

Proceedings of the Iowa Academy of Science

Volume 11 | Annual Issue

Article 22

1903

The Action of Chloric Acid on Metals

W. S. Hendrixson

Copyright ©1903 Iowa Academy of Science, Inc.

Follow this and additional works at: <https://scholarworks.uni.edu/pias>

Recommended Citation

Hendrixson, W. S. (1903) "The Action of Chloric Acid on Metals," *Proceedings of the Iowa Academy of Science*, 11(1), 150-162.

Available at: <https://scholarworks.uni.edu/pias/vol11/iss1/22>

This Research is brought to you for free and open access by the Iowa Academy of Science at UNI ScholarWorks. It has been accepted for inclusion in Proceedings of the Iowa Academy of Science by an authorized editor of UNI ScholarWorks. For more information, please contact scholarworks@uni.edu.

1.	5 c.c. of a solution of chloric acid gave 1.0639. HClO_3 .	
2.	5 c.c. of chloric acid gave 1.0619 HClO_3 .	
	The same solution of pure chloric acid titrated with standard barium hydroxide gave in 5 c.c. 1.0665 HClO_3 .	
		CALCULATED
3.	0.4595 grams KClO_3 gave 0.3158 HClO_3 .	.3165
4.	0.6709 grams KClO_3 gave 0.4628 HClO_3 .	.4622
5.	0.8300 grams KClO_3 gave 0.5731 HClO_3 .	.5718
6.	1.2744 grams KClO_3 gave 0.8778 HClO_3 .	.8778
7.	0.3350 grams KBrO_3 gave 0.2605 HBrO_3 .	.2585
8.	1.0983 grams KBrO_3 gave 0.8460 HBrO_3 .	.8478

The method above described seems to have some advantages. It is extremely simple. It can be carried out at room temperature, avoiding the danger of loss of hydrochloric acid by heat. In the reduction and the preparation of the solution for titration are necessary only iron and pure sulphuric acid and nitric acid which are always at hand in every laboratory, and no filtering or other operations likely to occasion loss of chlorine or loss of time are required.

Iowa College, Grinnell, Iowa.

April 11, 1904.

THE ACTION OF CHLORIC ACID ON METALS.

BY W. S. HENDRIXSON.

In the course of my work a year ago on Silver as a Reducing Agent, in which the action of finely divided silver on chloric, iodic and chromic acids was studied quantitatively, there was occasion to study the literature relating to the action of chloric and related acids on other metals. It soon appeared clear that the amount of information to be gained about the action of chloric acid in particular, on the metals was very meager, and it appeared also that there were several errors, whose origin in most cases could not

be traced, that had apparently come down from treatise to treatise to the present time. It seemed, therefore, desirable to attempt to make some contribution to the subject, and if possible to clear up some contradictions and doubtful points, and this seemed the more desirable since chloric acid is one of the few strong oxidizing acids, which can be obtained in the free state easily and in pure condition, and which is fairly stable.

So far as known to me scarcely any attempt has been made to study quantitatively the action of chloric acid on metals. It is a highly dissociated acid and it is also a strong oxidizing agent. As might be expected, its action on metals may take one or both of two courses. It may dissolve some metals with the liberation of hydrogen in about the same way as hydrochloric acid, and with very little oxidizing action; again, it may act purely as an oxidizing agent. The course depends upon the nature of the metal in any case and the concentration of the acid. Contrary to statements that have been made I do not find any metal that dissolves in chloric acid without the reduction of at least a small portion of the acid. On the other hand, there are several metals that simply disappear in the acid and that rapidly and at ordinary temperature, without the evolution of any gas whatever. Among these are cadmium, copper and iron.

Most of the chloric acid in the market is far from pure, and I have been able to obtain only one sample pure enough for use in this work. It was secured from Eimer and Amend, and it contained no sulphuric acid, barium or free chlorine, and only a trace of hydrochloric acid. This supply was some time ago exhausted and the delay in importing an additional supply has occasioned in some measure the incompleteness of this paper. The acid as received showed by titration that it contained 211.7 HClO_3 per liter, or almost exactly the amount corresponding to 2.5 normal acid.

It was very desirable in some of these experiments to hasten the action of the acid by heat. Since it is stated in the literature that chloric acid in water solution decom-

poses into chlorine and perchloric acid, water and oxygen, when heated above 40° , it was deemed necessary to test the stability of the 2.5 N. acid at higher temperatures, and this was done in the following way: A volume of 30 c.c. of the acid of 2.5 N. strength was placed in a tube so arranged that pure air from a gas cylinder could be passed through the acid and then by suitable exit tube into a flask containing potassium iodide. The tube was placed in a beaker of water which could be heated. While a slow current of air was passed through the acid the temperature was slowly raised to the boiling point of the water in the beaker, and the boiling was maintained for half an hour. At about 95° the solution of potassium iodide began to show a trace of color, due to separated iodine. At the end of the experiment the free iodine was titrated with N/10 thiosulphate and required 0.2 c.c., which corresponds to 0.6 mg. of chlorine. The strength of the acid then remaining in the tube was found to be 2.65 N. and on testing with silver it gave apparently only the usual slight opalescence. It seems clear, therefore, that one may heat even the strongest, pure chloric acid that is likely to be found in the market to temperatures near the boiling point of water without fear of essential decomposition. It seems probable that the statement that chloric acid decomposes when heated above 40° might be due to the fact that the author used impure acid, containing possibly hydrochloric acid which might decompose the chloric acid, or that the statement refers to an acid of about the maximum concentration.

The methods of experiment were in general very simple. In some cases where no hydrogen was evolved, the flask or tube containing the weighed metal and measured acid was allowed to stand at room temperature. In cases where the solution was slow, the vessel was placed in water which was heated to 40 or 50 degrees. The conditions are mentioned under the metals to which they apply. Save in two or three cases no attempt was made to exclude the air for the two reasons, that at best the acid would contain some air which could not with safety be expelled by heating, and that in two or three cases where

the solution was carried on in an atmosphere of carbon dioxide the results were not noticeably different from those in the experiments carried out with the same metals in the presence of air. From time to time suitable means were applied to determine whether any chlorine was evolved or any hydrochloric acid was being lost. The tests were negative in every case save in one experiment in the solution of iron. By accident the temperature was allowed to reach 80 degrees, and some chlorine was evolved, and was detected by aspirating a current of air through the acid and into a solution of potassium iodide and starch. To determine the amount of reduction in any experiment the solution was made up to a known volume and portions of it were titrated with N/20 silver solution after the method of Volhard, to determine the hydrochloric acid, from which the amount of chloric acid reduced could be calculated.

Action of Chloric Acid on Sodium and Potassium.

No information as to the action of chloric acid on potassium is known to me in the literature. Tommasi* tried the action of sodium amalgam on the acid and stated that the acid is not reduced to the least extent. I have repeated the experiment of Tommasi, using about two per cent sodium amalgam freshly prepared from carefully cleaned sodium and the usual redistilled mercury. The method of experiment in this instance was to add the amalgam slowly, while the solution of acid was kept cool, to a measured volume of chloric acid. When nearly all the acid was neutralized the solution was poured off, and, together with the washings, was acidified with nitric acid and titrated in the usual way. A blank experiment using water was made to test the freedom of the amalgam from traces of chlorine.

1. 25 c.c. 2N HClO_3 treated with 10 grams sodium amalgam required 1.4 c.c. N/20 silver solution, corresponding to 0.0025 grams HCl.
2. 25 c.c. 2 N HClO_3 treated with a large excess of sodium amalgam required 6.85 N/20 silver solution, corresponding to 0.0125 grams HCl

*Istituto Lombardo, 2 Ser. X, 799.

Similar results were obtained with potassium amalgam, and the reduction was about twice that produced under similar conditions by sodium amalgam.

1. 25 c.c. 2N HClO_3 treated with about 10 grams of potassium amalgam required 2.9 c.c. N/20 silver solution, corresponding to 0.0053 HCl.
2. 25 c.c. N HClO_3 treated with 10 grams potassium amalgam required 1.5 c.c. N/20 silver solution corresponding to 0.0027 grams HCl.

From the results there seems to be no doubt that both sodium and potassium amalgam are capable of reducing chloric acid, though the amount of the reduction is very small. In using mercury and an alkali metal there is the possibility that the reduction may be caused by the mercury. In the presence of such a strong electro-positive metal as sodium, however, this does not seem probable. Moreover, on attempting to dissolve mercury in chloric acid it was found that after heating at 40 degrees for four hours scarcely any reduction of the acid had taken place and the remaining mercury was collected, dried and weighed and corresponded within four milligrams to the original amount taken. The smallest amount of HCl found above corresponds to about 0.04 gram of mercury.

Action of Chloric Acid on Magnesium.

Magnesium in the form of the ordinary ribbon of commerce was used. It was cleaned with emery paper and dissolved in an excess of normal chloric acid, 50 c.c. of the acid being used in each case. The amount of metal considered, the reduction caused by magnesium is more pronounced than in the cases of the alkali metals.

1. 0.2918 grams of magnesium gave.....0.0065 grams HCl.
2. 0.2170 grams of magnesium gave.....0.0054 grams HCl.

The results show in fact that about one-twentieth of the magnesium was used in reducing the chloric acid. The remainder, of course, dissolved to form the chlorate with the evolution of approximately its equivalent of hydrogen. Since, as is well known, water containing salts in solution acts on magnesium with the evolution of hydrogen, it did not seem worth while to determine the amount of hydrogen produced in the solution of the metal.

Action of Chloric Acid on Zinc.

Concerning the action of chloric acid on zinc there are many statements in the literature and some contradictions. According to GayLussac* and Berzelius the acid dissolves zinc without decomposition and with the evolution of hydrogen; according to Vauquelin, Fordos and Gelis† with the formation of hydrochloric acid, but without the evolution of hydrogen; according to Gmelin* with both the reduction of the acid and the evolution of hydrogen. Tommasi‡ states that in one experiment zinc reduced 14 per cent of the free acid present in 100 hours, and that the acid was completely reduced by an excess of zinc and sulphuric acid. Zinc and zinc dust have been used as the reducing agents in determining chlorates, but not so far as known to me for the determination of the free acid, nor does there seem to be any record of quantitative study to determine the nature of the reaction of chloric acid and zinc so far as relates to the relative amount of zinc that reduces the acid and that which sets hydrogen free as the concentration of the acid is varied. In the present series experiments were made with an excess of acid and with an excess of zinc, but the series is not yet complete.

In these experiments and also in those with aluminium, there was used as the vessel in which the reaction took place a graduated tube made from a burette. It was fitted with a rubber stopper and a delivery tube of small bore, such as is used for water thermometers. The tube was filled with acid nearly to the stopper when in place and adjusted in a water bath. The weighed zinc was dropped in, the stopper quickly inserted and the hydrogen was collected in a graduated tube over water. Experiments thus far seem to show that the relative amounts of zinc that set free hydrogen and that reduced the acid may vary widely with the concentration of the acid. In the first two experiments weighed amounts of zinc were used and after the action had practically ceased the remaining zinc was weighed. In each case 25 c.c. of normal acid was used. The chloride

* Gmelin's Handbuch, Vol. 1, 370.

† J. Pharm 4, 346.

‡ Instituto Lombardi, 2 Ser. X, 739. Berichte 11, 345.

formed was titrated and the hydrogen was reduced to normal conditions and the amounts of zinc corresponding to each were calculated. The calculation of the reducing zinc was based upon the assumption that one molecule of the acid oxidized three atoms of zinc, or that when the acid is decomposed at all it is completely reduced to hydrochloric acid, and the whole series of experiments support this view. The volumes of hydrogen given below are in all cases reduced to normal conditions.

	ZINC DISSOLVED.	H. COLLECTED.	HCl. FOUND.	Zn. TO H.	Zn. TO HCl
1.....	0.7047	69.93	0.0925	0.2048	0.4979
2.....	.6627	63.11	.0892	.1857	.4803

In the following an excess of 2 N. acid was used and all the zinc weighed was dissolved, and it was of the same sample as used in (1) and (2). As may be observed in (3) and (4) the amounts of hydrogen collected were very small and the oxidizing action of the acid was very much more pronounced. It was observed in both experiments that the evolution of hydrogen seemed to be very much more rapid near the beginning of the experiment. Though there was scarcely a visible residue it seems possible that as the zinc dissolves, impurities collect at the surface and influence the character of the reaction. This influence would have been far less in (1) and (2) where the zinc taken was about three times the amount dissolved. It is the purpose to investigate this reaction farther, using several samples of redistilled zinc.

	ZINC DISSOLVED.	H. COLLECTED.	HCl. FOUND.	Zn. TO H.	Zn. TO HCl.
(3)	.3484	4.4 c.c.	.0619	.0129	.3332
(4)	.4966	5.7 c.c.	.0873	.0168	.4699

Action of Chloric Acid on Aluminium.

Except the statement of Tommasi * that a solution of chloric acid treated with aluminium showed after six hours only a trace of hydrochloric acid, there seems to be nothing in the literature concerning the action of the acid on this metal. Aluminium slowly dissolves in cold dilute

* l. c.

chloric acid, and whatever the concentration hydrogen is given off and the acid is reduced as in the case of the action of the acid on zinc.

For the following experiments the ordinary aluminium wire of commerce was used. An attempt was made to compare, as in the case of zinc, the action of the dilute acid on an excess of the metal with the action of an excess of the strong acid. In the former case, however, the metal dissolved as indicated by the loss of weight was always too small by about 5 per cent to account for the hydrogen set free and the chloric acid reduced. Determinations of the actual amounts of metal in solution and in the residue showed that in very dilute acid the metal becomes coated with a layer of oxide, which accounts for the above mentioned discrepancy. The ratio of the metal which replaced hydrogen to that which reduced the more dilute acid was found to be about 1 to 7, while in the experiments with the 2 N. acid below the ratio was about 1 to 5.

In the following experiments the aluminium was completely dissolved in 2 N. acid, the hydrogen was collected and reduced to normal conditions and the HCl was titrated in the usual way.

	AL. DISSOLVED.	H. COLLECTED.	HCl. FOUND.	AL. TO H.	AL. TO HCl.
(1)	.2435	47.8	.1363	.03876	.2027
(2)	.2637	55.4	.1386	.04487	.2210

In each experiment there was an insoluble residue of 0.7 milligram.

Action of Chloric Acid on Iron.

The treatises of Graham-Otto and Dammer quote apparently from a very old but undesignated work, that zinc and iron dissolve in chloric acid with the evolution of hydrogen. Schiff* in his correspondence states that Pellagri found that iron reduces chlorates, and Tommasi † partially reduced copper chlorate with iron. There seem to be no other references to the action of iron on either free chloric acid or its salts.

Contrary to the statement mentioned iron dissolves readily in dilute or strong chloric acid without the evolution

* Berichte, 8, 1350.

† (l. c.)

of hydrogen or any other gas. In the following the purest, soft iron wire such as used in standardizing permanganate was used. Even with two or three pieces of this large wire the action was so vigorous that a considerable rise in temperature was occasioned, when the 2N. acid was used. The solution took place in glass stoppered bottles standing in cold water. In several instances a brown coating was observed to form which scaled off and was soon dissolved in the excess of acid. The iron goes directly into the ferric condition, and in no instance, even while the solution was going on, could ferrous iron be detected by the usual tests. The solution has the usual brown color characteristic of solutions of ferric salts but remains perfectly clear so long as the acid is in excess. With a large excess of iron, oxides and probably basic salts are precipitated. In one such case the amount of reduction of the chloric acid was found to be approximately 95 per cent. The very ready reduction of the acid by iron suggests to the writer a method for the determination of chloric acid and chlorates by reduction with iron in the presence of sulphuric acid and the titration of the hydrochloric acid formed.

In the solution of iron, if anywhere, one might expect the oxygen of the air to exert an influence upon the relation of the metal dissolved to the amount of acid reduced. In experiment (4) the solution was carried out in an atmosphere of carbon dioxide. A distilling flask containing the acid was supported so that the neck in which the weighed iron was placed, was in a nearly horizontal position. When the air had been completely expelled by carbon dioxide the neck was raised so that the iron fell into the acid. The results of this experiment do not indicate that the air has any appreciable influence. In the following experiments the iron in column (3) is of course calculated on the basis that it was all oxidized to the ferric condition. In all cases the amounts of iron thus calculated and added to the residues of carbon and silica found in the respective experiments are somewhat smaller than the corresponding amounts of iron weighed. I am not at present able to account for this small difference, and the subject

will receive further attention. In (1) of the following experiments 35 c.c. of normal acid were used at 40 degrees, and in the others 20 c.c. of 2N were used in each case, and the acid was kept at about room temperature.

	IRON WEIGHED.	HCl. FOUND.	IRON CALCULATED.	RESIDUE.
1.	.1609	.0518	.1592	.0011
2.	.2262	.0699	.2148	.0046
3.	.3010	.0949	.2916	.0006
4.	.3220	.1023	.3143	.0014

Action of Chloric Acid on Tin.

The tin used was so-called pure tin obtained from Schuchardt, and the solution took place in glass stoppered bottles at room temperature. In the first experiment 25 c.c. of the 2N. acid were used and the solution occupied about thirty minutes. In the second case 50 c.c. of N. acid were used and the action occupied several hours. Contrary to what might be expected very little tin oxide or stannic acid remained. In each case the residue, which did not increase on long standing, weighed .0022 gram. The solution remained clear for a long time even after it had been diluted preparatory to titration. As in the case of iron, no hydrogen was set free and the tin went at once into the stannic condition, as shown by appropriate tests.

1. .3084 grams of tin gave .0618 HCl, corresponding to .3027 grams tin.
2. .3572 grams of tin gave .0721 HCl, corresponding to .3531 grams tin.

Action of Chloric Acid on Copper.

After the work on copper had been done there came to my notice the communication of Brochet on the solvent action of chloric acid on copper which appeared in Comptes Rendus January 25th of this year. His paper came into my hands after the next paragraph had been written. While granting to Brochet the priority in several particulars, since he gave no analytical data, I deem it best to submit for record the paragraph as originally written.

The action of chloric acid on copper offers no peculiarities. It is just what one in view of the foregoing would expect. The copper simply disappears, and this gives rise

to a clear blue solution due to salts of copper. The copper used was in the form of bright wire gauze, such as is commonly used in combustion in organic analysis. The metal dissolves rapidly in 2N. acid at 50 degrees.

1. .2778 grams copper gave .0528 HCl, corresponding to .2766 grams Cu.
2. .5288 grams copper gave .1000 HCl, corresponding to .5236 grams Cu.

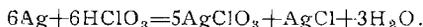
Action of Chloric Acid on Cadmium.

The action of chloric acid on cadmium is in every way similar to its action on copper, it being one of simple oxidation and the solution of the oxide in the excess of acid, no gas being given off. Ordinary commercial cadmium was used. The acid was 2 normal. In the first case the reaction went on at room temperature and in the second at 50°.

1. .4732 grams cadmium gave .0520 grams HCl, corresponding to .4810 Cd.
2. .4091 grams cadmium gave .0438 grams HCl, corresponding to .4052 Cd.

The action of chloric acid on certain other metals has been studied to some extent. It acts with exceeding slowness on mercury and antimony even when at full strength and at 70°, and no attempt was made to determine the quantitative relationship. Nickel dissolves readily and apparently in quite the same way as copper and cadmium. Bismuth is rather slowly oxidized and only a small portion of the product goes into solution. In one experiment .3693 grams of bismuth gave .0282 HCl, corresponding to .3624 Bi.

In a recent communication on silver as a reducing agent* it was shown that silver reduces chloric and iodic acid directly to hydrochloric and hydriodic acids, and according to the equation as there given for chloric acid.

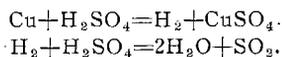


The same general reaction has since been found to hold true in the case of bromic acid and silver. There was no evidence in any case of the formation of any intermediate product, in the reduction of the acid, but in each case the reaction ran smoothly as above represented. Omitting the

* HENDRIXSON, Jour. Amer. Chem. Soc. 25.

matter of the evolution of hydrogen the same reaction holds true in general of the action of chloric acid on other metals. In no case when the temperature has been kept moderately low has there been evidence of the formation of a lower acid, an oxide of chlorine or free chlorine. Save in the case of iron, where the question of impurity is uncertain, the amount of metal dissolved has been accounted for by the amount of reduction of the acid, or the reduction and the hydrogen set free. It is possible that some irregularity in the reaction took place in the case of iron and in other instances, even though it was not detected. Since chloric acid is almost as highly dissociated as hydrochloric acid it must be that a large portion of the HCl formed by the reduction exists in the solution in the free condition, and it might be expected that the two acids would act upon each other according to some one of their known reactions. If such action occurs its extent must evidently be quite small.

There is yet a persistent tendency as shown in chemical literature to regard the reduction of an acid in its action on a metal, as in the case of the action of hot sulphuric acid on copper, as due to the "nascent" hydrogen first set free. Thus,



In the case of chloric acid, however, we have all varieties of reaction, from that of the action of the acid on sodium and potassium, where nearly the full equivalent of the hydrogen is set free and the reduction of the acid is extremely small, to that of the action of the same acid on iron, tin and copper, in which no hydrogen is set free and nearly or quite the full equivalent of the metal appears in the amount of reduced acid. It would seem, therefore, that since the temperature is practically the same in all cases, as well as the concentration of the acid, that the reduction can not be accounted for on the basis of nascent hydrogen. In each case it seems to be rather a mere question of the tendency of the metal, under the conditions, to oxidize at the expense of the oxygen of the acid, or, to go

into solution at the expense of the hydrogen which is set free. In the cases of iron, tin and bismuth it seems evident to the eye that oxides are first formed, and in all cases where reduction occurs the view is simplest and most nearly in accord with the facts, that the metal is oxidized and that the oxide dissolves in the excess of the acids, or remains insoluble as in the case of bismuth.

Iowa College, Grinnell, Iowa.

April 11, 1904.

PERIODICAL LITERATURE IN IOWA ON THE SUBJECT OF CHEMISTRY.

BY W. S. HENDRIXSON.

The following is a list of the chemical periodicals in the State of Iowa, with the extent of the files and the names of the libraries in which they may be found. The list is prepared and published for the information of chemists who may have occasion to refer to such periodicals in their work. So far as known the books of any file may be used for reference purposes in the libraries which contain them and under certain restrictions, in some cases, they may be taken out for purposes of reference. In some cases the books are in the private libraries of chemists connected with the institutions mentioned, but this does not preclude their use by outside parties.

In this list are not included fragments of sets consisting of only a few volumes, unless the periodicals are now being received. The extent of the files is indicated by years. The libraries in which the periodicals are to be found are designated as follows: State University of Iowa, S. U. I.; State Library, S. L.; Iowa State College, I. S. C.; Iowa College, I. C.; Morningside College, M. C.; Drake University, D. U.; Cornell College, C. C.; Coe College, Coe; Simpson College, S. C.; State Normal, S. N.; Sioux City Library, S. C. L.