

Electrolytic Oxidation of Hydrochloric Acid to Perchloric Acid^{1,2}

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Perchloric acid is not easy to prepare, hence the price is high. The uses of this very unusual and important acid and its salts are greatly limited by this high cost. Electrolysis of hydrochloric acid, a comparatively cheap starting material, was found by early experimenters (1) (2) to produce some perchloric acid but no yields were published. Later more extensive experiments (3) reported the electrolytic formation of perchloric acid but again no yields were published. The most complete and successful experiments (5) reported the making of small commercial quantities of perchloric acid by electrolysis of hydrochloric acid. The operation of this process was very soon superseded by chemical methods which have since become quite important developments. The best conditions are a high current density .1 to .2 amp./sq. cm., a low temperature of 20° and a very dilute solution of hydrochloric acid. Only dilute solutions of perchloric acid could be obtained which required much expensive evaporation for making a final product of 50%.

The idea being tested in these experiments was that the optimum condition for producing ozone by electrolysis would be the best conditions for the oxidation of hydrochloric acid to perchloric acid. Previous experiments had not reached these conditions because very dilute hydrochloric acid solutions are not best for ozone making. Sulfuric acid of maximum conductivity is a good electrolyte for ozone production. Therefore small concentrations of hydrochloric acid in sulfuric acid were electrolyzed at high current densities and low temperatures with good material yields. Sulfuric acid was quite satisfactory for experiments since it did not interfere with any of the titrations for determination of chloride, chlorate, and perchlorate.

Of course pure perchloric acid could not economically be separated from these solutions containing so much sulfuric acid. However, industrially, low concentrations of hydrochloric acid in concentrated perchloric acid would give the ozone conditions. Each day a quantity of the acid equal to the amount of hydrochloric oxidized could be taken from the cell. No experiments were made with the electrolysis in strong perchloric acid due to the great difficulty in accurately determining the small quantities of perchloric acid produced by the oxidation in the presence of the large amounts of perchloric acid already present.

Apparatus and Method of Experimenting

Platinum wires wrapped around glass coils for cooling with running water, served as anodes and cathodes. Beakers of 400 cc. capacity standing in cold running water served as electrolyzing vessels. Temperatures

1. Condensed from a thesis for the A.M. Degree at Indiana University by Mr. Donald Ballman. He is now in the Sales Department of the Dow Chemical Company, Midland, Michigan.

2. Contribution No. 630 from the Department of Chemistry.

lower than 30° could not be attained without ice since these experiments were run during summer weather.

Methods of Analysis

Chloride was determined by a direct application of Volhard's method. Chlorate was determined by a titration with excess ferrous sulfate and a back titration with potassium permanganate. Finally a measured quantity of the electrolyte was neutralized with sodium hydroxide, evaporated to dryness, mixed with sodium carbonate and a trace of potassium permanganate and fused. This changed both chlorate and perchlorate into chloride. A Volhard determination on this residue gave total chloride. From these data perchloric acid was calculated.

A series of experiments showed that acid concentration of 1:5 was best.

Yields were highest at about .2 amp/sq. cm.

The percent conversion was highest at low concentrations of the hydrochloric acid whereby loss of free chlorine was minimized. The best yield in any experiment was 48% for .06 N. HCl.

In some long runs the data and results are:

Two beakers in series at 6 amp. with 6 inches of platinum wire each for both anode and cathode were run for 35 days, with tap water cooling (about 30°). Each day 2° ml. of 50% HCl were added to each. It would have been better if this acid could have been added continuously rather than in one daily batch. One beaker started with pure water, the other with 1:5 sulfuric acid. At the end, the experiment using sulfuric acid contained 96 grams of perchloric acid and the one with pure water contained 98.8 gms. It is thought that the lower final yield with water was due to a very low yield at the start until the concentration of perchloric acid built up sufficiently for ozone conditions. These results calculated out to a material yield of 12.4 percent based on the hydrochloric acid used. Loss of free chlorine was the cause of the low yields. The higher yields reported used much less conc. of hydrochloric acid and lower currents.

Yields were a little higher at 20° than at 30° but not enough better to warrant the trouble of operation at the lower temperature.

Conclusions

While perchloric acid can be made by electrolysis of hydrochloric acid at high currents the slowness of the process and the lower material yield when attempts were made to speed the action and the low current efficiencies indicate possibility of an economical way to prepare perchloric acid.

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