tion of a methanol solution of oxalic acid and can be recovered unchanged under the above conditions.

Aldehydo-Cellobiose Oxime Octaacetate.—Cellobiose oxime (3 g.)[10] was acetylated with pyridine (24 cc.) and acetic anhydride (12 cc.) by stirring at 0° for two hours, followed by forty hours of standing at ice box temperature. The sirup ($(\alpha)\mathrm{D}$ +36°, $CHCl_3$) that was precipitated by pouring into ice and water was combined (total, 4.6 g.) with the sirupy material ($(\alpha)\mathrm{D}$ +35°, $CHCl_3$) obtained by chloroform extraction of the mother liquor and precipitated several times from benzene by means of heptane; $(\alpha)\mathrm{D}$ +37°, $CHCl_3$. The material resisted crystallization but produced crystalline cellobionic acid nitrile octaacetate when heated in the solid state to incipient decomposition.

The acetylated product obtained from 12 g. of cellobiose oxime as described above, was refluxed for thirty minutes with a solution of 13 g. of oxalic acid dihydrate in 160 cc. of methanol. The material obtained after solvent removal was dissolved in water, extracted with chloroform, the extract washed with an aqueous solution of sodium bicarbonate, dried, and the solvent removed. The residue was obtained crystalline from ether; yield 10.4 g.; m. p. 150–151°. Pure material was obtained by dissolving in chloroform and adding ether; m. p. 154–155°; $(\alpha)^{28}\mathrm{D}$ +30° (*c*, 3; $CHCl_3$).

Anal. Calcd. for $C_{12}H_{15}O_3N(OCOCH_3)_8$: total acetyl, 11.5 cc. of 0.1 *N* NaOH per 100 mg.; O-acetyl, 11.5 cc. Found: total acetyl, 11.6 cc.; O-acetyl, 11.6 cc.

De-oximation of *Aldehydo*-Cellobiose Oxime Octaacetate.—*Aldehydo*-cellobiose oxime octaacetate (2 g.) was dissolved in 60 cc. of glacial acetic acid and a solution of 20 g. of sodium nitrite in 60 cc. of water was dropped in during one hour with slow stirring. The stirring was continued for an additional hour with the rate greatly increased during the last ten minutes. The reaction mixture was poured into ice and water, extracted with chloroform, the extract washed with an aqueous solution of sodium bicarbonate, dried, and the solvent removed under reduced pressure. The product so obtained was purified three times by precipitation from methanol by the addition of water; $(\alpha)\mathrm{D}$ +17.1° (*c*, 3.6; alcohol-free $CHCl_3$). This procedure was repeated four more times; $(\alpha)\mathrm{D}$ +17.7° (*c*, 3.4; $CHCl_3$). The substance was obtained as a snow-white, amorphous solid that resisted crystallization but was nitrogen-free. It reduced Fehling's solution and reacted with hydroxylamine to produce the original crystalline *aldehydo*-cellobiose oxime octaacetate.

Anal. Calcd. for $C_{12}H_{14}O_{11}(COCH_3)_8$: acetyl, 11.8 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 12.1 cc.

Summary

1. Maltose semicarbazone has been synthesized. This compound on acetylation yields a crystalline octaacetate of ring structure.

2. Mild acetylation of cellobiose semicarbazone produces crystalline cellobiose semicarbazone heptaacetate. Evidence is presented to show that it is the ring form. More vigorous acetylation yields the crystalline octaacetate which also has the ring form.

3. A crystalline cellobiose oxime nonaacetate has been synthesized and evidence is presented to show that it has a ring structure.

4. *Aldehydo*-Cellobiose oxime octaacetate has been synthesized in crystalline form from cellobiose oxime. Evidence is presented to show that it has the true oxime structure.

5. Cellobiose oxime octaacetate has been de-oximated to give an amorphous *aldehydo*-cellobiose octaacetate which re-forms the original oxime on treatment with hydroxylamine.

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[10] P. A. Levene and M. L. Wolfrom, *J. Biol. Chem.*, **77**, 677 (1928).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Pyridinium Vanadate

BY S. KATZOFF AND R. ROSEMAN

In the course of some work on vanadium, crystals were obtained which we have identified as a new compound, of formula $(C_5H_6N)_3V_5O_{14}\cdot H_2O$.

Preparation

1. The compound can be prepared by double decomposition between ammonium metavanadate and pyridine hydrochloride. A 7% water solution of the metavanadate is prepared by saturating at the boiling point (filtering, if necessary), and to the cooled solution is added one-fifth of its volume of a cool 2:1 mixture of pyridine and concentrated hydrochloric acid. Addition of an equal volume of alcohol, and cooling, result in nearly complete precipitation of the crystalline compound.[1] The precipitate is collected on a Büchner funnel and washed with a pyridine–water mixture (1:1), 95% alcohol and, finally, ether.

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[1] The cool solution sometimes remains supersaturated for remarkably long times, but crystallization is readily initiated by the usual methods.

2. The compound can also be prepared directly from vanadium pentoxide and pyridine, with the aid of hydrogen peroxide. To 1 part by weight of vanadium pentoxide powder (prepared by gently warming ammonium metavanadate) is added 3 parts of pyridine, 1 part of water, and then 2 parts of 30% hydrogen peroxide in small portions, not allowing the temperature of the mixture to rise above 50° at any time. Crystals of the compound soon appear,[1] and the conversion is essentially complete after several hours. The function of the hydrogen peroxide is, presumably, to help dissolve the vanadium pentoxide, giving a solution containing pervanadate ions which, either by subsequent decomposition of the peroxide group or simply by maintaining equilibrium with the vanadate ions, leads to the desired compound.

3. The compound is purified by recrystallization, which is easily carried out since there is a large variation of the solubility in water with temperature. The procedure is to dissolve the material in 3 times its weight of hot water (80°) containing a little pyridine, filter through a quantitative paper, and cool.[1] Rapid performance of the operations is desirable, since hydrolysis occurs at the high temperature, with precipitation of vanadic acid. The crystalline product is collected, washed, and dried on a Büchner funnel, as previously described.

Analysis

The compound was analyzed for vanadium and pyridine.

1. Vanadium was determined by direct ignition of a sample (in a platinum crucible) to vanadium pentoxide. Treatment of the residue with a little nitric acid and reignition did not, in general, result in a change in weight.

2. Pyridine was determined by the following method. A sample (0.5 to 1 g.) is dissolved in 25 cc. of water in a 50-cc. Kjeldahl flask, and 3 cc. of 6 *N* sodium hydroxide is added. The solution is then distilled, using a trap, into a slight excess of standard hydrochloric acid (0.25 *N*), the distillation being carried nearly to dryness. The excess hydrochloric acid is titrated with standard sodium hydroxide (0.25 *N*), using methyl orange or brom phenol blue as indicator.[2]

Following the methods outlined above, the ratio of pyridine to vanadium in the compound was found to be 3:5. For the water content, we depend on an accurate determination of the vanadium. Determinations of the V_2O_5 content of our best products gave values between 61.55 and 61.75%. This corresponds satisfactorily to the compound of simple formula $(C_5H_6N)_3V_5O_{14}\cdot H_2O$, the theoretical V_2O_5 content of which is 61.71%.

Properties

The compound has an orange color, which appears of a lighter or a darker shade according as the crystals are small or large. The density is 2.04, as determined with a pycnometer, using pyridine as the immersion liquid. The crystals are monoclinic, generally appearing as parallelepipeds, sometimes with truncated edges or corners. Pyridine, ether, alcohol, benzene, and acetone do not dissolve the compound appreciably. Water dissolves it, giving an orange solution which reacts acid to litmus. Molten phenol was also found to dissolve it.

When exposed to the atmosphere, the compound slowly loses its volatile constituents. For example, a sample kept on a watch glass in the laboratory for one month lost 5% of its weight. Analysis showed that the percentage of vanadium pentoxide had correspondingly risen, proving that no vanadium had been lost. On the other hand, a sample kept in a glass-stoppered container did not change its composition over a period of two weeks.

Some excellent crystals, of a deep orange color, and perfectly transparent, were prepared by using the previously described recrystallization technique without, however, rapid cooling of the filtrate. The crystallography is being studied by Dr. J. D. H. Donnay, of this University, in collaboration with Dr. J. Mélon, of the University of Liége.

We are greatly indebted to Mr. Jerome Strauss, Vice President of the Vanadium Corporation of America, for the generosity with which he supplied us with pure vanadium compounds for our work.

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(2) Care must be taken to choose the end-point color according to the concentration of pyridine hydrochloride in the solution. The *p*H corresponding to this concentration is calculated, and the end-point color is obtained from a previously prepared set of color standards made up in potassium acid phthalate–hydrochloric acid buffers [Clark and Lubs, *J. Biol. Chem.*, **25**, 479 (1916)].

Our method of analysis was checked by showing, first, that the titration method for pyridine gives accurate results over a wide range of concentrations, and, second, that essentially all of the pyridine is recovered in the distillation. The accuracy of the method is about 1%.