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Education

SYNTHESIS AND QUALITATIVE REACTIONS OF ACRYLIC ALDEHYDE (ACROLEIN)

(ORGANIC CHEMISTRY LABORATORY AND DEMONSTRATION EXPERIMENT)

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Unsaturated primary alcohols are easily oxidized to their corresponding aldehydes. Acrolein, on the other hand, is usually generated from glycerol by elimination of water. Both $KHSO_4$ or H_2SO_4 can be used for this 'dehydration'. A simple and effective demonstration experiment is described, showing the properties of both vinyl and aldehyde groups.

Key words: acrylic aldehyde; acrolein; propenal; aldehydes; unsaturated compounds; glycerol; chemistry experiments

INTRODUCTION

Aldehydes are usually considered as first oxidation products of primary alcohols [1–5]. Indeed, the oxidation is fairly easily performed, and a number of chemical demonstrations have already been offered. If a mixture of air and methanol (or ethanol) vapor passes over a hot catalyst (platinum [6] or copper [7] have successfully been used for that matter), the corresponding aldehyde is easily obtained. Jones reagent can also be used [8] although it is claimed that it is a too strong oxidizer, and the oxidation may proceed to the corresponding carboxylic acid [9]. Other demonstrations are also known [10–12].

To the best of our knowledge, no demonstrations have been offered to cover the properties of unsaturated aldehydes, the simplest representative of which is acrylic aldehyde (acrolein, propenal). All textbooks used [1–5] consistently recommend that acrolein be synthesized by elimination of water from glycerol with $KHSO_4$. We used this as a starting point in our experiment of acrolein synthesis. In a parallel experiment, H_2SO_4 (being a very strong dehydration agent) was used for water elimination, instead of $KHSO_4$. Both attempts were successful, as will be presented shortly.

PROPERTIES OF ACROLEIN

According to literature data, acrolein is a water soluble colorless liquid with $T_b = 326$ K and a specific smell, and it is claimed that its vapors are strong eye irritant [13]. Being unsaturated compound, it is expected to show all characteristic reactions of both aldehydes and alkenes, but also some specific properties due to the existence of conjugated double bonds. As a demonstration of the above 'specific' properties it is mentioned [1, 13] that acrolein can easily be polymerized or oxidized (even with air oxygen), resembling in these reactions 1,3-dienes. Consequently, it must be kept in tightly closed vessels.

ACROLEIN GENERATION AND TEST REACTIONS

Chemicals and equipment. Solid $KHSO_4$ or concentrated H_2SO_4, glycerol, Fehling, Tollens and Nylander reagents, bromine water, distilled water, ice, large test-tube, test-tube with side arm, a test-tube rack with test-tubes, a 400 mL beaker, bent glass tube ("П" shaped), few droppers, 2 corks with holes (matching the large and side-armed test-tubes, as well as the glass tube), a quartz (or pyrex) tube with heater made of high-resistance wire, regulation transformer.

Acrolein synthesis. 3–5 milliliters of glycerol are mixed with 2–3 grams of $KHSO_4$ in the large test-tube. We checked that one could use concentrated sulfuric acid instead of $KHSO_4$ with equal success. The test-tube is corked and connected (via the "П" shaped bent glass tube) with the side-armed test-tube, the latter being put in a beaker with chunks of ice. The large test-tube is carefully heated in the quartz tube (the voltage applied to the heater is selected in such a way as to prevent generation of large quantities of foam). The experimental setup is shown in Fig. 1.

Characteristic reactions. The product of the reaction is tested with Fehling, Tollens and Nylander reagents (their preparation is given elsewhere [8]), and also with bromine water (cf. Fig. 2). The results will be discussed in the subsequent heading.

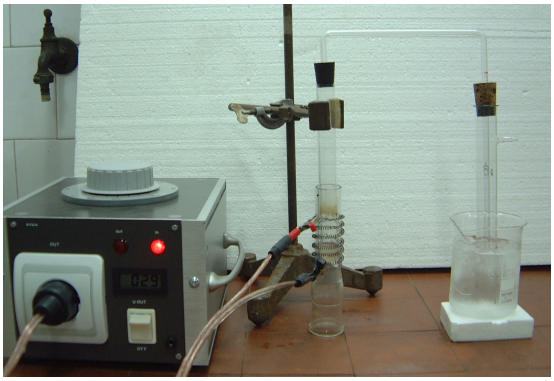

Fig. 1. Synthesis of acroleine (experimental setup)

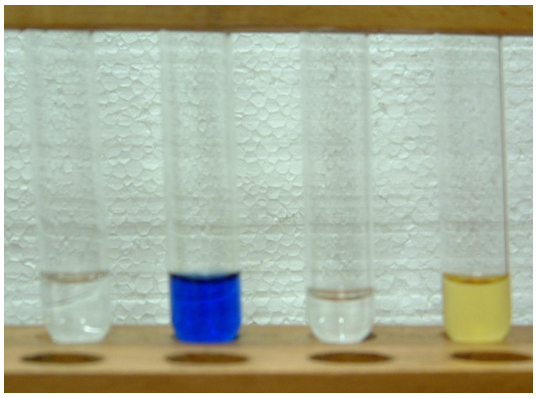

Fig. 2. Test-tubes in the rack are filled with (left to right): Nylander, Fehling, Tollens reagent and (the rightmost one) bromine water

RESULTS AND DISCUSSION

Upon heating, the reaction mixture in the large test-tube starts to generate a foam, while in the same time its color changes from white through brown, to black (compare the leftmost parts of Figs. 1 and 3). The foam is, probably, a mixture of the reaction product (acrolein) and glycerol. The color change results most likely from the product of a parallel reaction (glycerol carbonification). The latter is easily understood when using concentrated sulfuric acid (H_2SO_4 acts as strong oxidizer at high temperatures). When $KHSO_4$ is used, it might be useful to assume that (again at high temperatures) $KHSO_4$ may be considered as a mixture of K_2SO_4 and H_2SO_4, i.e.:

$$2KHSO_4(s) \varsigma K_2SO_4(s) + H_2SO_4 \qquad (1)$$

Let us mention in passing that a similar phenomenon (change of color, due to carbonification) is also observed during generation of ethene from ethanol and concentrated sulfuric acid [14] and could be explained analogously.

Fig. 3. Synthesis of acroleine – end of reaction (the black color is due to part of the glycerol being oxidized to carbon)

In 10–15 minutes it is possible to collect about 1 mL of liquid product in the cooled side-armed test-tube. The liquid exhibits a strong penetrating odor, resembling that of CH_3CHO and (to a lesser extent) HCHO. It is safe to identify the product as acrolein. Its color is pale yellow, probably due to traces of impurities.

In order to prevent polymerization or oxidation of the product, a safe method would be to dilute it with water (adding distilled water in the receiver, approximately ten times the volume of liquid acrolein). The diluted acrolein solution is practically colorless. Part of the solution (~ 1 mL) is poured off in an empty test-tube, and the rest should be sealed in a glass tube for later use (**caution: see safety tips**). The sealed tube containing aqueous solution of acrolein is shown in Fig. 4.

About 5 drops of the acrolein solution are added in each of the four test-tubes containing Tollens, Fehling and Nylander reagents, as well as bromine water. If Tollens reagent is prepared using NaOH first, it is immediately reduced by the aldehyde. Black color of elemental silver is an indication of –CHO group presence (a silver mirror of poor quality can occasionally be obtained). Discoloration of bromine water is instantaneous, while Fehling and Nylander reagents turn red (i.e. brown) only upon heating on a water-bath (cf. Fig. 5 and compare it with Fig. 2).

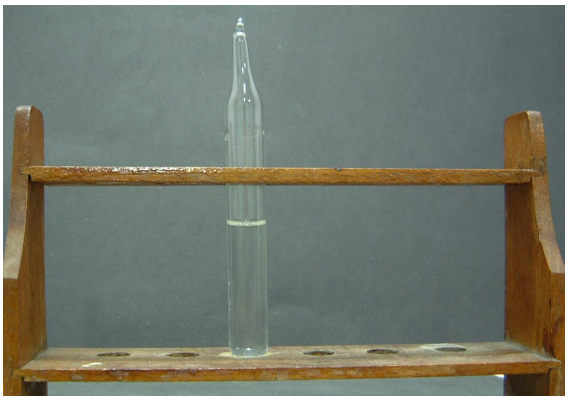

Fig. 4. Sealed glass tube with aqueous solution of acrolein

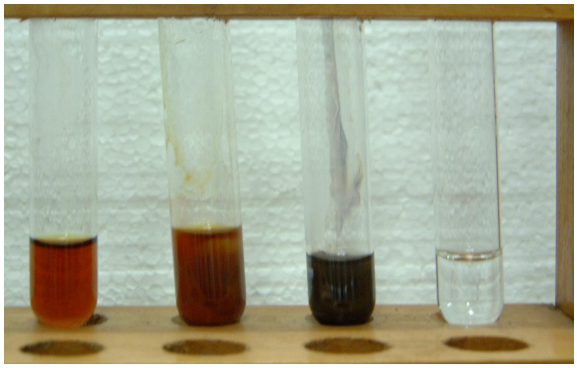

Fig. 5. Same as Fig. 2, but acrolein solution has been added

CONCLUDING REMARKS

The experiment described here might be a useful demonstration for an organic chemistry class (second year of university level). If the instructor finds it a bit lengthy, it is still possible to make the acrolein generation (the synthesis) earlier or as a lab experiment, and then to perform the tests for the –CHO and for the C=C groups as a lecture experiment. Usually it is enough to use Tollens reagent to identify the –CHO group, and bromine water for C=C.

SAFETY TIPS AND DISPOSAL

Acrolein is an irritating agent. Wear safety goggles or face shield when performing demonstrations with it. Whenever possible, perform the demonstrations in a hood. If not sealed as advised earlier, acrolein should be disposed as a water solution under the drain with lots of water. During sealing of the tube, usually a minor pop occurs (due to the mixture of acrolein vapor and air that catches fire while melting the glass). No real hazard exists when the instructor is aware of this fact. However, acrolein must be properly diluted with water.

Never attempt to seal a tube with more concentrated water solution of acrolein, for there is a serious risk of explosion that may shatter the tube and injure you!

Sulfuric acid is a strong dehydrating agent and is skin aggressive. Always wear face shield and gloves when working with it. Dispose it under the drain (dilute it previously, always adding the acid in water – never vice versa!) with a lot of water.

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Р е з и м е

СИНТЕЗА И НЕКОИ КВАЛИТАТИВНИ РЕАКЦИИ НА АКРИЛАЛДЕХИД (АКРОЛЕИН)

(ЛАБОРАТОРИСКИ И ДЕМОНСТРАЦИОНЕН ЕКСПЕРИМЕНТ ПО ОРГАНСКА ХЕМИЈА)

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Клучни зборови: акрилалдехид; акролеин; пропенал; алдехиди; несатурирани соединенија; глицерол; експерименти по хемија

Незаситените примарни алкохоли може лесно да се оксидираат до соодветните алдехиди. Од друга страна, акролеинот обично се добива со елиминација на вода од глицерол. При ваквата „дехидратација“ може да се употреби $KHSO_4$ или H_2SO_4. Во трудот е опишан еден едноставен и ефектен експеримент, преку кој може да се демонстрираат својствата како на винилната така и на алдехидната група.