

Preparation of Iodic Acid by Ozonization

GEORG BIEDERMANN and
ROLAND LENDEÚS

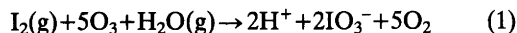
Department of Inorganic Chemistry, The Royal
Institute of Technology, S-100 44 Stockholm,
Sweden

Various redox equilibria of iodic acid (I(V)–I(III)–I(I)) are now being studied in this laboratory, and in connection with this work the need has arisen to use a pure specimen of this substance.

The preparation of iodic acid implies complications due to its high solubility in water which decreases but little as the temperature is lowered from 160 °C to the eutecticum.¹ It is hardly possible to obtain HIO₃ crystals with a practical yield from the very viscous saturated solutions. Hence the excess of the reagent used to oxidize iodine to iodic acid (fuming nitric acid, hydrogen peroxide, chloric acid and perchloric acid have been employed^{2,3}) must be driven off by heating and the crystallization must be carried out in the presence of another electrolyte (*e.g.* HNO₃). It also meets with difficulties to detect small amounts of these reagents in the final product.

Faced with these problems we have turned our interest to the observation that ozone can oxidize iodine in acidic solution to iodic acid. This fact was discovered by Engler and Wild about ninety years ago,⁴ and since then it was confirmed by many investigators.⁵ Iodic acid formation represents a serious source of error in the iodometric analysis of ozone and it must be avoided.

Within the frame of the present research project we have undertaken a systematic study to find the optimum conditions for iodic acid synthesis based on the reaction



The oxidation reaction is written in this way because mainly it takes place in the gas phase above the iodine solution. The first reaction product is I₂O₅ which forms an aerosol that dissolves only slowly in water.

At room temperature, where Engler and Wild⁴ worked, the ozonization proceeds only sluggishly but as the iodine solution is heated, it accelerates a great deal. However, the risk also increases that some of the iodine vapor escapes from the apparatus, and thereby the yield de-

clines. We have found 70 °C to be the best compromise.

The experiments were carried out in the simple apparatus illustrated in Fig. 1. Its main feature is the filter funnel provided with a sintered disc of porosity 3. The upper part of the funnel is filled, as indicated, with water. While the ozonization (1) proceeds, the condenser is filled with a heavy fog of iodine pentoxide which is mainly retained by the disc; the smallest particles which pass through are absorbed in the covering water layer. The washing flask is strictly unnecessary as it was found to contain only a few tenths of a percent of the total amount of the iodic acid produced.

In order to maintain a saturated solution and gas phase throughout the preparation, the iodine crystals must be kept finely dispersed. As iodine is very soft, it conglomerates easily and the reaction velocity of (1) decreases accordingly. This may be counteracted by stirring the solution with *two* reflon covered magnet bars.

In the final series of experiments we weighed in about one gram of iodine and added it to 100 ml of distilled water. Two iodine preparations were used. The first one was of exceptional purity, it was donated to us by Dr. Signar Sundstrand who prepared⁶ and tested the sample. The other one was a commercial product of pro analysis quality. The two preparations behaved identically in our experiments.

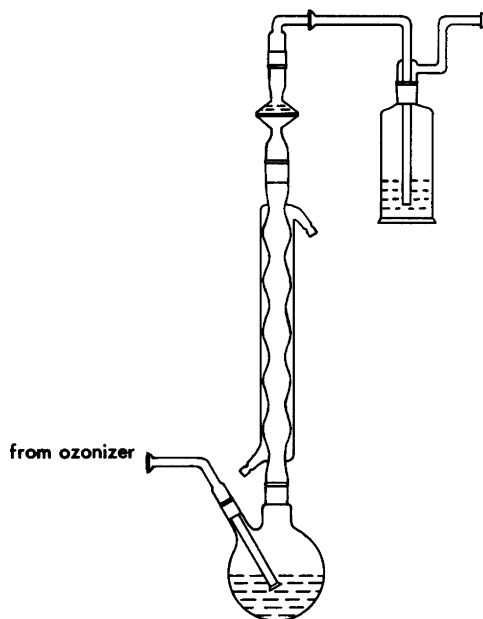


Fig. 1. Preparation of iodic acid.

Ozone was generated in the conventional way by electric discharge from commercial oxygen. This was prior to its introduction to the ozonizer dried with sulfuric acid and cooled to -78°C . By iodometric analysis⁷ the ozone content of our gas stream was found to lie within $5.0 \pm 0.1\%$. The streaming velocity was maintained close to 3 ml/s. At higher values the ozone stream carried along some iodine which decreased the yield.

In each experiment the ozonization was continued until the solution became colorless, and the iodine pentoxide fog in the condenser disappeared. Then the solution in the vessel and on the filter disc were united, the apparatus was washed with water which was added to the combined iodic acid fractions. Finally, the total volume was adjusted to an exact level in a volumetric flask. An aliquot was then taken, and its iodic acid content was determined by titration with a 0.05 M NaOH solution.

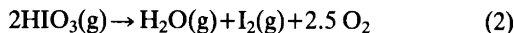
In the final series of experiments, comprising six syntheses, we have found that 2.5 h are required to get from one gram iodine a clear, colorless solution, and an average yield of $95 \pm 2\%$ is obtained in our apparatus. These conclusions are supported by many preliminary experiments. The losses are probably due to the escape of extremely fine iodine pentoxide particles which were sometimes visible at the outlet of the washing flask as a thin jet. In our apparatus (Fig. 1) of course only small amounts can be prepared, about 10 g/day corresponding to 60 mmol of iodic acid. However, the ozonization requires but little attention, and a continuous production is easy to maintain.

The resulting iodic acid solution was evaporated *in vacuo*. It is important at this stage to avoid the contamination by dust and organic vapors, which a pump inevitably generates by separating the solution with a sintered glass disc of fine porosity 4. The evaporation started at 40°C , and as the iodic acid solution became more concentrated, the temperature slowly was lowered to 20°C . Without this precaution decomposition occurred, and a yellow colored product formed. The last traces of water were removed by drying the residue, obtained by evaporation, with premelted KOH in an exhausted desiccator.

The X-ray powder photograph of the dried crystals was found to consist of sharp lines which could be ascribed to the reported spectrum of rhombic iodic acid.⁸

We have also tested whether any appreciable contamination occurred because of the frequent exposition of the stock solution and the crystals to the laboratory air. Our iodic acid crystals were therefore slowly heated in a stream of nitrogen to

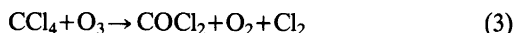
600°C where complete decomposition takes place:



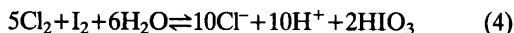
No weighable residue was found.

It was also important to see whether any appreciable amounts of foreign substances were introduced with the ozone. As this was generated from commercial oxygen, prepared from air, ozonization might give rise to the formation of nitric acid. In a special experiment ozone was led through water for many hours but no nitric acid was found. Test for sulfate was also negative and the pH remained unchanged.

We also tried to ozonize concentrated iodine solutions of carbon tetrachloride and of hexane. The experiments failed, however, because the resulting HIO_3 solutions contained large amount of Cl^- , presumably due to the reactions

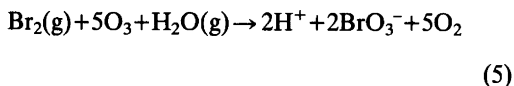


and



while ozonization of hexane gave rise to the formation of an organic acid of a penetrating smell.

Finally, we have also found that the ozonization of a mixture of bromine and water gas provides a dilute (about 10 mM) HBrO_3 solution:



However, the yield was only a few percent, as most of the bromine escaped during the ozonization. We are now experimenting with an improved synthesis apparatus and the results will be reported in another article.

Acknowledgements. This work is part of a research project financially supported by *Statens Naturvetenskapliga Forskningsråd* (Swedish Natural Science Research Council).

1. Groschuff, E. Z. *Anorg. Chem.* 47 (1905) 331; Linke, W. D. *Solubilities*, American Chemical Society, Washington D.C. 1958, Vol. 1, p. 1126.
2. Brauer, G., Ed., *Handbuch der Präparativen Anorganischen Chemie*, 3rd rev. Ed., F. Enke Verlag, Stuttgart 1975.

3. Hayes, J. M., Diehl, H. and Smith, F. G. *Talanta* 13 (1966) 1019.
4. Engler, C. and Wild, W. *Ber. Dtsch. Chem. Ges.* 29 (1895) 1929.
5. Biedermann, G. and Ferri, D. *Chem. Scr.* 2 (1972) 57.
6. Sundstrand, S. *Acta Chem. Scand. A* 37 (1983) 787.
7. Birdsall, C. M., Jenkins, A. C. and Spadinger, E. *Anal. Chem.* 24 (1952) 662.
8. Swanson, H. E., Gilfrich, N. T. and Ugrinic, G. M. *Natl. Bur. Stand. Circ.* 5 (1955) No. 539.

Received July 9, 1984.