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The Hydrolysis of Iodine Monochloride

BY FREDERICK ARTHUR PHILBRICK

The object of the present work was to examine the hydrolysis of iodine monochloride

$$5ICl + 3H_2O \rightleftharpoons HIO_3 + 5HCl + 2I_2$$

a reversible reaction which up to the present appears to have escaped quantitative investigation. It was also hoped that the results might throw some light on the constitution of iodine monochloride in aqueous solution, and particularly on the disputed existence of the iodine cation.[1]

The solutions used were very dilute, and on account of analytical difficulties the measurements were confined to solutions saturated with the iodine produced by hydrolysis. Concentrated solutions of iodine monochloride were diluted in a known proportion, and the weight of iodine precipitated was determined by analysis of the solution filtered from it.

The concentrated solutions were prepared from weighed quantities of iodine, concentrated hydrochloric acid (the constant-boiling mixture, corrected for pressure) and an excess (about 20%) of a solution of iodic acid whose exact concentration had been determined by iodimetry. These ingredients were mixed in glass tubes which were then sealed and kept cool. No free chlorine could be detected, even after months, and before use the concentrations were checked by analysis. The resulting solutions were diluted with water in a known proportion by weight, varying from 35 to 115 times, and were transferred to long-necked flasks in a thermostat at 25°. In some of the experiments weighed quantities of potassium chloride were also placed in the flasks. The time necessary for the solutions to reach virtual equilibrium was measured in a series of preliminary experiments, while in the experiments reported at least twice as long was allowed (eleven to twenty-eight hours). While still in the flasks the solutions were freed from precipitated iodine by upward filtration through glass wool filters inserted through the neck. Immediately on leaving the filters the solutions were received in bottles containing hydrochloric acid, with which they were diluted in a known proportion by weight. This precaution is necessary not only to prevent the precipitation of iodine on cooling, but also to allow the oxidation of dissolved iodine by the excess of iodic acid, with the object of avoiding loss of iodine by volatilization in the subsequent analysis.

The solutions were analyzed by adding excess of potassium iodide and titrating the liberated iodine with thiosulfate. Analytical errors are multiplied in the calculations, so the analyses were duplicated and the titrations were carried out by weight on account of the precision which this method allows. Since the solutions were made up by weight, no density corrections were involved. The usual precautions of precise iodimetry were adopted, and after the titrations had been taken with a weight buret to within two or three drops of completion they were finished with a very dilute solution of thiosulfate freshly prepared by dilution of the more concentrated solution and added from a volume buret. The standard was a solution of potassium iodate, and the other solutions used in the analysis were frequently checked against it, and against one another. The weights were standardized for the work. The average concordance of duplicate analyses was ±0.02% and the greatest divergence was ±0.05%.

The purification of most of the materials has been described in a previous paper.[1] The iodic acid left no residue on gentle ignition.

The results are shown in the table, the solutions being in order of increasing chloride ion concentration. All the concentrations are in millimoles per kilogram of solution. Let the

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[1] Philbrick, *J. Chem. Soc.*, 2254 (1930); Faull and Baeckström, THIS JOURNAL, **54**, 620 (1932).

concentrations of iodine monochloride before hydrolysis and at equilibrium be a and a', respectively, and let those of iodic acid be b and b', while the concentration of dissolved iodine in the solution at equilibrium is c. Then $b' = b + (a - a')/5$, and on the addition of excess of potassium iodide one kilogram of the solution will produce

$$a' + 3\left(b + \frac{a - a'}{5}\right) + c = \frac{3a + 2a'}{5} + 3b + c$$

millimoles of iodine

c was calculated from the results of Carter and Hoskins.[2] a' and b' can then be calculated from the results of the titration and the known values of a, b and c. The hydrogen ion concentration can be calculated in a similar way. The ionic concentrations were calculated on the hypothesis of complete dissociation.

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Concentrations in millimoles per kg. of solution. K_1, K_2 and K_3 are calculated with these units of concentration

Experiment	1	2	3	4	5	6	7	8	9	10	11	12
$[Cl^-]$	20.09	31.30	31.67	32.71	37.28	39.74	40.36	46.31	48.50	59.24	60.06	65.64
$[IO_3^-]$	1.232	1.606	1.800	1.737	1.924	2.235	1.504	1.507	2.347	2.496	1.186	3.122
$[H^+]$	20.88	31.47	32.06	33.25	37.55	40.09	30.85	30.86	47.92	56.31	28.91	62.80
$[K^+]$	...	..	..	..	..	..	9.077	15.04	..	..	28.83	..
Positive iodine, as $[I^+]$	0.4455	1.432	1.412	1.198	1.648	1.892	1.933	1.916	2.925	5.424	3.512	5.959
Iodine solubility	1.411	1.439	1.440	1.443	1.455	1.461	1.463	1.478	1.483	1.510	1.513	1.527
$10^5 \times K_1$	3.04	2.58	2.37	1.75	1.62	1.49	2.20	1.64	1.31	1.54	2.14	1.15
$10^2 \times K_2$	1.11	2.08	1.96	1.60	1.87	1.92	2.91	2.94	2.37	3.58	5.99	3.30
$10^5 \times K_3$	56.9	69.7	64.9	51.0	52.5	50.9	75.9	66.3	52.2	66.7	106.2	55.5

The existence of a complex between chloride ions and positive iodine was established by the conductivity and transference experiments of Faull and Baeckström.[1] Their transference experiments do not however cast any light on the existence of an iodine cation. If such an ion exists it will be in equilibrium with the complex and with chloride ions according to some such scheme as

$$I^+ + 2Cl^- \rightleftharpoons ICl_2^-, \text{ whence } [ICl_2^-]/[I^+] = K[Cl^-]^2$$

In Faull and Baeckström's experiments the cathode liquid consisted of pure hydrochloric acid, and any iodine cation emerging from the middle liquid would be progressively converted to the complex anion in a solution of this chloride ion concentration and would be carried back toward the anode. It should also be pointed out that chlorine water and starch are unsuitable reagents for the detection of traces of iodides, since a slight excess rapidly removes any blue color. The results of the present work, however, do indicate that the concentration of iodine cations in all but the most dilute solutions of hydrochloric acid is negligible.

If the positive iodine is wholly in the form of a complex anion, to which we may give the provisional formula ICl_2^-, the hydrolytic equilibrium can be represented by

$$5ICl_2^- + 3H_2O \rightleftharpoons 2I_2 + IO_3^- + 6H^+ + 10Cl^-$$

Since all the solutions were saturated with iodine the expression $[\text{Positive iodine}]/([IO_3^-]\ [H^+]^6)^{1/5}\ [Cl^-]^2$ should be approximately constant. In the table this expression is denoted by K_1. In calculating it the chloride ion concentration shown in the table must be diminished by twice the concentration of positive iodine and also by the concentration of ClI_2^-. K_1 is found to decrease with rising chloride ion concentration, indicating dissociation of the complex in the more dilute solutions. The specially high values of K_1 found for the solutions in which the total ionic concentration has been increased by the addition of potassium chloride are probably due to salt effect.

The hypothesis of complete dissociation of the iodine monochloride leads to greater variation, as can be seen from the values of K_2, which represents the expression $[\text{Positive iodine}]/([IO_3^-]\ [H^+]^6)^{1/5}$. As would be expected, K_2 increases with rising chloride ion concentration. Better agreement can be obtained for the expression $[\text{Positive iodine}]/([IO_3^-]\ [H^+]^6)^{1/5}\ [Cl^-] = K_3$, corresponding with the reaction:

$$5ICl + 3H_2O \rightleftharpoons IO_3^- + 6H^+ + 5Cl^-$$

There are however cogent objections to the view that these solutions contain undissociated molecules of iodine monochloride. Efforts to extract any iodine monochloride from them with inert solvents have been unsuccessful. Cremer and Duncan[3] tried carbon tetrachloride and the

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(2) Carter and Hoskins, *J. Chem. Soc.*, 580 (1929).

(3) Cremer and Duncan, *J. Chem. Soc.*, 2031 (1932).

present writer tried carbon tetrachloride, benzene and nitrobenzene. A solution of iodine monochloride in dilute hydrochloric acid was diluted with water and rapidly shaken with the inert solvent before hydrolysis had gone far. No iodine monochloride could be found in the solvent, and no difference in the oxidizing power of the aqueous layer on potassium iodide could be detected before and after extraction.

While the present results do not allow a final decision on the many factors which may influence equilibrium in this system, the most probable view is that the positive iodine is in the form of a complex anion ICl_2^-, and that at great dilution this ion suffers partial dissociation into I^+ and Cl^-. In concentrated hydrochloric acid the concentration of iodine cation must be negligible, and some other explanation must be sought for the solvent power of these solutions on iodine noted in a previous paper. As to the titration of iodine in concentrated hydrochloric acid with an iodate, calculation from the observed values of K_1 shows that a very small excess of iodate is sufficient to reduce the equilibrium concentration of iodine below the level at which it can be detected—*i. e.*, the end-point is very sharp. This is in agreement with experience. The high acid concentration used in the titration is not necessary to reduce hydrolysis but is needed to make the reaction a rapid one, as already noted by Swift.[4]

Summary

1. The equilibrium between iodine monochloride and water at 25° has been investigated quantitatively.

2. The results indicate that in chloride solutions iodine monochloride is present chiefly as a complex ion ICl_2^-, which at great dilutions suffers dissociation into I^+ and Cl^-. In concentrated hydrochloric acid this dissociation is negligible.

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[4] Swift, THIS JOURNAL, **52**, 894 (1930).

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[CONTRIBUTION FROM THE THERMOCHEMICAL LABORATORY, INORGANIC DEPARTMENT, UNIVERSITY OF LIVERPOOL]

Systematic Investigation of a Hitherto Undetected Source of Error in Chemical Measurements of High Precision which Depend upon the Use of Compressed Oxygen. I

BY L. J. P. KEFFLER

Introduction.—The accuracy of the results obtained with the calorimetric bomb for the heats of combustion of organic substances depends in a large measure upon the accuracy with which the water equivalent of the calorimetric system has been determined. The water equivalent, in turn, or at least its apparent value, depends upon the amount of combustible impurity contained in the oxygen used for the combustion. Hitherto it has been assumed that no error was introduced into the measurements as the result of such contamination of the oxygen, on the condition that the amount of impurity be slight and that the same oxygen be used for the determination of a heat of combustion as had been used previously for the determination of the water equivalent.[1]

It is now going to be shown that such a procedure is not safe, since the oxygen delivered from a newly refilled cylinder may vary quite appreciably in purity when the pressure in the cylinder decreases.

(1) **Data Obtained with Oxygen (G) from Unknown Origin.**—A first series of measurements of the water equivalent of the calorimeter was carried out with standard benzoic acid from the Bureau of Standards, using oxygen from a hundred-foot cylinder supplied by the British Oxygen Company; the source of the gas could not be ascertained. The results obtained with that oxygen (G) have been collected in Table I.

(2) **Data Obtained with Oxygen (K) Derived from Liquid Air.**—A request was made to the British Oxygen Company to deliver two hundred-foot cylinders of the purest oxygen from liquid air which they could possibly supply. Both of these cylinders (K and L) when tested with a view to finding whether they were really identical, gave the same value for the water equivalent when this was determined under similar conditions. This appears clearly from Table II which contains besides the results corresponding to the new cylinders, those obtained previously with oxygen E (preheated) and oxygen G (unheated).

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[1] Richards, THIS JOURNAL, **42**, 1604 (1920).