

## UNITED STATES PATENT OFFICE

2,683,741

## PRODUCTION OF N-ALKYLACRYLAMIDES

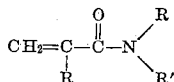
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7 Claims. (Cl. 260—561)

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This invention relates to a process for the production of N-alkylacrylamides from esters of acrylic acid and of the  $\alpha$ -alkylacrylic acids and primary or secondary amines. Representative N-alkylacrylamides which may be produced by the process of my invention are N-methyl acrylic acid amide, N-ethyl acrylic acid amide, n-butyl acrylic acid amide or the corresponding N-di-alkylacrylamides, e. g. N-dimethyl acrylic acid amide. My invention may also be employed for the production of the homologs of the foregoing acrylamides, e. g. N-methyl methacrylic acid amide or N-ethyl ethacrylic acid amide, or the analogous N-dialkyl methacrylic or ethacrylic acid amides, such as N-dimethyl methacrylic acid amide, N-methyl-N-ethylmethacrylic acid amide, or N-dimethyl ethacrylic acid amide. Thus, the products which may be produced by the process of my invention are represented by the formula



where R is hydrogen or an alkyl radical and R' is an alkyl radical.

It is known that primary and secondary alkylamines, such as methylamine or diethylamine, may be reacted with acrylic acid esters to form N-alkyl-beta-aminopropionic-N-alkylamides or N-alkyl-beta-aminopropionates, depending upon the conditions employed. With ratios of amine to ester up to about equal mol ratios, there is little, if any, formation of the aminoamides, the product being almost wholly aminopropionates. With higher ratios of amine to ester, e. g., 2 mols or more of the amine for every 1 mol of ester, the aminoamide may be obtained as the principal product of the reaction.

I have discovered that the N-alkyl-beta-aminopropionic-N-alkylamides may be decomposed by heat to form the corresponding N-alkylacrylamides. Thus, in reacting an ester of acrylic acid or of an  $\alpha$ -alkyl-acrylic acid with a primary or secondary amine, the amine more readily adds to the unsaturated carbon atoms of the ester molecule to form an amino compound than it reacts with the —COOR group of the ester to form an amide. Nevertheless, on heating the aminoamide, the amino radical and a hydrogen alpha thereto are readily split out of the molecule to reform the amine and reestablish the alpha, beta-unsaturated structure of the acrylic compound.

I have further discovered that the homologs of acrylic acid esters, such as esters of methacrylic or ethacrylic acid also may be reacted with pri-

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mary or secondary amines to form the corresponding N-alkyl-beta-amino-alpha-alkylpropionic-N-alkylamides under conditions similar to those under which the aminoamides may be formed from acrylic acid esters and that the resulting alpha-substituted homologs of N-alkyl-beta-aminopropionic-N-alkylamides may be heated to form the homologs of the N-alkyl acrylic acid amides, e. g. N-methacrylic acid amides and N-ethacrylic acid amides.

The process of my invention, therefore, involves heating an N-alkyl-beta-aminopropionic-N-alkylamide or an alpha alkyl-substituted homolog thereof at temperatures at which the aminoamide is decomposed to form an N-alkylacrylamide.

The aminoamide may be produced in known manner by reacting an alkylamine with an ester of acrylic acid or of an  $\alpha$ -alkyl-acrylic acid. I have discovered, however, a particular procedure for carrying out this reaction to produce the aminoamides from the primary and secondary methyl or ethylamines reacting with either methyl or ethyl acrylates, methacrylates or ethacrylates. These acrylic esters have very low solubilities in water. Accordingly, it has heretofore been regarded as desirable to exclude from the reaction mixture substantial amounts of water and also to have present in the reaction mixture an alcohol or other organic solvent for the acrylic ester, for example, by mixing the ester with an alcoholic solution of the amine. I have now discovered, however, that in reacting the methyl or ethylamines with methyl or ethyl acrylate, methacrylate or ethacrylate, it is advantageous to have water present in the reaction mixture by, for example, employing the amine as about a 25% (by weight) solution in water which is mixed with the ester. The resulting reaction mixture may contain about 62 to 91 mol percent water, depending upon the particular amine used and whether 2 or 4 mols of the amine are employed for every 1 mol of the ester. These represent preferred amounts of water but improved results may be obtained employing smaller or greater proportions of water. In general, the water may amount to about 40 to 95 mol percent based on the total water, ester and amine supplied to the reaction mixture.

The second step of the complete process for producing the amides from amines and acrylic esters which embodies my invention, involves heating an aminoamide described above to temperatures at which it is decomposed to form the corresponding alpha, beta-unsaturated amide with evolution of amine corresponding to the

amino substituent of the aminoamide. Before thus heating the aminoamide it may be recovered from the reaction product of the procedure used for its preparation. I prefer, however, to heat the reaction product of the amine and acrylic ester containing the aminoamide to form the acrylamide without first separately recovering from that reaction product the aminoamide. I have found that high yields of acrylamide are thus obtained by treating the crude reaction product and at the same time the procedural steps for making the acrylamide are simplified and made more economical.

The temperature to which the aminoamide must be heated in order to decompose it varies according to the particular aminoamide being treated. For example, in the case of the methyl and ethylaminoamides temperatures in the range 100° to 150° C. have been found to decompose these materials to form the corresponding unsaturated amides. With an n-butylaminoamide temperatures of about 200°–220° C. have been found desirable in order to decompose these materials with reasonable rapidity to form the corresponding unsaturated amides.

The reaction involved in thus decomposing the aminoamides by heat appears to be an equilibrium reaction which, in order for it to go to substantial completion, is favored by removing one or both of the products of the reaction; i. e., the amide and the amine. Accordingly, a preferred method of carrying out my process involves heating and simultaneously distilling the material containing the aminoamide. The temperature is maintained high enough to cause decomposition of the aminoamide present and the pressure is maintained during this heating-distillation treatment high enough to prevent the aminoamide distilling over and being removed from the material being heated and low enough to permit the amine produced by decomposition of the aminoamide to distill out and be removed. The amide may or may not simultaneously be distilled out with the amine. I prefer to maintain during the distillation of the amine a pressure high enough so that the N-alkylacrylamide formed is retained in the material being heated while the amine is distilled over until the desired decomposition of the aminoamide has been obtained. The undistilled product is then further distilled to carry over the amide, which is recovered as a distillate separate from the amine previously distilled over. In some cases, however, particularly when the amine formed has a much lower boiling point than the N-alkylacrylamide, both the amine and amide may be distilled over simultaneously and the vapors fractionally condensed first to condense out the amide and separate it from the vapors of the amine. It is characteristic of either of the foregoing methods of operation that the amine is vaporized and the vapors of the amine are separated from the N-alkylacrylamide which is recovered from the amine.

The following examples are illustrative of processes within the scope of my invention. The reaction conditions for decomposing the aminoamides to form the acrylamides disclosed in these examples are suitable conditions for the particular materials being treated and are illustrative of, but not limitations to, the conditions described above suitable for carrying out this step of my process for these and other materials.

*Example 1.*—Ethyl acrylate is slowly added to a stirred solution of primary methylamine in

water (a 25% solution by weight) in amount supplying 1 mol of ethyl acrylate for every 2 mols of methylamine. The temperature of the mixture is kept below 15° C. by cooling during the addition of the ethyl acrylate. After thorough incorporation of the materials with each other the mixture is allowed to stand at room temperature for a period of time, for example for about 16 hours, after completion of the addition of the ethyl acrylate to the solution of methylamine. The resulting reaction product is distilled under a vacuum to remove water. The residue left after removal of the water is fractionally distilled under a reduced pressure and the material boiling at 109° to 111° C. under a reduced pressure of 7 mm. Hg is recovered as a crude product containing about 91% to 92% of N-methyl acrylamide. This crude product may be refractionated to recover a purified N-methyl acrylamide.

By operating under the conditions described about an 82.5% yield of the crude methyl acrylamide product was obtained based on the ethyl acrylate. By modifying the foregoing process to mix the methylamine and ethyl acrylate in the mol ratio of 4:1, the yield of crude N-methyl acrylamide was increased to 90%. Further increasing the mol ratio to 4 mols methylamide to 1 mol ethyl acrylate increased the yield of crude N-methyl acrylamide to 92%.

The procedures of the foregoing example may be modified by heating the aqueous mixture of ethyl acrylate and methylamine to boiling under a reflux condenser for a period of about 6 hours. While this shortens the time of the materials in the process, in general it decreases the yield of N-methyl acrylamide, although this tendency to decrease in yield may be in part offset by employing the higher ratios of methylamine to ethyl acrylate described above.

*Example 2.*—A 25% solution of diethylamine in water is mixed with ethyl acrylate in amounts supplying 3 mols of diethylamine for every 1 mol of ethyl acrylate. This mixture is boiled under a reflux condenser at atmospheric pressure for a period of 24 hours, and is then concentrated under a reduced pressure to evaporate off water. Three grams of p-tert.-butylcatechol are added to the concentrated reaction product for every 1 mol of ethyl acrylate; the p-tert.-butylcatechol serving to inhibit polymerization of the materials present during the subsequent treatment of the reactants and their reaction products. This residue from which water has been evaporated is then distilled with rectification of the evolved vapors in a still and rectification column from which air is displaced by nitrogen gas, the distillation being carried out under a reduced pressure of 4 mm. Hg. Water, alcohol and amine first distill over after which a fraction distilling over at a top of column temperature of 81° to 92° C. under the reduced pressure of 4 mm. Hg is separately recovered as a crude N-diethyl acrylic acid amide product in about 72% yield based on the ethyl acrylate supplied to the process. The crude product may be refractionated in a nitrogen atmosphere under reduced pressure to give a purified product, about 1% of p-tert.-butylcatechol being added to the crude product to inhibit polymerization during this refractionation.

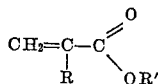
*Example 3.*—n-Butylamine and ethyl acrylate are mixed in the ratio of 3 mols of the amine for every 1 mol of the acrylate and the mixture boiled under a reflux condenser at atmospheric pressure for a period of 18 hours. At the end of this time the reaction product is heated in the boiler

of a still provided with a rectifying column. Excess amine and ethyl alcohol and water are first distilled over under a reduced pressure. The contents of the still are then heated under a pressure of 265 mm. Hg and the fraction distilling over at 210–211° C. under 265 mm. Hg is separately recovered as a crude N-n-butyl acrylic acid amide which may be refractionated under reduced pressure to recover a purified product.

*Example 4.*—A 25% solution of methylamine in water is mixed with ethyl methacrylate in proportions supplying 3 mols of the methylamine for every 1 mol of the methacrylate, and the mixture is boiled under a reflux condenser for 24 hours at atmospheric pressure. Low boiling material is then removed by evaporation under reduced pressure until the temperature of the residue reaches 75° C. There is then added to the unvaporized residue about 3 grams of p-tert-butylcatechol for every 1 mol of the ethyl methacrylate initially supplied and the residue heated in a nitrogen atmosphere to slowly distill it under a reduced pressure of 6 to 8 mm. Hg. After distillation of methylamine is completed the distillation is carried on under a reduced pressure of 2.5 mm. Hg and a fraction distilling over at 65–80° C. is separately recovered and redistilled in a nitrogen atmosphere with the addition of 1% p-tert-butylcatechol to recover N-methyl methacrylic acid amide as the product of this process.

It will be noted that in the foregoing examples in some cases a polymerization inhibitor is added to the material. This is desirable in some cases, while in other cases the acrylates ordinarily available for use in my process already contain materials which adequately inhibit polymerization during the production and recovery of the N-alkylacrylamides by the process of my invention. Any of the known inhibitors of polymerization of acrylic compounds, such as hydroquinone, may be employed in place of the p-tert-butylcatechol used in some of the above examples.

The process described in this application is applicable to the production of N-alkylacrylamides from the esters of acrylic acid and its homologs having the general formula



where R is hydrogen or an alkyl radical and R' is an alkyl radical.

I claim:

1. A process for the production of an N-alkylacrylamide which comprises heating an N-alkyl-beta-aminopropionic-N-alkylamide in which each of the N-alkyl groups contains 1 to 2 carbon atoms at temperatures in the range 100° to 150° C. and thereby decomposing the aminopropionicamide to form an N-alkylacrylamide and an alkylamine, said heating of the aminopropionicamide being carried out under pressures below atmospheric at which the alkylamine is vaporized and distilled off and the aminopropionicamide and N-alkylacrylamide are retained as liquid separated from the vaporized alkylamine.

2. The process of claim 1 in which the N-alkyl-

beta-aminopropionic-N-alkylamide is N-methylaminopropionic-N-methylamide.

3. The process of claim 1 in which the N-alkyl-beta-aminopropionic-N-alkylamide is N-diethylaminopropionic-N-diethylamide.

4. A process which comprises destructively distilling beta-(di-loweralkylamino)-N,N-di-(lower alkyl) propionamide to form di-loweralkylamine and N,N-di-(lower alkyl) acrylamide at a temperature and pressure at which the di-lower alkylamine is vaporized and distilled off, while the N,N-di-(lower alkyl) acrylamide remains in the liquid residue, and recovering the N,N-di-(lower alkyl) acrylamide from said liquid residue.

5. A process for the production of an N-alkylacrylamide which comprises heating at elevated temperatures an N-alkyl-beta-aminopropionic-N-alkylamide in which each of the N-alkyl substituents consists of a lower alkyl radical containing 1 to 5 carbon atoms to produce an N-alkylacrylamide and an alkylamine and separating said N-alkylacrylamide from the alkylamine.

6. A process which comprises destructively distilling an N-mono-(lower alkyl)-beta-aminopropionic-N-mono-(lower alkyl) amide in which each of the N-alkyl groups contains 1 to 5 carbon atoms, to form alkylamine and an N-alkylamide, said destructive distillation being carried out at a temperature and pressure at which the alkylamine is vaporized and distilled off, while said N-alkylamide is retained in the liquid residue, and recovering said N-alkylamide from said liquid residue.

7. A process which comprises destructively distilling an N-lower alkyl-beta-aminopropionic-N-lower alkylamide in which each of the N-alkyl substituents contains 1 to 5 carbon atoms to vaporize therefrom alkylamine and an N-alkylamide, and cooling the resulting vapors to temperatures below the condensation temperature of said N-alkylamide and above the condensation temperature of said alkylamine, thereby separating N-alkylamide as condensate from vapors of said alkylamine.

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