tions of 100 cc. of chloroform. The chloroform extracts were combined, washed with dilute ice cold 3% sodium bicarbonate and then with ice water, the chloroform layer separated and dried over calcium chloride. Upon evaporation at gentle heat aided by an air current, a finely divided crystalline deposit was obtained. Filtered and washed with ether the yield was 18.0 g. (54%). The mother liquors yielded further material on concentration, the average yield being about 70%.

The compound could be recrystallized readily and practically quantitatively from 15 parts of boiling 95% alcohol; 6.3 g. recrystallized from 90 cc. of 95% alcohol gave a yield of 5.8 g. of material whose $[\alpha]^{20}_{D}$ value was $-88.3°$ (0.2109 g. in 25 cc. $CHCl_3$ rotated 1.49° to the left). A further single recrystallization gave $-88.4°$ (0.1485 g. in 25 cc. $CHCl_3$ rotated 1.05° to the left). It can also be recrystallized without decomposition from water at 80–90°, being soluble to the extent of about 0.4 g. in 100 cc.

The compound crystallizes in colorless brilliant needles 2 to 3 mm. long and melts at 201° (corr.) to a clear colorless oil.

An analysis for acetyl groups by the method of Kunz and Hudson showed the presence of four acetyl groups, 0.2378 g. substance consumed 20.30 cc. of 0.1 *N* sodium hydroxide; calcd. 20.14 cc.

Anal. Calcd. for $C_{20}H_{23}O_{13}$: C, 50.94; H, 4.92. Found: C, 50.83; H, 5.29.

5-β-*d*-Glucosidokojic Acid (2-Hydroxymethyl-5-β-*d*-glucosido-1,4-pyrone).—Attempts to deacetylate the tetraacetyl compound by ammonia in methyl alcohol solution were not successful. Incomplete deacetylation resulted even after allowing the deacetylation mixture to remain overnight, followed by gentle refluxing and resaturation of the resultant solution with ammonia and subsequent standing. However, sodium methylate brought about the desired result very smoothly.

Nine grams of the tetraacetylglucosidokojic acid was dissolved by warming in 300 cc. of chloroform and cooled to 10°. A solution of 75 cc. of 0.9 *N* sodium methylate and 25 cc. of anhydrous methyl alcohol was added and the mixed solutions allowed to stand in the ice-bath for one-half hour. A white gelatinous precipitate came down. The suspension was treated with the exact amount of dilute sulfuric acid to neutralize the original amount of sodium methylate and concentrated *in vacuo* at 60° to dryness. The dry residue was extracted with 75 cc. of 95% alcohol and the extract concentrated *in vacuo*. Colorless needles separated as the solution concentrated and the resulting yield of crude material was 2.8 g. The substance was recrystallized from 5 parts of 95% alcohol. The recrystallized glucoside gave $[\alpha]^{20}_{D}$ $-107.2°$ in water (0.1797 g. in 25 cc. H_2O rotated 1.54° to the left) and a further recrystallization gave $-107.4°$ (0.1470 g. in 25 cc. H_2O rotated 1.26° to the left); therefore the value $-107.3°$ is accepted as the true rotation. The compound melts at 197–198° (corr.) to a clear colorless oil.

Anal. Calcd. for $C_{12}H_{16}O_9$: C, 47.35; H, 5.30. Found: C, 47.42; H, 5.66.

The writer wishes to express appreciation for the assistance of Dr. F. H. Goldman in the analyses.

Summary

Kojic acid (2-hydroxymethyl-5-hydroxy-1,4-pyrone) has been condensed with acetobromoglucose to form 5-β-tetraacetyl-*d*-glucosidokojic acid. By deacetylation of this acetate with sodium methylate crystalline 5-β-*d*-glucosidokojic acid has been isolated and characterized.

WASHINGTON, D. C. RECEIVED DECEMBER 1, 1933

NOTES

Auto-Oxidation and Ionization Potentials of Molecules

BY NICHOLAS A. MILAS

Some years ago[1] the writer showed that the tendency to auto-oxidize of the hydrides, alkyl and aryl derivatives of the elements of the fifth group of the periodic table increases as the "effective nuclear charge" of these elements increases. This seems to be true also with similar derivatives of the elements of the sixth and seventh groups. Diethyl telluride, for example, is far more easily oxidized than diethyl ether. Similarly, ethyl iodide is more easily oxidized than ethyl chloride. If the auto-oxidation of these substances proceeds through a preliminary addition of molecular oxygen to the reactive unshared electrons present in each molecule, then there ought to exist a relationship between the tendency of these substances to auto-oxidize and the ionization potentials of the reactive electrons.

If one makes a simple calculation of the ionization potentials of the hydrides of these elements, on the assumption that the ratio of the first ionization potentials of any two elements in each group varies directly as the ionization potentials of their hydrides, one would find that the ionization potentials of the different hydrides are inversely proportional to their tendency toward auto-oxidation. The ionization potential of NH_3, for example, is 11.2 volts[2] while that of

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[1] Milas, *J. Phys. Chem.*, **33**, 1204 (1929).

[2] Mackay, *Phys. Rev.*, **24**, 319 (1924); "Handbuch der Physik," **23**, Part I, 142 (1933).

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

BY C. M. SUTER AND EUGENE W. MOFFETT[1]

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. (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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[1] Eastman Kodak Company Fellow, 1931–1932.

Inhibition of Oxidation of Phenylhydrazine

BY R. H. HAMILTON, JR.

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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