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Abstract

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On the Preparation of Acetone Cyanohydrin (α-Hydroxyisobutyronitrile) from Acetone and Sodium Cyanide*

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It is known that acetone cyanohydrin can be obtained from acetone and cyanide salts of alkali metals in two ways: by the action of a mineral acid on a mixture of acetone and a solution of an alkali-metal cyanide salt ([1]), or by the action of a previously obtained bisulfite derivative of acetone on a solution of an alkali-metal cyanide salt ([2]).

On the other hand, Raschig established ([3]) that acetone absorbs an equimolecular amount of sulfur dioxide and forms the molecular compound $CH_3 \cdot CO \cdot CH_3 \cdot SO_2$ with $d^8 = 1.08$, which on prolonged contact with water is converted into propane-2-sulfonic-2 acid, and on interaction with alkali solutions is readily converted into the bisulfite derivative.

In view of the facts stated above, and also of the circumstance that sulfurous acid is a stronger acid than hydrocyanic acid, as a result of which H_2SO_3 can displace HCN from its salts, the possibility was studied of obtaining acetone cyanohydrin by the interaction of $CH_3 \cdot CO \cdot CH_3 \cdot SO_2$ with acetone and NaCN in the presence of water, according to the following equations:

$$CH_3 \cdot CO \cdot CH_3 \cdot SO_2 + NaCN + H_2O \longrightarrow CH_3 - \underset{SO_3Na}{\overset{OH}{C}} - CH_3 + HCN, \quad (1)$$

$$\begin{aligned} &CH_3 - \underset{SO_3Na}{\overset{OH}{C}} - CH_3 \xrightarrow[-Na_2SO_3]{+NaCN} CH_3 - \underset{CN}{\overset{OH}{C}} - CH_3 \\ &HCN \xrightarrow[(NaCN)]{+CH_3 \cdot CO \cdot CH_3} CH_3 - \underset{CN}{\overset{OH}{C}} - CH_3 \end{aligned} \quad (2)$$

It was established by a large number of experiments that these reactions proceed smoothly and practically to completion if they are carried out at a temperature below 25°.

If this condition is observed, it is necessary to work not in the presence of 1 gram-mole of water, as is evident from equation (1), but in the presence

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8 gram-moles of water per 1 gram-mole of $CH_3 \cdot CO \cdot CH_3 \cdot SO_2$, since the secondary product formed (1 gram-mole of Na_2SO_3) adds 7 gram-moles of water in the form of a crystalline hydrate.

It was also established that, when the indicated amount of water is used, most of the NaCN introduced into the process passes into solution, while the cyanohydrin is obtained practically as a product containing no water. When a 20–30% excess of acetone is introduced into the process, an increase in yield to more than 95% of the theoretical yield with respect to NaCN is observed.

The excess acetone can easily be regenerated by distillation of the product obtained.

Extraction of the acetone cyanohydrin retained by the precipitate of $Na_2SO_3 \cdot 7H_2O$ is most expediently carried out with acetone.

Unreacted acetone, as well as acetone used for washing, may be used to replace part, or even all, of the amount of acetone in subsequent experiments.

The acetone cyanohydrin obtained, purified from unreacted acetone, has an average concentration of about 95% and can be used in this state as the starting material for some synthesis. For example, methyl methacrylate was successfully synthesized from it.

The proposed method has the following principal advantages in comparison with other methods described in the literature for obtaining acetone cyanohydrin from acetone and NaCN:

1. Whereas, to obtain 1 gram-mole of acetone cyanohydrin by these methods, no less than 1 gram-mole of mineral acid, or correspondingly $NaHSO_3$, is required, in the new method the consumption of SO_2 amounts on average to 1/2 gram-mole.
2. The reaction product is obtained anhydrous and does not require additional drying, as is done when the product is obtained in an aqueous medium by other methods.
3. Owing to the absence, at the end of the process, of an aqueous layer with acetone cyanohydrin dissolved in it, the need to use organic solvents for its extraction is also eliminated.
4. The yield of acetone cyanohydrin by the new method is considerably higher than by other methods, which require the work to be carried out in an aqueous medium.

Experimental Part

1. Saturation of acetone with sulfurous gas. Into a conical Erlenmeyer flask fitted with a rubber stopper with two tubes, a definite amount of acetone is poured and saturated, with cooling, with SO_2 from a cylinder. The gas outlet tube is connected by means of a rubber tube with the outside atmosphere to remove sulfurous gas which, toward the end of the process, can no longer be absorbed by the acetone. Saturation is continued until weighing establishes that the acetone has absorbed an equimolecular amount of SO_2.

2. Preparation of acetone cyanohydrin. Into a three-necked flask of 1 l capacity, fitted with a mercury seal, mechanical stirrer, dropping funnel, and thermometer, 155 g of 95% NaCN are charged, and 210 g of water and 150 g of 95% acetone are added. The latter may be partially or completely replaced by regenerated acetone from preceding experiments.

The flask containing the reaction mixture is cooled below 25° with tap water. The stirrer is then switched on, and after 15 min, 180 g of $CH_3 \cdot CO \cdot CH_3 \cdot SO_2$ are begun to be added dropwise from the funnel. This amount of $CH_3 \cdot CO \cdot CH_3 \cdot SO_2$ is added over $1\frac{1}{2}$ hours, while not allowing the temperature of the reaction mixture to rise above 25°.

When the first portions of $CH_3 \cdot CO \cdot CH_3 \cdot SO_2$ are added, a white precipitate of $Na_2SO_3 \cdot 7H_2O$ begins to separate. Subsequently, the soluble part of the reaction product acquires the consistency of an oil and takes on a yellow color, which gradually changes to orange.

After the addition of $CH_3 \cdot CO \cdot CH_3 \cdot SO_2$ is complete, the reaction mixture is stirred for 1 hour, until the reaction mixture becomes alkaline (pH 8–9 according to universal indicator). The mixture is then filtered through a Büchner funnel.

Regardless of whether unused acetone or wash acetone regenerated from preceding experiments is taken for the experiment, 300–360 g of filtrate is obtained, containing 70–73% acetone cyanohydrin, which amounts to 80–84% of the theoretical yield based on NaCN.

When the precipitate of $Na_2SO_3 \cdot 7H_2O$ is washed with pure acetone, an additional 100–130 g of filtrate is obtained, containing 40–35% acetone cyanohydrin, which amounts to 18–10% of the theoretical yield based on NaCN. It is evident that the total yield is almost quantitative.

Subsequently, the main filtrate, to which the wash acetone may also be added, is acidified with concentrated sulfuric acid to pH 2 and distilled at 60–70° and 70 mm Hg to remove unreacted acetone.

Under these conditions, acetone cyanohydrin with a concentration of 94–96% is obtained, as well as acetone containing 2–3% hydrogen cyanide. The average loss of acetone cyanohydrin during distillation of the unreacted acetone is about 2–3%.

In the present work the concentration of acetone cyanohydrin was determined in all cases by Liebig' s method: 0.5 g of product was dissolved in 25 ml of 10% KOH and titrated with 0.1 N $AgNO_3$ solution.

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Note: Figure translations are in progress. See original paper for figures.