

BiH_3 is about 5.6 volts (calcd.). Similarly, the ionization potential of H_2O is 13.2 volts,² while that of H_2Te is 8.7 volts (calcd.). A similar trend is found with the hydrides of the seventh group. In other words, as one passes down in each group of the hydrides, from the lightest to the heaviest central element, there is a regular decrease in the ionization potentials, which means an increase of looseness of the reactive unshared electrons. With an increase of looseness of these electrons there is a relative increase in the tendency toward auto-oxidation.

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The Reduction of Aliphatic Cyanides and Oximes with Sodium and *n*-Butyl Alcohol

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The usefulness of *n*-butyl alcohol in the sodium reduction of a number of aliphatic cyanides and oximes has been investigated. In a considerable number of preliminary experiments upon the reduction of *n*-butyl cyanide it was found that: (1) better results were obtained by adding the sodium to the boiling solution of the cyanide than by adding the cyanide solution to the sodium; (2) if the temperature of the reaction mixture were kept below the boiling point mechanical stirring increased the yield of amine, but it was of no advantage to stir the refluxing solution; (3) the use of more than 7 atoms of sodium per mole of cyanide did not appreciably increase the yield of amine; and (4) all of the sodium dissolves within a convenient time if slightly more than 3 moles of *n*-butyl alcohol is used per atom of sodium. It is probable that (3) would not be true for all reductions of this type.

The yields of amines from a series of methyl alkyl ketoximes varied from 69 to 86% of the theoretical amounts. Heptaldoxime gave 69% of the amine. *n*-Butyl and *n*-amyl cyanide gave 86 and 78%, respectively, of the corresponding amines.

Procedure.—A solution of 1 mole of cyanide or oxime in 2300 cc. of *n*-butyl alcohol in a 5-liter two-necked flask fitted with a 2.5×100 cm. Pyrex condenser was heated to boiling and 161 g.

(1) Eastman Kodak Company Fellow, 1931-1932.

(7 moles) of sodium added in 10-20 g. pieces at short intervals through the large neck of the flask. This required from ten to fifteen minutes. After the reaction had moderated the mixture was refluxed until practically all of the sodium had dissolved. The reaction mixture was allowed to cool, 1.5 liters of water added and the mixture distilled to remove the amine and alcohol. More water was added as necessary. The distillate was made slightly acid with hydrochloric acid and distilled to a volume of 300 cc., 500 cc. of water added and distillation continued until no more alcohol came over. The water solution of amine hydrochloride was saturated with sodium hydroxide, the upper oily layer of amine separated and further dried over sodium hydroxide and then over sodium. The amine was now distilled from sodium in a 250-cc. special Claisen flask. If the amine is properly dried there is very little forerun and no high boiling residue.

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Inhibition of Oxidation of Phenylhydrazine

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In the course of a quantitative study of the osazone reaction, in which quantities of glucose of the order of magnitude of 10 mg. were used, it was necessary to find means of preventing tar formation. This end was attained by carrying out the reaction in sealed tubes from which all air had been evacuated.

It was later discovered that the presence of sodium bisulfite in the reaction mixture entirely prevented tar formation, even though air were present. A tube containing 1 mg. of glucose, 1 cc. of 50% acetic acid saturated with sodium acetate, 0.1 cc. of phenylhydrazine, 1 cc. of 50% NaHSO_3 , and 8 cc. of water was heated for one hour in boiling water and cooled. The crystals separating were left in contact with the mother liquor for several months, the tube being stoppered to prevent evaporation. No discoloration of either crystals or mother liquor resulted, although a tarry precipitate quickly developed in a similarly prepared tube lacking the bisulfite.

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