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PREPARATION OF METHACRYLAMIDE

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The present study was undertaken to develop a convenient laboratory method for the preparation of small quantities of methacrylamide. Methacrylamide has been prepared by the reaction of acetone cyanohydrin with concentrated sulfuric acid (1, 2, 3, 4, 5, 6) and by the hydrolysis of methacrylonitrile (7). Trial experiments indicated that the procedure described by Crawford and McGrath (3) was operable on a laboratory basis to give 46% yields of isolated amide. This procedure requires the following steps: (a) heat acetone cyanohydrin with concentrated sulfuric acid, (b) dilute, (c) neutralize with calcium carbonate, (d) filter off calcium sulfate, (e) evaporate to dryness, and (f) recrystallize from benzene. This isolation procedure is necessary because methacrylamide is very soluble in both water and organic solvents. It is also inconvenient and laborious and results in loss of amide through polymerization and hydrolysis. A technique has been developed for isolating the amide from the acetone cyanohydrin-sulfuric acid reaction mixture, and used to determine conditions of time and temperature which give maximum conversion of cyanohydrin to amide.

The procedure used in isolating methacrylamide from the acetone cyanohydrin-sulfuric acid mixture is based on a combined neutralization of the sulfuric acid and salting out of the amide. The feasibility of this process was demonstrated by the following experiment. Dissolving 20 g. of anhydrous sodium sulfate in a solution of 5 g. of methacrylamide in 50 ml. of water salted out 90% of the solid amide. This technique was shown to be adaptable to the isolation of methacrylamide from the sulfuric acid reaction mixture by forming the sodium sulfate through neutralization of the sulfuric acid. Thus, 17 g. of amide in 80 ml. of water and 30 g. of concentrated sulfuric acid was neutralized with 32.5 g. of sodium carbonate at below 25°. The salted out material was recrystallized from benzene to give a total of 15 g. or 88%.

With this technique of isolating the methacrylamide, one can follow the course of the conversion of acetone cyanohydrin to amide by actual isolation of the product. A series of experiments was designed to determine the effect of time and temperature on the reaction. The acetone cyanohydrin-sulfuric acid reaction mixture was heated quickly to reaction temperature, 100–150°, and sampled at 15-minute intervals. Yield of amide was determined on each sample and plotted as a function of time. The data for runs at 100, 130, and 150° are given in Figure 1. From these data it is seen that a maximum yield of 20 g. (71%) is obtained by heating at 150° for 22 minutes, 7 of which are required to reach 150°.

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At each temperature there is an optimum time at which maximum yield is obtained, and after which the yield drops off. It is possible that shorter heating times at higher temperatures would give slightly higher yields than those recorded here. On the basis of an isolation which recovers 90% of the product, an isolated yield of 71% corresponds to a conversion of about 80%. The data show that the time and temperature are determining factors and reproducible operation requires careful specification of these variables. A preferred procedure based on the optimum conditions is given in the experimental part.

EXPERIMENTAL PART

Study of time and temperature variations. In a 1-liter round-bottomed flask equipped with stirrer, dropping-funnel, and thermometer were placed 300 g. of 98% sulfuric acid and 2 g.of flowers of sulfur. To this was added, over forty minutes, 170 g. (2 moles) of acetone cyanohydrin (Rohm and Haas Co.), while keeping the temperature at 70–80° by external cooling. The flask was immersed in an oil-bath preheated to 135°. Aliquot portions (78.5 g., one-sixth of total volume) were withdrawn at intervals. The methacrylamide content of each sample was determined quickly as follows. The sample was cooled to room temperature, poured into 125 ml. of cold water, filtered, and neutralized with 53 g. of sodium carbonate. The salted out solid was collected, dried, extracted with 200 ml. and two 100-ml. portions of hot benzene. The benzene extracts were treated with Norit, filtered, and cooled. The first crop of crystals was separated and the mother liquor evaporated to give a second crop. The combined weight of the two fractions was taken as the yield of amide. The theoretical yield from each portion is one-third mole, 28.3 g.

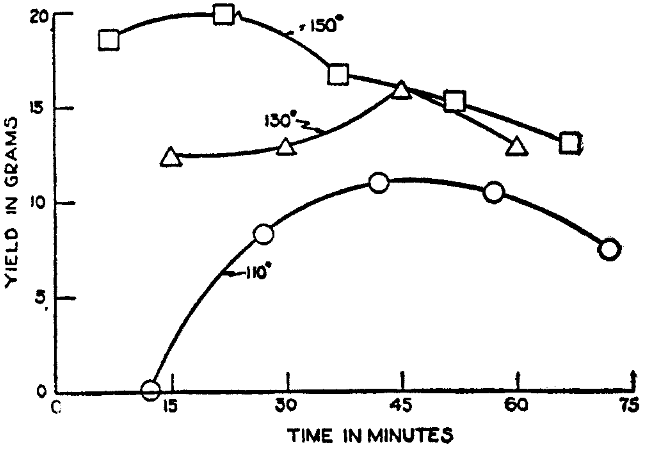

Fig. 1. Yield of methacrylamide isolated from acetone cyanohydrin-sulfuric reaction as a function of time and temperature of reaction. Theoretical yield 28.3 g.

In experiments at different temperatures, the heating was varied by starting with the oil-bath preheated to 5° above the desired temperature and holding it at the desired temperature. Samples were withdrawn as the temperature rose, the first at 100–110°, when the yield was never over 7%, and then at the temperature of the run. The yield data are summarized in Figure 1. An attempt to carry out the process at 170° gave results which indicated that the highest yield was obtained at 150° before the contents of the flask reached 170°. This indicated that the procedure described is not so well suited to rapid, high temperature operations as the continuous unit used by Crawford (2).

Preferred procedure for synthesis of methacrylamide. In a 1-liter round-bottomed flask fitted with an efficient stirrer, a dropping-funnel, and a thermometer, were placed 150 g. (1.5 moles) of 98% sulfuric acid, prepared by the addition of 33.5 ml. of fuming sulfuric acid (15% SO_3) to 48 ml. of acid of sp. gr. 1.84, and 1 g. of flowers of sulfur. To this was added, with rapid stirring, 85 g. (1 mole) of acetone cyanohydrin, as prepared in Organic Syntheses (8) or as furnished by Rohm and Haas Company, over a period of 25 minutes keeping the temperature of the contents of the flask at 75–80° by cooling in a water-bath. At the end of this period, the water-bath was replaced with an oil-bath preheated to 155°. With continued stirring, the temperature of the reaction mixture was raised to 150° within 5 minutes and maintained at 150° for 15 minutes. The reaction mixture was quickly cooled to room temperature by replacing the oil-bath with an ice-bath and was then poured into 375 ml. of cold water. The diluted mixture was filtered to separate a small amount of polymer. The filtrate was neutralized and the crude product salted out of solution by adding, while holding the temperature below 30°, 160 g. of sodium carbonate. The salted out material, which rises to the top of the solution, was separated and, after drying 10–24 hours in a vacuum desiccator over calcium chloride, gave 320 g. of a light tan solid which contains some sodium sulfate.

The crude solid obtained in the preceding paragraph was placed in a 2-l. flask and heated and stirred with 500 ml. of boiling benzene. The solvent was decanted and the extraction was repeated with four 200-ml. portions of benzene. The combined benzene solutions were heated to boiling, treated with Norit, and filtered. On cooling, 50–52 g. of methacrylamide separated, m.p. 105–107°. An additional 6–8 g., m.p. 103–105°, were obtained when the mother liquor was concentrated to 150 ml. and cooled. The yield of methacrylamide was 56–60 g. (66–71% of the theoretical amount).

SUMMARY

A procedure for isolating methacrylamide from aqueous sulfuric acid solution has been developed and used in a study of the effect of time and temperature on the conversion of acetone cyanohydrin-sulfuric acid solutions to methacrylamide. In the procedure described, yields of 70% of isolated methacrylamide are obtained by heating the reaction mixture at 150° for 15 to 20 minutes.

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