[Contribution from the Chemistry Department of the University of Illinois]

The Explosive Reaction of Bismuth with Perchloric Acid

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In a study of the use of perchloric acid as a solvent for alloys, violent explosions were encountered in the cases of alloys containing bismuth. This explosive reaction of bismuth with perchloric acid has been previously reported by Fichter and Jenny,[1] who attributed it to chloric acid or chlorine dioxide. For reasons given below, such an explanation does not seem adequate.

When bismuth is heated with 70% perchloric acid at temperatures below 100°, the metal dissolves very slowly, and small amounts of chloride appear in the solution. In the neighborhood of 110°, a brownish coating forms on the metal, which, upon further heating, explodes violently, shattering the container and throwing the acid considerable distances. A convenient and less hazardous procedure for preparing the explosive material is to dip the metal in the acid by means of forceps and heat it over a Bunsen flame until fumes appear. These fumes consist mainly of perchloric acid, but contain small amounts of hydrogen chloride, and no bismuth salts. After explosion, the metal is bright again, though roughened, as by pitting. Usually fractures appear in the crystal, and frequently it is broken into smaller pieces. The violence of the explosion seems to increase with repetition, suggesting a surface effect. If a piece of bismuth that has been activated by heating in concentrated perchloric acid is allowed to remain in the acid, an explosion is always found to take place sooner or later, even in the cold. On the other hand, if the metal is exposed to the air for some time or dipped in water, the dark layer disappears and the explosive property is lost.

The fact that the explosion is characteristic of bismuth, and is not shown by other metals, suggested at first the formation of a metastable form of bismuth, analogous to the explosive antimony of Cohen.[2] This assumption is improbable for the following reasons. (1) It has not been possible to prepare an explosive form of bismuth by heating the metal with sulfuric acid, or phosphoric acid or other acid of high boiling point. (2) Explosive antimony is formed electrolytically at the cathode of a cell, while "explosive bismuth" forms at the anode when concentrated perchloric acid is electrolyzed on bismuth electrodes. (3) Antimony cannot be activated in an analogous way, by heating with perchloric acid. (4) The activity of bismuth is instantly destroyed by contact with water.

The explosive material is not bismuth perchlorate. This salt was prepared by evaporating bismuth oxide with an excess of perchloric acid, and was found to be perfectly stable at ordinary temperatures, and to decompose only slowly upon ignition. It was tried to catalyze the decomposition by mixing powdered metallic bismuth with the salt, using both the bright form and the black form prepared by the reduction of bismuth hydroxide with sodium stannite, but without success. Fusion of the mixture with contact agents, as boric acid and borax, was also without effect.

The above experiment also shows that the explosions are not due to the dehydration of the acid by bismuth perchlorate, forming the explosive anhydrous perchloric acid.

There is no evidence of the presence of chloric acid or chlorine dioxide. The activated material does not have the odor of these substances. When a piece of active bismuth is dipped in water, the solution gives no coloration with aniline sulfate, nor does it liberate iodine from potassium iodide solution. No explosion could be obtained from the perchloric acid after the removal of the bismuth, though chloric acid and chlorine dioxide appear to have an appreciable solubility in concentrated perchloric acid. An electrolytic cell was set up in which concentrated perchloric acid was kept flowing over a bismuth anode. The explosions obtained were always at the surface of the metal.

It is not likely that impurities in the bismuth (carbon, for example) are responsible for the effect. Metallic bismuth prepared by reducing bismuth compounds with inorganic reagents showed the same property.

Mixtures of perchloric acid and sodium bismuthate can be heated without explosion, indicating that the unstable substance is not a derivative of pentavalent bismuth.

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(1) Fichter and Jenny, *Helv. Chim. Acta*, **6**, 225 (1923).

(2) Cohen and Ringer, *Z. physik. Chem.*, **47**, 1 (1904).

All the evidence indicates that the explosiveness is inherent in the dark coating that forms on the metal. Attempts to analyze this coating were unsuccessful. No solvent was found that would remove the excess perchloric acid without reacting with the dark layer. When the activated surface was washed with water, the deposit was instantly hydrolyzed, giving an acid solution containing Bi^{+++}, ClO_4^- and Cl^- ions. Analyses of these solutions gave varying results, impossible of interpretation. For example, in one series of three analyses, the Bi^{+++}–Cl^- ratios (in gram atoms) of the hydrolyzed products were 1:0.104, 1:0.185 and 1:0.084. This variation is doubtless due to the loss of hydrochloric acid by volatilization during the activation process, while the Bi^{+++} was left behind as a perchlorate.

The over-all reaction, including the preliminary action, the formation of the dark coating, and its hydrolysis, was studied as follows. A piece of bismuth embedded in glass wool was placed in one arm of an inverted V-shaped tube, and a few cubic centimeters of concentrated perchloric acid were added to the other arm. The apparatus was then evacuated and sealed off. The acid was then run into the arm containing the bismuth and the apparatus heated until the dark coating appeared. The solution was then run back into the other arm, and the product exploded by a slight blow on the tube. After several failures, a series of several explosions was obtained without demolishing the tube. The white fumes formed condensed on the surface of the tube, and were subsequently found to contain bismuthyl chloride. The tube was opened, and the solution and deposit analyzed, giving a Bi^{+++}–Cl^- ratio very close to 8:3. This indicates that the gross reaction may be represented as

$$8Bi + 24HClO_4 \longrightarrow 7Bi(ClO_4)_3 + BiCl_3 + 12H_2O$$

This equation, however, gives no information about intermediate reactions.

There remains the possibility that the explosion is due to salts of monovalent or divalent bismuth. The strongest evidence against such an assumption is that there appears to be no metallic bismuth in the explosion products.

Summary

Various hypotheses are considered to account for the explosive reaction of bismuth with hot, concentrated perchloric acid. The explosiveness seems inherent in the dark layer formed on the bismuth during the heating. Owing to its instability, this product has not been separated, and no analysis has been possible.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Reaction between Nitrous Oxide and Hydrogen on Platinum

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The catalyzed reaction of hydrogen on nitrous oxide has recently been the subject of several investigations. The reaction affords a means of comparing the rates of reaction of hydrogen and deuterium,[2] and its behavior on different catalysts is interesting, particularly in view of the various relationships between the kinetics of the reaction and the adsorption of the two reacting gases.[3] At one extreme, hydrogen may be so strongly adsorbed by the catalyst that the rate of reaction is practically independent of the hydrogen pressure, and at the other extreme the primary process may be a decomposition of nitrous oxide on the catalyst so that the rate is largely independent of the nitrous oxide pressure, as is the case on a reduced silver surface.[3]

Between these two extremes have been found[4,5,6] cases in which the mechanism changes, depending upon which of the two gases is in excess. The reaction as reported here belongs to the first class and since it has been possible to establish the simple mechanism applying, it seems desirable to present the results.

The characteristics of the reaction on a platinum filament have been determined previously by static methods.[4,6] By using flowing gases we have been able to eliminate some of the un-

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[1] Sterling Fellow of Yale University, 1932–1933. Present address Calco Chemical Company, Bound Brook, New Jersey.

[2] H. W. Melville, *J. Chem. Soc.*, 797 (1934).

[3] For a review of the literature, see for example, Benton and Thacker, THIS JOURNAL, **56**, 1300 (1934).

[4] Hinshelwood, *Proc. Roy. Soc.* (London), **A106**, 292 (1924).

[5] Hutchison and Hinshelwood, *J. Chem. Soc.*, 1556 (1926).

[6] Cassel and Glückauf, *Z. physik. Chem.*, **B19**, 47 (1932).