron nail in concentrated ammonia water to which commercial ammonium carbonate had been added, rusted rapidly.

6*a*. Into one bottle was put concentrated ammonia water, ammonium carbonate, carbon tetrachloride and an iron nail, in the order given. No sign of rusting was observed in ten months.

6*b*. Into another bottle was put concentrated ammonia water and ammonium carbonate, as above. An iron nail was then put in and after about five minutes the carbon tetrachloride was added. In this case very pronounced rusting took place within a few hours, and the nail was practically destroyed in a few weeks.

Expt. 3 indicates that the theory of simple hydrolysis is not sufficient to explain the effect of the ammonia water in accelerating the action of the system carbon tetrachloride–water–iron, nor does it explain the effect of carbon tetrachloride on the system ammonia–water–iron.

The following experiments were performed to get some idea of the rate at which carbon tetrachloride is hydrolyzed when metals are not present.

7. Water and carbon tetrachloride were placed in a 250-cc. tightly stoppered bottle and allowed to stand, with frequent shaking, for twelve weeks. The color of litmus paper was not changed by the water layer, nor was any test for chlorides obtainable.

8. Concentrated ammonia water and carbon tetrachloride were allowed to stand, as above, for ten weeks. A 25-cc. portion of the aqueous layer, after dilution, gave a decided test for chlorides, but not a heavy precipitate.

9. Carbon tetrachloride and 50% acetic acid, allowed to stand as above for ten weeks, gave no test for chlorides in the aqueous layer.

10. Carbon tetrachloride and sulfuric acid, sp. gr. 1.233, gave no test for chlorides in the aqueous layer after standing for ten weeks. All of these experiments were at room temperature.

11. Carbon tetrachloride and sulfuric acid, as in Expt. 10, were heated in a sealed tube for 24 hours at 120°. There was no perceptible change in relative volumes, but, after dilution, a very heavy test for chlorides was obtained.

These expts., 7–11, show that if hydrolysis is responsible for the corrosion of the iron in the earlier experiments, the iron is at least as much responsible for the hydrolysis of the carbon tetrachloride. As iron stands above hydrogen in the electro-potential series, it seemed worth while to observe the effect of substituting for iron some other metal which is below hydrogen in that series, so as to eliminate the formation of hydrochloric acid as a factor in the corrosion of the metal. Also, since the action of ammonia water on iron salts is to form an insoluble substance, it was decided to use a metal whose salt would not give a permanent precipitate with excess of ammonia water. Copper was chosen as satisfying both of these requirements. Copper is not attacked by either hydrochloric acid or ammonia if oxygen is excluded, and the color of the ammono-cupric ion makes it easy to discover the slightest amount of action upon it by the liquids used.

The method used in experimenting with copper was the same as with iron, except that the copper was not in contact with the air, but immersed completely. Excepting in Expt. 15, the copper was in contact with both liquids. About 0.5 g. of very thin copper foil was used in each experiment, all traces of oxide being removed by washing with ammonia water. Test tubes were used for the experiments and in each case the tube was filled with liquid almost to the top, a cork stopper was fitted tightly into it, leaving a very small air space, and the stopper was varnished with shellac to exclude air. The tubes were shaken frequently. All experiments with copper were made at room temperature.

12. *Water, Carbon Tetrachloride and Copper.*—After five days the aqueous layer showed acid reaction and gave a slight test for chloride, but showed no trace of copper, even with acetic acid and potassium ferrocyanide, though the copper was somewhat discolored in the carbon tetrachloride layer. After fourteen days a chloride test gave a heavy precipitate of silver chloride. The aqueous layer was still colorless, but addition of ammonia turned it blue, showing that a very small amount of copper had dissolved. The copper foil had become dark in the water layer.

Comparing Expts. 7 and 12, it is evident that the presence of the copper accelerated greatly the hydrolysis of carbon tetrachloride, although the amount of copper dissolved was very small, and may have been due to admission of air in making the first test.

13. *Concentrated Ammonia Water, Carbon Tetrachloride and Copper.*—Action began immediately at the line of contact of the copper with the two liquids and a dark blue color appeared. Within twelve hours the copper was entirely dissolved, apparently as ammono-cupric chloride. A control experiment, without the carbon tetrachloride showed no effect at all on the copper, and the addition of ammonium salts did not change this result.

It might appear, at first sight, that the ammonia acts by destroying the equilibrium between the copper and cupric or cuprous ions, thereby accelerating the solution of the copper, but this does not explain the increased rate of hydrolysis, for the rate of hydrolysis without the ammonia is enormously greater than the rate of solution of the copper, and it will be shown that there are many cases in which hydrolysis takes place without any action at all on the copper. Neither does this suggestion account at all for the necessary negative ions.

14. *Concentrated Ammonia Water, Methyl Alcohol and Carbon Tetrachloride* were mixed so as to form a solution, to which copper foil was added. The

action was immediate and very vigorous, with evolution of heat. An odor like that of methyl amine was noticed. The copper dissolved very rapidly. After *fifteen minutes* a diluted portion of the dark blue liquid gave a very heavy precipitate with silver nitrate and nitric acid. A control experiment without copper gave no test for chlorides.

15. *Carbon Tetrachloride, Ammonia Water and Copper.*—In this case the copper foil was suspended in the ammonia layer about 2 cm. above the plane of contact between the two liquids, and the tube was not shaken after filling. The action was slow, but after one week the aqueous solution was dark blue in color just above the carbon tetrachloride, and colorless around the copper. Comparing with 13 it seems probable that the copper goes into solution as the cuprous ion, which changes to ammonocuprous ion and is then oxidized by the carbon tetrachloride at the zone of contact of the liquids. If this suggestion is correct, examination of various classes of organic halides might be expected to enable us to make a classification, at least. A number of compounds have been examined, qualitatively, and the results of these experiments will be given below.

16. As ammonia water alone brings about hydrolysis of carbon tetrachloride in time, and more rapidly than acids, it was desired to determine whether the hydroxyl ion is the chief agent in accelerating hydrolysis in Expts. 13, 14 and 15, or, indeed, if hydrolysis is really more rapid in 13 and 15 than in 12. A solution was prepared by dissolving solid ammonium nitrate in concentrated ammonia water to form approximately a 20% solution of the salt. This solution did not redden phenolphthalein and, therefore, may be considered to contain an almost negligible concentration of hydroxyl ions. A portion of this solution with carbon tetrachloride gave no trace of chloride after fourteen days. To another portion of the same solution carbon tetrachloride and copper foil were added in the usual manner. Action on the copper began at once, and after three days the copper was dissolved and the solution gave a very heavy precipitate when tested for chlorides.

Expt. 16 shows conclusively that the presence of copper very greatly accelerates the hydrolysis of carbon tetrachloride, and that the effect of the ammonia solution is due to the ammonia alone, and not to the hydroxyl ion in so far as the solution of copper is concerned. The question that remains to be answered is, does the solution of the copper depend upon hydrolysis or is the answer to be found in the nature of the organic halide itself? The experiments listed below show that hydrolysis can take place without any action at all on the copper in the case of certain classes of halides, but solution of the copper is always accompanied by hydrolysis of the organic halide.

The following table shows briefly the effect of various halides in causing copper to dissolve in concentrated ammonia water. Certain cases will be discussed more in detail.

I. Rapid solution.
- Carbon tetrachloride
- Chloroform
- Bromoform
- Hexachloroethane
- Pentachloroethane
- Chloral
- Chloropicrin
- Ethyl trichloroacetate
- Dichloroacetic acid
- Trichloroacetic acid

II. Slow solution.
- Iodoform (very slow)
- Ethylene chloride
- Ethylidene chloride
- Acetylene tetrachloride
- Benzotrichloride

III. No solution.
- Ethyl bromide
- Ethylene bromide
- Ethyl iodide
- Benzyl chloride
- Epichlorohydrin
- Allyl bromide
- Monochloroacetic acid
- Tetrachloroethylene
- *p*-Dichlorobenzene
- *p*-Chlorotoluene
- Tribromophenol

It will be noticed that all of the substances in Col. I contain the trichloromethyl group excepting dichloroacetic acid and bromoform, which latter contains the tribromomethyl group. While the rate of solution of copper varies considerably with the individual substances, it is measured in terms of days (two or three) for members of Group I, weeks for members of Group II, and members of Group III gave colorless solutions with no action at all on the copper, or such very slightly colored solutions as to indicate only negligible action, even after months. Hydrolysis took place in all cases except those in which the halogen was in the benzene nucleus. In the case of tetrachloroethylene there was considerable action on the copper, but the solution was red, not blue. A few of these experiments require a word of comment.

17. *The Chloroacetic Acids.*—It was seen in 14 that solubility plays a very important part in the rate of solution of copper in at least one case, as, indeed, might be anticipated. The question might therefore arise whether or not the differences tabulated might not be due chiefly to differences in solubility. The three chloroacetic acids enable us to answer this question very satisfactorily, for they all dissolve very easily in ammonia water, and so the question of solubility is eliminated in experiments with these acids. Monochloroacetic acid is very freely hydrolyzed under the conditions of these experiments, but after two weeks the solution was just perceptibly blue, and after three weeks the blue color could barely be recognized in acid solution. Dichloroacetic acid acted with about the same speed as carbon tetrachloride, but it should be remembered that there is a tremendous difference in solubility between the two substances. The rate of reaction with carbon tetrachloride in methyl alcohol-ammonia water solution was many times faster than that of dichloroacetic acid in ammonia water solution. Trichloroacetic acid acted very vigorously, so much heat being produced that the tube had to be cooled in running water to control the reaction, and the copper dissolved in a few hours.

18. A solution of trichloroacetic acid in concentrated ammonia water was divided into two parts. A piece of copper foil was added to one portion and the other portion was allowed to stand as prepared. After five minutes the portion containing the copper was diluted and tested for chlorides with nitric acid and silver nitrate. A heavy precipitate of silver chloride was formed. The other portion gave no test for chlorides after ten minutes. Evidently, in this case hydrolysis was very greatly accelerated by the presence of copper.

19. *Benzotrichloride, Ammonia Water and Copper.*—Violent action took place when the ammonia water and benzotrichloride were brought together, but there was little effect upon the copper. This was something of a surprise, for it is known that benzotrichloride reacts violently when heated with copper alone. It is seen to be the only substance examined which contains the trichloromethyl group which does not cause rapid solution of copper in ammonia water. The probable explanation is that the action of ammonia with benzotrichloride is so rapid that we really do not have the latter substance to deal with for any considerable length of time.

20. *Tetrachloroethylene, Ammonia Water and Copper.*—The commercial tetrachloroethylene used was very impure. It was purified by washing, drying with calcium chloride and fractionating by distillation. Fractions were obtained boiling at 100–118°, 119–122°, 123–128°. The portion used boiled at 119–122°. When allowed to stand with ammonia water and copper the aqueous layer developed a rich red color, like that of port wine, and a brown coating appeared on the copper in the organic layer and was later found in considerable quantity as a precipitate. As this is the only substance examined which gives a red color with copper and ammonia water it may well serve as a test for tetrachloroethylene. The crude commercial product gave the same test, but the fraction obtained from it which boiled at 123–128° gave no pink or red color, but did give a greenish blue solution and a brown solid substance.

It is evident that a very large amount of quantitative work must be done before it is safe to offer any explanation of these results. No work of this sort has yet been done, nor have any of the organic products of the reactions been isolated. Whatever the explanation may be, attention is directed to certain features of these experiments, even though they are only qualitative.

It has been accepted as a generalization that the reactivity of organic halides, that is, their readiness to enter into double decompositions or metathetical reactions, becomes less as the number of halogen atoms attached to one carbon atom becomes greater, but in these experiments it is precisely the most highly halogenated group-trichloromethyl that is most active in causing the solution of copper. The role of copper in accelerating the hydrolysis of these halides may or may not be entirely that of a catalyzer. Expts. 7 and 12 indicate that in absence of ammonia the action of copper is strictly catalytic, at least in relation to the hydrolysis of carbon tetrachloride. The function of the organic halide in causing solution of the copper in ammonia water is evidently not that of a catalyzer but rather that of an oxidizing agent, for with both iron and copper the action is one of oxidation. The mechanism of the reaction is by no means apparent, but it is a suggestive fact that in most, if not all, cases a discoloration of the copper takes place at or below the surface of the organic layer if the copper goes into solution at all. It is possible that these experiments may have some significance in connection with a preliminary paper by J. M. Nelson[1] which has recently appeared, concerning the electromotive force developed in cells containing nonaqueous liquids, in which he suggests that the solution of metals by alkyl halides may be a process very similar to the solution of metals by aqueous solutions of acids.

As soon as circumstances permit, work will be resumed in this laboratory upon this problem, to determine the rates of hydrolysis under different conditions and with various halides, the organic products of the reactions, and the effect of using other metals in place of copper.

Summary.

1. The hydrolysis of carbon tetrachloride by pure water at ordinary temperatures is so slow as to be entirely negligible, but the presence of iron or copper greatly accelerates the hydrolysis. The hydrolysis is also accelerated by both hydrogen and hydroxyl ions, particularly at elevated temperatures.

2. Contemporaneously with this acceleration of hydrolysis there is a corrosive action on the metal, which is well marked with iron, but is very slight and even doubtful with copper. This effect is very greatly increased by the presence of ammonia. It does not take place in the absence of the carbon tetrachloride nor in absence of water. In the case of iron the product is ferric hydroxide and with copper a solution of ammonocupric chloride is formed. Both are oxidation processes.

3. Certain organic halides act towards copper in the presence of ammonia water in a manner similar to carbon tetrachloride. The action is most pronounced with compounds containing the trichloromethyl group. Monohalogen derivatives have practically no action on copper under these conditions, and where more than one halogen atom is present in the compound there is no increased effect unless two are joined to the same carbon atom, and then the effect is very much less than in cases where three chlorine or bromine atoms are joined to the same carbon atom.

4. While all of the aliphatic compounds studied are hydrolyzed in time

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[1] THIS JOURNAL, **39**, 82 (1917).

by ammonia water, the rate of hydrolysis is greatly increased by the presence of copper in all the cases examined.

5. No effect is observed in the case of halogen substituted in the benzene nucleus.

6. A color test is described for tetrachloroethylene.

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XIII. MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. THE DECOMPOSITION PRODUCTS OF THE METHYL ESTER OF ISOAMINOCAMPHONANIC ACID. A NEW REACTION INVOLVING THE FORMATION OF THE METHYL ETHER OF A HYDROXY ACID.

BY WILLIAM A. NOYES AND GLENN S. SKINNER.[1]

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Several years ago, L. R. Littleton[2] and one of us were engaged upon the study of the decomposition of isoaminocamphonanic acid with nitrous acid. Cis-camphonololactone was the only product identified. We have undertaken the study of the decomposition of the methyl ester with the intention of separating the products by fractional distillation under diminished pressure. The products that would normally be expected are a methyl ester of a hydroxy (trans-camphonolic) acid with hydroxyl in place of the amino group and a methyl ester of a Δ_3 unsaturated acid containing a gem methyl. Neither of these products has been found but instead at least six compounds involving rearrangements. Our results show that the methyl ether and methyl ester of cis-camphonolic acid and the methyl esters of lauronolic acid, 1,2,2-trimethyl-1-carboxy-cyclopentene-4, cis 1,2,3-trimethyl-2-hydroxy-1-cyclopentanoic acid, and a secondary β-hydroxy acid are formed. The method of preparing the hydrochloride of methyl isoaminocamphonanate and the nature of the decomposition products will be most clearly understood from the following diagram:

The *d*- and *l*-camphoric acids[3] allow racemization of the secondary but not of the tertiary carboxyl when sufficient strain is produced in the molecule by heat, being converted respectively to *l*-isocamphoric and *d*-isocamphoric acids in 50% yield if equilibrium is established. The hydroxy compound that would ordinarily be expected in this decomposition is the methyl ester of trans-camphonolic acid, but no trans compound has thus far been identified. It is not clear whether the cis compounds we have

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[1] An abstract of a thesis submitted by Mr. Skinner in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the University of Illinois.

[2] THIS JOURNAL, **35**, 75 (1913).

[3] *Ber.*, **27**, 2005 (1894).