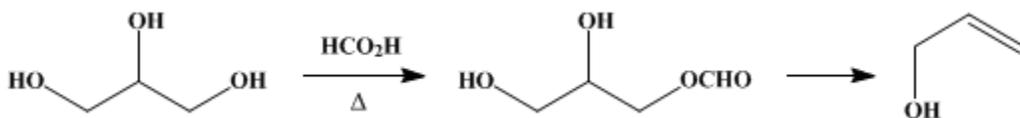


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## ALLYL ALCOHOL



Submitted by Oliver Kamm and C. S. Marvel.

Checked by H. T. Clarke and E. R. Taylor.

### 1. Procedure

In a 5-l. round-bottomed flask are placed 2 kg. (1587 cc., 21.7 moles) of **glycerol** and 700 g. (585 cc., 12.9 moles) of technical 85 per cent **formic acid** (Note 1). The flask is connected with a condenser set for downward distillation and the temperature within the reaction mixture is indicated by a thermometer, the bulb of which is immersed in the liquid. It is advisable to use as a receiver a distilling flask attached tightly to the lower end of the condenser. A tube is then run from the side arm of the distilling flask to a bottle of strong caustic soda to dissolve and decompose any **acrolein** which may be formed; a few pieces of clay plate are added to the distillation flask containing the reactants in order to prevent bumping, and it is then heated *rapidly* over a good ring burner (Note 2). The first runnings should come over within fifteen minutes and a temperature of 195° should be reached in thirty to forty-five minutes. Slow heating causes charring and formation of much **acrolein**, and thus gives a very low yield of **allyl alcohol**. The distillate collected up to the point where the thermometer registers 195° is saved separately (Note 3). Heating is continued until the temperature reaches 260°, the main reaction taking place between 225° and 235°. At 260°, when the heating should be stopped, a white smoke appears and decomposition apparently begins. The distillate (about 750 cc.) coming over between the thermometer readings between 195° and 260° is saved. For this operation about four hours are required.

The contents of the flask are now allowed to cool to a temperature between 100° and 125°, and 500 g. (9.2 moles) more of the technical 85 per cent **formic acid** is added. The distillation is then repeated in exactly the same manner as described above and 500 cc. of distillate is collected between the temperatures from 195–260°. The reaction mixture is allowed to cool again and a third portion of 500 g. of **formic acid** is added. This distillation yields not more than 350 cc. of the desired fraction, indicating that the **glycerol** is used up and that further addition of **formic acid** is unnecessary; moreover, the residue left behind is now small, amounting only to 100–200 cc. The three distillations require from one to one and one-half days.

The 195–260° fractions of the distillates are treated with **potassium carbonate** to salt out the **allyl alcohol** and to neutralize the little **formic acid** present. This **allyl alcohol** is then distilled and the fraction boiling up to about 103° is collected, or if a column is used, up to 98°. In this way, 845 g. of an **allyl alcohol** is obtained, which by **bromine** titration shows a purity of about 68–70 per cent (Note 4). This is equivalent to 570–590 g. of pure **allyl alcohol** (45–47 per cent of the theoretical amount) (Note 5).

The alcohol may be made practically anhydrous by refluxing with successive portions of fused **potassium carbonate** until no further action is observed. The **carbonate** will remain finely divided and will not become sticky when water is absent. A considerable amount of **allyl alcohol** is lost mechanically during the drying in this way, so that the **potassium carbonate** which is used here should be employed for the salting out of fresh portions of **allyl alcohol** in the first part of subsequent preparations. The **allyl alcohol** thus produced is dry enough for all practical purposes (98–99 per cent), and it is unnecessary to dry with lime or **barium oxide** as advised in the literature in order to remove all the water. The **allyl alcohol** obtained by this process boils at 94–97°.

The checkers have used the following method with success for obtaining a completely anhydrous product. The **allyl alcohol** obtained after one salting out with **potassium carbonate** is distilled as indicated above to give a product of about 70 per cent purity and then mixed with one-quarter of its volume of **carbon tetrachloride** (Note 6). The mixture is then slowly distilled from a round-bottomed

flask fitted with a fractionating column at least 80 cm. long, collecting the low-boiling mixture of carbon tetrachloride, water, and allyl alcohol, drying it with potassium carbonate, and returning it to the flask (Note 7). This process is repeated several times, until only very little water passes over. The mixture is then completely distilled, taking the following cuts: Up to 80°, 80–90°, 90–95°, 95.5–97°, the last being alcohol which titrates 100 per cent pure. The lower fractions are dried separately and refractionated, thus giving an additional portion boiling at 95.5–97°.

## 2. Notes

1. The reaction between formic acid and glycerol runs very smoothly and without the tendency toward foaming which results when oxalic acid is used.
2. Unless heating is rapid, the yields are very unsatisfactory.
3. The lower fraction which distils up to the point where the thermometer registers 195° contains a considerable amount of formic acid, and in large-scale production it would undoubtedly pay to recover it.
4. To determine the purity of any sample of allyl alcohol, 1 cc. is run into 15–25 cc. of carbon tetrachloride and this solution is then treated in the cold with a carbon tetrachloride solution of bromine (standardized with potassium iodide and sodium thiosulfate) until a permanent bromine coloration is obtained. The amount of allyl alcohol present in any solution may also be determined roughly by conversion to allyl bromide. From several experiments it was found that the allyl bromide obtained was equivalent to the amount of allyl alcohol as determined by bromine titration.

When the crude allyl alcohol is distilled from a steam bath under reduced pressure, the distillate is considerably richer in allyl alcohol (sometimes up to 90 per cent). The strength can be readily determined by measuring the specific gravity and comparing with the following figures:

|                          |        |        |        |        |        |        |        |       |
|--------------------------|--------|--------|--------|--------|--------|--------|--------|-------|
| Per cent allyl alcohol.. | 65     | 70     | 75     | 80     | 85     | 90     | 95     | 100   |
| Density at 20°.....      | 0.9200 | 0.9110 | 0.9020 | 0.8930 | 0.8840 | 0.8750 | 0.8650 | 0.854 |

The best results are obtained when working at a pressure of 200–300 mm. Some boiling points of the watery alcohol are: 60°/200 mm., 70°/300 mm., and 78°/500 mm.

5. A large amount of work was carried out upon the oxalic acid and glycerol method for the production of allyl alcohol. The results were not satisfactory and therefore are not included here. It might be said, however, that, when oxalic acid is used in place of formic acid, the reaction requires a longer time for completion and is not nearly so smooth. There is a much greater tendency toward foaming and the reaction must be continually watched in order to prevent this, especially after the first distillation with oxalic acid, when more oxalic acid is added and heating is continued. Another disadvantage is that large amounts of acrolein are produced when oxalic acid is used. In general, the yield by this method amounts to not over 20–30 per cent, whereas with formic acid a yield of 45–47 per cent is easily obtained. As far as the preparation of allyl alcohol is concerned, in amounts such as are used in the above experiments, the formic acid method is greatly to be preferred. The method of employing anhydrous oxalic acid, which has been reported as giving particularly good yields, did not give satisfactory results when tried. Experiments were also made with 90 per cent formic acid, and yields of 50–54 per cent of allyl alcohol were obtained.
6. It is suggested that ethylene chloride rather than carbon tetrachloride be used to dehydrate the allyl alcohol because of its more rapid effect. (W. W. Hartman, private communication.)
7. The apparatus described on p. 262 may be used for these operations.

## 3. Discussion

The two most practical methods for the preparation of allyl alcohol are by the action of either formic<sup>1</sup> or oxalic acid<sup>2</sup> on glycerol. Both methods have been studied, and the formic acid method has been shown to be much the superior. Improved yields are obtainable<sup>3</sup> by reworking the fractions obtained in accordance with the procedure described in this volume, but such improvement was found to be only 2 per cent in an experiment carried out by one of the editors.

Allyl alcohol has also been prepared, together with propionaldehyde, by passing propylene oxide mixed with nitrogen over activated alumina at 200–400°,<sup>4</sup> and from propylene oxide, an alkali alum, and

an oxidation catalyst such as [vanadium pentoxide](#) at 200–300°. <sup>5</sup> The thermal decomposition of [allyl sulfite](#) also furnishes [allyl alcohol](#). <sup>6</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 25](#)

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## References and Notes

1. Tollens and Henninger, *Ann.* **156**, 139 (1870); Koehler, *Bull. soc. chim.* (4) **13**, 1103 (1913); Hoff, *Oversigt Kgl. Danske Vidensk. Selsk. Fork.* 199 (1915) [*C. A.* **10**, 1035 (1916)]; Delaby and Dubois, *Compt. rend.* **187**, 767, 949 (1928), **188**, 710 (1929); *Bull. soc. chim.* **47**, 584 (1930); Dewael, *Bull. soc. chim. Belg.* **39**, 40 (1930).
2. Bigot, *Ann. chim. phys.* (6) **22**, 464 (1891); Tollens and Henninger, *Ann.* **156**, 134, 149 (1870); 167, 222 (footnote) (1873); Chattaway, *J. Chem. Soc.* **105**, 151 (1914); **107**, 407 (1915); Coffey and Ward, *ibid.* **119**, 1301 (1921).
3. Dewael, *Bull. soc. chim. Belg.* **39**, 40 (1930).
4. Carbide and Carbon Chemicals Corp., U. S. pat. 1,917,179 [*C. A.* **27**, 4546 (1933)].
5. Carbide and Carbon Chemicals Corp., U. S. pat. 2,159,507 [*C. A.* **33**, 6874 (1939)].
6. Carré and Libermann, *Bull. soc. chim.* (5) **1**, 1248 (1934).

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## Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

caustic soda

formic

alumina

[alcohol](#) (64-17-5)

[potassium carbonate](#) (584-08-7)

[Acrolein](#) (107-02-8)

[glycerol](#) (56-81-5)

[bromine](#) (7726-95-6)

[Allyl bromide](#) (106-95-6)

[Allyl alcohol](#) (107-18-6)

[carbonate](#) (3812-32-6)

[formic acid](#) (64-18-6)

barium oxide

carbon tetrachloride (56-23-5)

Oxalic acid (144-62-7)

potassium iodide (7681-11-0)

sodium thiosulfate (7772-98-7)

ethylene chloride (107-06-2)

Propionaldehyde (123-38-6)

propylene oxide (75-56-9)

nitrogen (7727-37-9)

vanadium pentoxide

allyl sulfite