# EXPLOSIVE REACTION OF PERCHLORIC ACID WITH METALLIC BISMUTH

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In studying the use of perchloric acid as a solvent for alloys, violent explosions were met in the cases of alloys containing bismuth. Muir[1] has reported that bismuth is soluble in dilute perchloric acid forming the insoluble bismuthyl perchlorate. Fichter and Jenny[2] worked with concentrated perchloric acid and obtained soluble bismuth perchlorate. They state that the reaction is often accompanied by explosions due to chloric acid and chlorine dioxide formed by the reduction of the perchloric acid.

There is no apparent reaction of bismuth with 70 per cent perchloric acid at room temperature. Upon heating to 105-110° centigrade the metal becomes coated with a brown-to-black layer which explodes upon either continued heating or a sudden shock such as dropping, with terrific violence shattering the vessel and throwing the hot acid for surprising distances. After such a decomposition the metal again takes the bright appearance as before. The same procedure may be repeated indefinitely as long as the crystal of metal remains of suitable size. The fact that after explosions the metal is badly shattered, suggests that the acid had penetrated the cleavage planes of the crystal prior to the explosion.

The violence of the reaction is reduced by alloying the metal with other metals. High temperature or sudden shock favor the decomposition, while on the other hand the activated metal loses its dark color and activity if allowed to remain in air for some time. A convenient and less hazardous method of preparing the explosive metal is to dip a fragment in the acid by means of tongs, and carefully heat above a Bunsen flame.

The unstable nature of the material made a chemical analysis impossible. Analysis of the products formed by the decomposition showed them to consist largely of bismuthyl chloride. The ratio of chloride to bismuth ions present in this residue was approximately three to eight. This indicated that there was direct solution of the metal, in all probability to the normal perchlorate, as well as the formation of the metastable material. The presence of the bismuthyl chloride was verified by X-ray analysis.

Proof has been established to show that this unstable material is not an amphoteric form of bismuth, it is not due to impurities in the metal, and it is not due to formation of anhydrous bismuth perchlorate. Electrolysis of a solution of this perchloric acid using bismuth electrodes resulted in an explosion at the anode, while the cathode was coated with a fine very stable layer of bismuth. Thus it must be an oxidation product of bismuth in some metastable condition. One possibility would be pentavalent bismuth, although sodium bismuthate is stable when mixed with 70 per cent perchloric acid.

Plunging the darkened metal into water results in the solution of the dark colored material with no further reaction. Aqueous solutions of perchlorates are without reaction with the metal. Dilute perchloric acid likewise gives no explosive material. Plunging a blackened piece of the metal into potassium iodide solution liberated no free iodine.

The explosions are not due to reduction products of perchloric acid as tests for chloric acid with aniline sulfate were negative.

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[1] Chem. News. *33*, 15 (1876).
[2] Hel. Chim. Act. *6*, 225 (1923).