THE RATE OF OXIDATION OF HYDRIODIC ACID BY SULPHURIC ACID

Thesis

by

Willard H. Tracy

In partial fulfillment of the requirements
for the degree of Bachelor of Science
in Chemistry

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California

1924

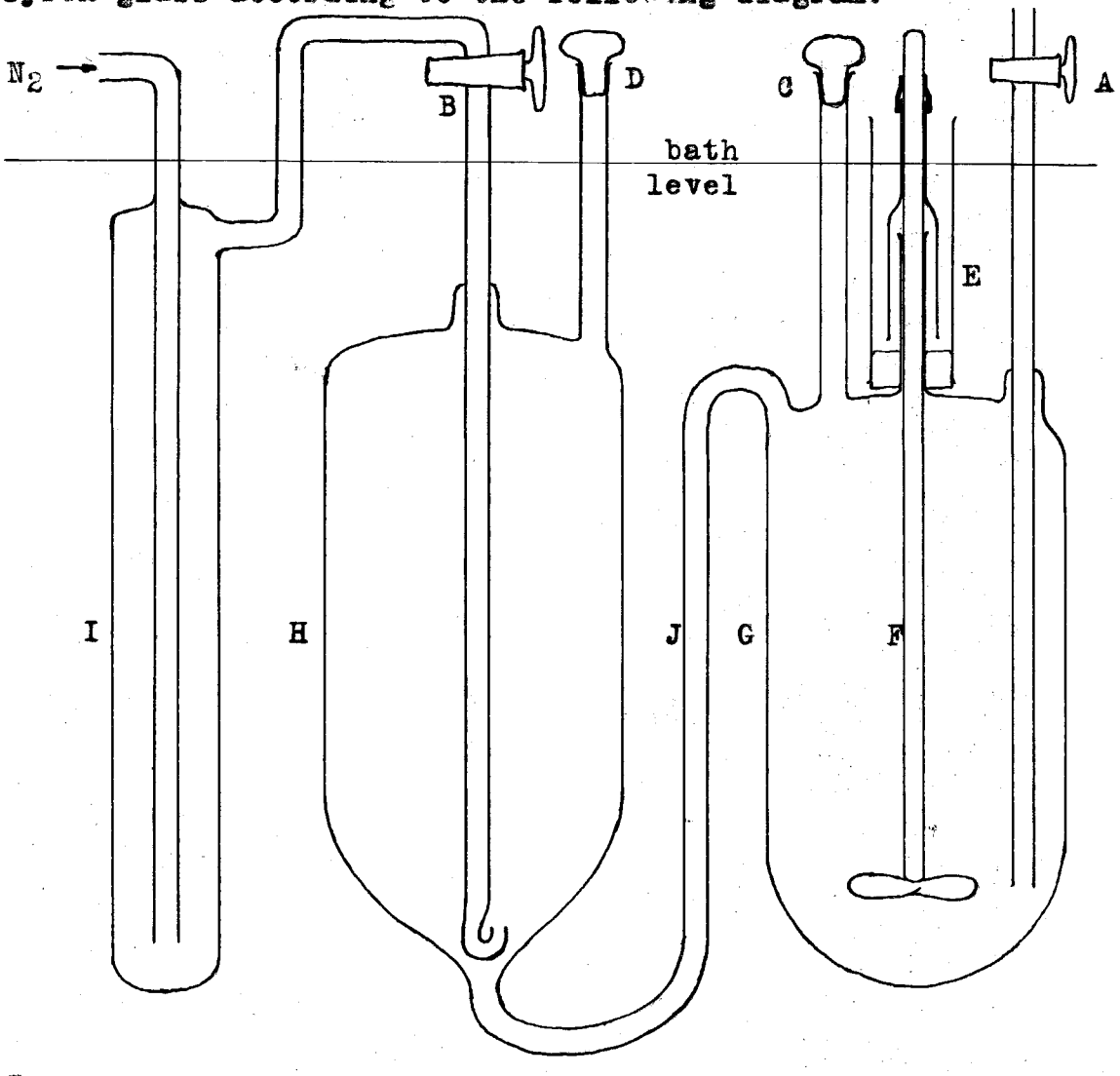
The Rate of Oxidation of Hydriodic Acid by Sulphuric Acid.

At the suggestion of Dr. D.F. Smith a determination of the rate at which hydriodic acid is oxidized by relatively concentrated solutions of sulphuric acid, with the formation of free iodine and sulfur, was attempted. The purpose of the investigation was to ascertain whether or not the rate of this oxidation was substantially proportional to the activity of the sulphuric acid in the solution, at a constant concentration of hydriodic acid, since the activities of sulphuric acid solutions of various concentrations at a temperature of 80°C. have recently been calculated by Smith and Mayer. (J. Am. Chem. Soc. 46, 79-80 (1924).) The course of the reaction was to be followed by titration of the liberated iodine. This investigation has had to be discontinued: the work already accomplished is reported in this paper.

Method and Apparatus

The work of Smith and Mayer above referred to had shown that the reaction occurred with measurable velocity in its initial stages at a temperature of 80°C. This temperature was accordingly fixed upon, and a water thermostat covered with a layer of "Transil Oil" to reduce evaporation was adjusted to maintain this temperature to within .02°, as indicated on a thermometer graduated in .1° and calibrated by the Bureau of Standards.

As hydriodic acid is rapidly oxidized by atmospheric oxygen at this temperature, an all-glass apparatus was designed which permitted of carrying out the reaction in an atmosphere of nitrogen. This apparatus was constructed of Pyrex glass according to the following diagram.



The apparatus was supported in the thermostat with the bath level at the point indicated. Nitrogen, previously passed through the glass bead saturator I filled with a solution of sulphuric acid prepared to approximate the

vapor pressure of the hydriodic acid solution used, was passed into the apparatus through the stopcocks A and B, and allowed to escape through tubes C and D and around E. After having swept out the air from the bulbs and connecting tubes, mercury was poured into the mercury seal E of the stirrer F. The stream of nitrogen was reduced in amount and the solutions were weighed into the bulbs G and H by means of weighing pipettes provided with long, narrow tips, capable of extending into the bulbs. The hydriodic acid pipette carried a glass stoppered side tube and a stopcock on the top tube. In filling it with hydriodic acid a stream of nitrogen was first passed through the bulb, after which acid was allowed to run into the pipette from the stock receptacle through the unstoppered side tube from which a current of nitrogen was permitted to escape, thus preventing the influx of air. The hydriodic acid was placed in G and the sulphuric acid in H. The stopcocks A and B were then closed and the ground glass stoppers at C and D inserted, after which the solutions were allowed to come to the temperature of the bath. The glass propeller stirrer F, connected directly to the shaft of a small motor by means of a short length of rubber tubing, was then started. The stopper C was removed, and, at an accurately noted time, a measured volume of nitrogen was admitted through B, thus forcing the contents of H over into G. The amount of solution remaining in H and J was determined by calibra-

tion of the apparatus with a constant amount, 500cc, of nitrogen passed through. This calibration was used rather than a determination of the residual solution in H after each experiment in order that the composition of the reaction mixture could be so adjusted as to maintain a constant concentration of hydriodic acid in all the experiments. Standard sulfuric acid was used for the calibration. After blowing over the charge, the tube J and bulb H were rinsed out with water and the rinsings titrated with standard alkali. The residual volume was found to be quite constant, values obtained being .40, .38, and .43 cc. At noted times after mixing the solutions, samples of about 5cc were withdrawn through C, with pipettes previously filled with nitrogen, and quickly discharged into 150cc flasks containing 100cc water, previously weighed. The flasks were reweighed and the solutions titrated for iodine at once, using starch as indicator.

Preparation of Materials

Sulphuric Acid: C. P. sulphuric acid of commerce was diluted to the requisite concentration and the solution boiled to expel air, after which it was kept in full bottles until it was used.

Hydriodic Acid: The so-called C. P. hydriodic acid of commerce available contained large quantities of reducing substances, as was demonstrated by adding a little iodine,

warming, and noting that the solution was decolorized. Distillation of this product did not remove the impurities. A supply of hydriodic acid was available which had been made from iodine by means of hydrogen sulfide. This material contained a large amount of free iodine. Repeated attempts to remove this, as by reduction with sulphur dioxide and precipitation of the sulphate formed with barium iodide, followed by distillation at a low pressure in an atmosphere of hydrogen or carbon dioxide, proved unavailing. At the time when the work was discontinued, an apparatus for the production of pure hydriodic acid by catalytic combination of hydrogen and iodine vapor over platinized asbestos, according to Bodenstein, (Z. physik. Chem. 13, 56(1894)) had been set up.

Nitrogen: A quantity of nitrogen was generated by slowly dropping a strong solution of sodium nitrite into a strong, hot solution of ammonium chloride, washing the gas with strong sodium hydroxide solution, and storing over water in a gasometer.

Standard Alkali: Crystallized C. P. barium hydroxide of commerce was used for the preparation of standard alkali solutions.

Standard Acid: Constant boiling hydrochloric acid prepared according to the method of Foulk and Hollingsworth, (J. Am. Chem. Soc. 45, 1220(1923)) was used for standardizing the alkali.

Standard Iodine Solution: On account of a shortage of potassium iodide, the standard iodine solution used was borrowed from Mr. H.M. Winegarden. It was later found to contain large quantities of iodate. A sample of potassium iodide was afterwards obtained which contained little iodate; this was then used, together with thrice sublimed iodine, for the standard iodine solution.

Standard Thiosulphate Solution: Imported sodium thiosulphate, "for analysis", was used.

Standard Arsenite Solution: This solution was prepared as recommended by Washburn, (J. Am. Chem. Soc. 30, 18(1908)) and diluted as required.

Preliminary Experiments

Some preliminary experiments were made to ascertain what concentrations of hydriodic acid and sulphuric acid would give measurable reaction velocities. The results obtained indicated that the range from 2 to 6 mols of sulphuric acid at 1 mol of hydriodic acid per kilogram of solution might be studied. It was afterward found that the hydriodic acid used for these experiments contained a large quantity of reducing substances. The results obtained are therefore certainly unreliable if not totally meaningless.

The Titration of Small Amounts of Iodine in the Presence of Concentrated Acid

A great deal of time was spent in attempting to discover a method of accurately determining small quantities of iodine in the presence of large amounts of strong acid. In the use of sodium arsenite as a reducing agent the hydrogen ion concentration must be very carefully controlled; this is also true to a less extent with sodium thiosulphate as the reducing agent. With sodium thiosulphate, in addition, the acid concentration must at no time exceed a rather small value if the formation of sulphurous acid is to be avoided. Some of the schemes tried will be mentioned.

In the first place, the addition of sodium bicarbonate to neutralize the acid seemed inadmissable on account of the probable loss of iodine vapor with the escaping carbon dioxide. In order to test this point, a stream of carbon dioxide was passed into a .01 N solution of iodine in 2% potassium iodide solution for several minutes. The iodine solution was then titrated with thiosulphate, when it was found to have lost some 7% of its strength. The use of sodium bicarbonate was therefore abandoned.

Direct neutralization with sodium hydroxide was tried, but extremely low values always resulted. Apparently the fairly high concentration of hydroxyl ion present locally even with good stirring resulted in the production of hypo-

iodite ion, even when the solution was only partially neutralized. The equilibrium constant of the reaction represented by the equation $I_2 + 2\ OH^- = IO^- + I^- + H_2O$ indicates that in solutions of greater pH than 9, only a negligible proportion of hypoiodite ion can exist at equilibrium. It would seem that the attainment of equilibrium must be slow, as the iodine value did not appear to return on standing, after partial neutralization with sodium hydroxide.

The addition of sodium monohydrogen phosphate as a neutralizing agent was attempted. In order, however, to attain the ratio of sodium monohydrogen phosphate to sodium dihydrogen phosphate necessary for proper control of the hydrogen ion concentration, a very large volume of solution, of the order of 1 liter, would be required, owing to the relatively small solubility of sodium monohydrogen phosphate. Beside this disadvantage, the end-point in such concentrated phosphate solution was very insensitive.

The following procedure was tried in an attempt to employ sodium arsenite as the reducing agent. The sample was weighed into water, after which an excess of standard sodium arsenite solution was added from a weight pipette. A drop of methyl red indicator was then added, and the solution titrated with a solution of ammonium hydroxide and ammonium chloride so prepared that the pH was not greater than 9, thus presumably avoiding the production of hypoiodite ion. In this titration the strong iodine color faded com-

pletely before the end-point for methyl red was reached, so that no trouble was experienced in observing this point. A phosphate buffer solution containing 2 mols of sodium monohydrogen phosphate per mol of sodium dihydrogen phosphate was then added to bring the solution to pH 7. After the addition of starch and potassium iodide, the excess of standard sodium arsenite was titrated with standard iodine solution. This complicated procedure also gave low results, presumably owing to the occurrence of the reaction represented by the equation $N_2H_3I_3 = N_2 + 3HI$. No base of suitable ionization constant except ammonium hydroxide could be discovered, so that this method had to be abandoned.

Extraction of the iodine from the strongly acid solution with carbontetrachloride and titration of the extract with thiosulphate was tried, with low results. Care was taken to prevent evaporation of iodine: perhaps the iodine reacted with some unknown impurity in the carbon tetrachloride.

The use of sodium thiosulphate in slightly acid solution (see W. C. Vosburgh, J. Am. Chem. Soc. 44, 2125(1922)) was at first tried, with erratic results, and given up. The poor results obtained were later found to be due to the presence of a large amount of iodate in the iodine solution with which the experiments were made. The method finally adopted, as the only feasible one, consisted in the simple

dilution of the acid solution to an acidity of .2 N and titration with thiosulphate, using color standards for determining the end-point. These standards were made up with cobalt nitrate, copper nitrate, and picric acid. The picric acid was found greatly superior to ferric chloride, sometimes recommended for this purpose. The accuracy obtained was of the order of 1% on 25cc of .01 N iodine solution.

Summary

1. An apparatus and method for determining the rate of oxidation of hydriodic acid by sulphuric acid are described.

2. Difficulties with the titration of small quantities of iodine in strongly acid solution are described. The only practicable method tried is the dilution of the acid solution to a concentration of .2 N in acid, and titration with thiosulphate, using color standards.