alcohol, and difficultly soluble in ether and benzene. It melts with gas evolution at 134.5°.

Calc. for $C_6H_{12}O_4N_4$: C, 35.29; H, 5.88; N, 27.45. Found: C, 35.51; H, 5.97; N, 27.31.

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[CONTRIBUTION FROM THE OTHO S. A. SPRAGUE MEMORIAL INSTITUTE, LABORATORY OF CLINICAL RESEARCH, RUSH MEDICAL COLLEGE.]

# THE PREPARATION OF ACROLEIN.

BY EDGAR J. WITZEMANN.

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Although numerous methods have been proposed for the preparation of acrolein, it has remained relatively difficult to obtain it pure and in large quantities. The most practical method for obtaining pure acrolein hitherto has been the phosphoric acid method proposed by Nef,[1] used by McLeod,[2] and investigated in some detail by Bergh.[3] More recently Wohl and Mylo[4] have described a method for preparing acrolein in which anhydrous magnesium sulfate was used as the catalyst. However, the apparatus used by Wohl and Mylo is composed entirely of especially constructed parts so that the method, as described by them, cannot be used except after a large outlay in time and money for the construction of the apparatus. The present note is an account of a much simpler way of using magnesium sulfate in an apparatus composed of ordinary stock materials. The results obtained by this modification are not so good as the best results obtained by Wohl and Mylo, but the method, as described here, is much more available for ordinary use.

Before discussing the modification of Wohl and Mylo's method I wish to record my experience with the phosphoric acid method. The apparatus used was essentially like that used by Bergh. A three liter Kavalier round-bottom flask standing in a Babo funnel and heated by a ring burner was used instead of the iron retort employed by Bergh. That is, the apparatus was like that in Fig. 1, except that there was no dropping funnel in the generator flask and that the thermometer was pushed down into the glycerol.

Using an apparatus arranged in this way, a charge of 500 g., consisting of 475 g. of commercial glycerol and 25 g. of a pure phosphoric acid (d. 1.7), regularly gave 40–45 (sometimes 50 g.) of very pure acrolein. It is necessary to regulate the flame of the ring burner carefully because more

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[1] *Ann.*, **335**, 221 (1904).

[2] *Am. Chem. J.*, **37**, 35 (1907).

[3] *J. prakt. Chem.*, [2] **79**, 351 (1909).

[4] *Ber.*, **45**, 2050 (1912).

tar and less acrolein are formed the higher the temperature is raised above the point necessary to maintain active distillation. This is usually about 220° during the first part of the distillation. The temperature must usually rise to about 240° as distillation progresses. The end point of the distillation is very definitely indicated by the fact that the tar suddenly begins to foam up and fill the flask. If the temperature has been properly regulated, the flame may be turned down when the foaming begins and the tar foam will only rise part way in the flask. But if the tar is too hot it will boil over and accomplish one of several things, the least of which is to fill the distilling tube and condenser with tar.

When amounts of phosphoric acid are used corresponding to between 3 and 4.5% of the reaction mixture, the acrolein distillate is somewhat heavier (50–55 g.) but the acrolein thus obtained is slightly inferior. The temperature of decomposition rises as the percentage of phosphoric acid is decreased.

It was thought that perhaps the yield could be increased by continuing the distillation after the foaming stage. It was possible to heat the tars after the foaming but the yields were not very markedly increased and the quality of the acrolein was reduced by the last runnings. Apparently, the subsequent heating only tends to further dehydrate the tar without producing additional amounts of acrolein.

Attempts were made to increase the yield by placing only 200 g. of the charge in the generator and dropping the other 300 g. into the generator flask through a separatory funnel during the distillation. This proved to be unsatisfactory, because the reaction mass was likely to foam up at any moment unless very closely watched, and the yield of acrolein was not improved.

The tars formed in this process are relatively easily soluble in 5–10% alkali solutions. The solubility diminishes as the degree of dehydration increases.

After having prepared about 1.5 kilos of acrolein in this way the method was abandoned in favor of the following:

## Modification of Wohl and Mylo's Method.

The method of Wohl and Mylo[1] has but one defect and that is, it can only be used after a heavy outlay for special apparatus. The modification here described was made in an attempt to utilize magnesium sulfate as a catalyst under less expensive conditions. After some experimentation with the use of distilling tubes, etc., the apparatus of Bergh's phosphoric acid method was modified as shown in Fig. 1. *A* is a ring burner resting on an asbestos board supported by a large ring attached to the ring stand. *B* is a Babo funnel. *C* is a three liter round-bottom Kavalier long neck (about 12 cm.) flask connected by an ordinary glass tube con-

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[1] *Loc. cit.*

nection to a short condenser. A short bent adaptor connects this with the first receiver (a one liter flask), which contains 100–125 g. of common salt and is immersed in boiling water. The bent glass connecting tube leading from *D* is constricted at its lower end and has a hole blown about 2.5 cm. from the lower end, in order to allow vapors to pass through it without forcing them through the water drops which continually fall from the lower end of this connecting tube. The receiver for the acrolein is kept immersed in an ice-water bath *E*. The uncondensed acrolein vapors are disposed of by means of a rubber tube attached to the side arm of the receiving flask and which terminates in a good hood or outside of the building. The two ring stands supporting the condensers are not shown.

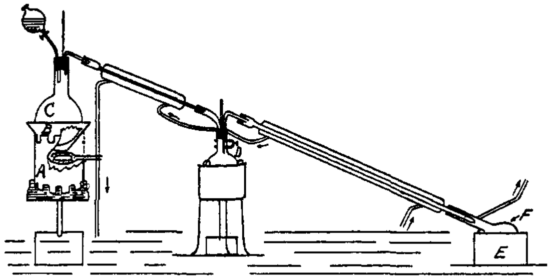

Fig. I.

The hydrated magnesium sulfate was dehydrated by heating it with a good Bunsen burner in an iron pan. Dehydrated layers at least three-eighths of an inch thick were obtained. This material was broken up between the fingers into pieces varying from one-fourth to one-half inch in dimensions. The smaller particles and dust were carefully removed. One hundred and sixty grams of this were placed in the three liter flask. If dust and fine particles cover the bottom of the flask to any marked extent, the flask will probably be broken during the distillation, hence the care in removing the fine magnesium sulfate.

Just before beginning the distillation 200 g. of commercial glycerol are poured on the magnesium sulfate. The flask and contents are now warmed up fairly slowly by keeping the flame low at first. Meanwhile, the Bunsen lamp under *D* is lighted in order to heat the water bath to boiling. When acrolein begins to pass over into the second receiver (the water is held back by the salt in the first receiver) glycerol is slowly dropped into the generator through the dropping funnel. The glycerol must be added as fast as that already present is decomposed, but not much faster. If the glycerol is not added as fast as it is decomposed, the bottom of the flask burns dry and breaks, although the magnesium sulfate mass may be foaming actively and developing acrolein freely. The glycerol in the generator darkens in color and becomes more syrupy and tarry as the distillation proceeds. The rate of the tarring depends somewhat on the height of the flame on the ring burner. After having studied the reaction and learned the optimum conditions, I found that I could operate with three sets of apparatus simultaneously and could thus obtain about 500 g. of very good acrolein in about five hours. The process requires very close attention, especially during the first few runs, but later on other work can be carried on easily.

Occasionally generator flasks break during distillation, but there is nothing to fear from this, since the odor given off is mostly that of hot sugar tar. This was a great surprise. It was expected that the odor of acrolein would be overpowering. Usually flasks are broken in this way because they are heated too rapidly at the beginning of the distillation. If the distillation has not progressed too far, so that the magnesium sulfate is not clogged with tar, the glycerol-soaked magnesium sulfate may be transferred to another flask and distillation continued. This was done a number of times.

Wohl and Wylo have suggested that the yield of acrolein might be increased, when distilling from a metallic retort containing the whole charge, by stirring the contents. From my experience in watching the operation in a glass flask it is apparent that the tar clogs up the pores and lumps of the magnesium sulfate; if this tar could be drained away from the catalyst the same catalyst could be used with much larger amounts of glycerol. This tar probably arises at first solely from acetol and it is possible that, as the amount of acetol tar increases, that either relatively more acetol is formed or that much of the acrolein is also resinified. At least it is certain that the yield in acrolein hour for hour diminishes somewhat as the distillation proceeds.

The acrolein as obtained in the second receiver is lemon-yellow in color and nearly always begins to polymerize at once. There are always a few grams of water in the bottom of each acrolein distillate. If this water is not removed, the polymerization does not proceed very far, so that the crude acrolein, if kept in a cool place, may be redistilled the next day without very great loss.

After having made some practice runs the following yields were obtained:

| | | |
|---|---|---|
| 450 g.<br>460 g.<br>470 g.<br>480 g. | crude acrolein from 1800 g. glycerol. Average yield 43%. | When redistilled 320–60 g. of purified acrolein were obtained. |
| 495 g. | from 1850 g. glycerol | 370 g. pure acrolein |
| 547 g. | from 2000 g. glycerol | 425 g. pure acrolein. |

The crude, moist acrolein began to boil at 51° and distilled over almost entirely between 52–54°; only a very small amount boiled between 54° and 58°, which was obviously due to the presence of water. Acrolein thus distilled polymerizes quite rapidly and should be agitated for a few minutes with granular calcium chloride until it clears up and then be used at once. The calcium chloride must not be alkaline to litmus in aqueous solution, because such calcium chloride causes very rapid polymerization.

Under normal conditions the tar in the generator flask can be readily and quickly washed out with warm water. At other times there is a small amount of non-acid tar, which can be removed easily with the chromic acid cleaning mixture.

CHICAGO, ILL.

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# THE PHOSPHATES OF 2,3-DISTEARIN.[1]

BY R. R. RENSHAW AND R. R. STEVENS.

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Grun and Kade[2] have recently described a number of distearyl phosphates obtained by the action of phosphoric anhydride on 2,3-distearin. It would appear that the publication of their researches was delayed and that their results were obtained, in part at least, as early as 1910. We also began the study of the phosphatization of distearin in the summer of 1910, but our object was to obtain a definite substance and not *per se* to study the interaction of phosphorus pentoxide and distearin. Our investigation is not as complete as that of Grun and Kade, and we bring up no question of priority. There are, however, certain similarities and differences in our results which we think desirable to indicate at this time.

Under certain conditions, Grun and Kade obtained the mono-2,3-distearyl glyceryl phosphate and from the decomposition of this, by standing or by recrystallization from alcohol, ether or ligroin, they seem to have obtained primary, secondary, tertiary and quinquenary esters of *o*-phosphoric acid. Suggesting as probable, the intermediate formation of metaphosphates, they propose the following scheme to represent the decomposition, where R represents the distearyl radical:

$$RH_3P_2O_7 \longrightarrow RH_2PO_4 \longrightarrow R_2HPO_4 \longrightarrow R_3PO_4 \longrightarrow R_5PO_5$$

That is, for instance, the primary distearyl glyceryl phosphate breaks down in part into distearin and phosphoric acid and the distearin formed reacts with some of the undecomposed primary phosphate to form the secondary phosphate, and similar reactions yield the tertiary and quinquenary phosphates. The evidence offered seems to be sufficient with the possible exception of the quinquenary phosphate.[3]

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[1] Presented at the 49th General Meeting of the Am. Chem. Soc., Cincinnati, Ohio, April 8, 1914.

[2] *Ber.*, 45, 3358.

[3] In connection with this, it may be recalled that Grun himself has shown that diglycerides form very stable addition products with the fatty acids, as for instance, dimyristin forms $C_3H_5(OH)(OCOC_{13}H_{27})_2 + 2HOOCC_{13}H_{27}$. The phosphorus content of the quinquenary ester and of such an addition product of the tertiary phosphate with four molecules of stearic acid differ within the allowable analytical error.