AMINATION OF ALKYL HALIDES
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ABSTRACT OF THE DISCLOSURE

Alkyl halides are aminated by reacting them with dialkyl secondary amines in a two-phase aqueous-organic system wherein alkaline material is added at a controlled rate.

This invention relates to the amination of alkyl halides to form tertiary amines. More specifically, the instant invention relates to a process for aminating higher alkyl chlorides preferably having from 4 to 22 carbon atoms with secondary amines such as dimethylamine. These tertiary amines are useful for the preparation of surface active agents.

Broadly, the amination of alkyl halides with ammonia and amines has been known for many years. For example, U.S. Patent 1,836,047 and German Patent 676,331 showed the reaction of alkyl bromides and chlorides with secondary amines. At the termination of the reaction an alkaline material was added to neutralize the liberated hydrogen halide. In these systems the use of large excesses of the amines, e.g., several times the theoretical requirements, was suggested; this excess served to fix or react with the liberated hydrogen halide. Such procedure is not satisfactory because the large excess of amine, though favorable to the reaction equilibrium, necessitates large equipment and the separation and handling of the unreacted amine.

Later developments in this basic amination reaction included the use of an alkaline material other than the amine to neutralize the hydrogen halide during the reaction. See, for example, U.S. Patents 2,172,622 and 2,870,207 and German Patent 1,022,417. In these latter patents, the alkaline material was added at the beginning of the process.

While the addition of the alkaline material instead of or in conjunction with the amine represents an improvement over the earlier process using the great excesses of the amine per se, the resultant process still fails to achieve the desired conversion to the higher amines and the necessary product quality.

In accordance with this invention, it has been found that high conversions of the reactants to the aminated product can be obtained by using from 1.6 to 4 times the theoretical amount of the secondary amine and adding the alkaline material at a controlled rate during the reaction. The reaction is carried out in a two phase system consisting of an aqueous phase and an organic phase. It is essential to the practice of the invention that the alkaline material not be completely added at the beginning of the reaction. It has been found that if all the alkaline material is added at the outset, or very rapidly at the beginning of the reaction, the conversion to the desired product is considerably decreased. It is hypothesized that this decrease in conversion results from the hydrolysis of the alkyl chloride to the corresponding alcohol; the hydrolysis being catalyzed by the alkaline material. Additionally, the alkyl chloride is dehydrohalogenated to an alpha-olefin. Not only does the formation of the alcohol and olefin reduce the amount of the desired end-product, but it also makes subsequent purification procedures far more difficult, since these materials are separable only with complex high vacuum distillation apparatus.

The rate at which the alkaline material is added is related to the rate of formation of the amine hydrohalide. As is well known in the art, the amine hydrohalide is formed by the reaction of the alkyl amine with the hydrohalide evolved from the basic reaction between the amine and the alkyl halide. The alkaline material is added at a rate sufficient to convert the amine hydrohalide back to the free amine as it is formed, but not so rapidly as to permit the accumulation of a substantial excess of the alkaline material. This procedure serves to make available the maximum amount of free amine, a factor favorable to the desired reaction, while minimizing the formation of the aforesaid undesired by-products by eliminating excess alkaline material.

The alkaline material is suitably added continuously over the course of the first 1/2 hours of the reaction, a period in which over 90% of the reaction takes place. In practice a substantially constant rate of addition for about one hour gives the desired result if the addition commences about 15 minutes after a significant rate of reaction begins.

As previously noted the reaction is carried out in a two phase system. Sufficient water must be present to dissolve the bulk of the salt formed during the reaction. If less water is used salt accumulates and complicates phase separation and handling. Generally at least one and one-half parts by weight of water are present for each part of salt.

The basic amination reaction of the invention may be summarized as follows:

\[ RX \rightarrow 2HR'R'\rightarrow RNH'RN' \rightarrow \left[ \text{NH}_2 \text{RNH}_2 \right] + X^{-} \]

R is an alkyl group having from 4 to 22 carbon atoms, preferably from 8 to 18. It may be straight or branched chain with an odd or even number of carbon atoms. R' and R'' are alkyl groups having from 1 to 4 carbon atoms, preferably 1 to 2. X is a halide group, such as iodide, chloride, or bromide, most preferably the chloride.

The tertiary amines of the instant invention include octyl dimethylamine, dodecyl dimethylamine, tridecyl di-
methylamine, heptadecyl dimethylamine, octadecyl di-
methylamine, hexyl diethyamine, pentadecyl diethyl-
amine, decyl dipropylamine, dodecyl dibutylamine, eycyl methylthethylamine, nonyl ethylpropylamine and undecyl methylpropylamine.

The reaction is exothermic and the rate of reaction is a function of the temperature, the molecular weight of the alkyl group and the particular halide. At a constant temperature the lower molecular weight alkyl compounds are the more reactive. Iodides are more reactive than the bromides; the bromides more reactive than the chlorides.

The reaction temperature may be from 50 to 190° C., most preferably, from 80 to 150° C. After the reaction is almost complete, it is often desirable to heat the reactor to a higher temperature, e.g., from 140 to 170° C., for a period of 15 min. to 3 hrs. to insure complete reaction. When the reactor is heated to reaction temperature an exotherm will occur. At this time the addition of the alkaline material may be commenced. The pressure is 125 to 225 p.s.i. during the course of the reaction and the reaction time may vary from 3 to 8 hrs. depending on the particular reactants employed.

The alkaline materials which may be employed are the soluble inorganic strong bases such as metal hydroxides, carbonates and bicarbonates, and, also the basic metal oxides and salts. Such materials may be readily selected by those skilled in the art. Preferred materials are the alkali and alkaline earth metal hydroxides. These include sodium hydroxide, potassium hydroxide and calcium hy-
droxide. As a matter of convenience these materials may be added to the reaction mass as a 10 to 50% aqueous solution.

Sufficient alkaline material is employed to neutralize the amine hydrohalide formed in the reaction. A slight molar excess is advantageous to ensure that no amine hydrohalide is left unconverted to free amine in the system. At the end of the reaction an excess of alkaline material is not detrimental.

In order to illustrate the invention more fully the following examples are set forth:

EXAMPLE I

The amination is conducted in a 2300-gallon, stainless steel clad, 500 p.s.i. internal reactor. The agitator is set for 10 minutes prior to the charging of reactants. Dodecyl chloride is pumped in from a storage tank until 35 moles are fed to the reactor. After charging the dodecyl chloride, a 50% aqueous solution of dimethylamine is charged until 70 moles are fed. This is a 2:1 molar ratio of the amine to the chloride or a 100% molar excess. During the charging of the dimethylamine, heat is applied to bring the temperature up to 116°C. At the end of the dimethylamine charge and when the batch is up to the 116°C temperature, a solution of 50% of sodium hydroxide is pumped into the batch at a constant rate of 51#/min. in the interval of one hour. A 10% molar excess is added based on the dimethylamine hydrochloride formed.

At 116°C the batch is maintained on automatic temperature control during which the heat from the exothermic reaction is taken away from the batch with cold water in the coil. Little cooling is required after the first one and one half hours, since the reaction is almost complete. After three hours the batch temperature is raised to 140°C. steam in the coil, and maintained there for fifteen minutes. This final heating at high temperature insures complete reaction. The batch is then cooled to 260°F. and agitation is turned off. The batch is allowed to settle in the reactor for fifteen minutes, during which time it separates into an amine and salt water phase, both saturated with dimethylamine.

Thereafter the two phases are separated, the unreacted dimethylamine recovered, and the amine phase distilled. The product of the distillation is 33 moles of high purity dodecylamine. This represents a conversion of 94%. After flash distillation an overhead stream consisting of 97% purity dodecyl dimethylamine is obtained. This product is water white and meets an APHA 25 color specification.

EXAMPLE II

The procedure described in Example I is repeated with n-octyl chloride and stearyl chloride. In both cases the same reaction conditions are used. The n-octyl dimethylamine and stearyl dimethylamine are obtained in yields of 93% and 92%, respectively. The product quality after flash distillation is about 97% of the alkyl dimethylamine meeting an APHA 25 color specification.

EXAMPLE III

Following the procedure of Example I a primary tri-

decyl chloride containing mixed branched chain isomers is aminated. The reaction temperature, however, is maintained at 150°C for 6 hours. A yield of 94% of the tri-decyl dimethylamine is obtained at a 92% purity after flash distillation. The APHA 25 color specification is met.

EXAMPLE IV

Using the procedure described in Example III an alkyl chloride derived from a C12–C15 mixed primary alcohol obtained from the wax cracking process is aminated. The yield is 90%, the purity 87% and color is water white meeting the APHA 25 specification.

Having thus described our invention, what we claim and desire to protect by Letters Patent is:

1. A process for the amination of an alkyl halide which comprises: reacting an alkyl halide, wherein said halide is a chloride, bromide or iodide, with 60 to 300% of a molar excess of a lower dialkyl secondary amine in a two phase aqueous-organic system at a temperature from 50 to 190°C, and thereby evolving an amine hydrohalide; adding an alkaline material continuously over the course of the first one and one-half hours of said reaction so as to form, with said amine hydrohalide as it is evolved, a halide salt of said alkaline material, such continuous addition being controlled so as to prevent the formation of a substantial excess of said alkaline material, at least one and one-half to four parts by weight of water being present for each part of said salt in said aqueous-organic system to dissolve the bulk of said salt; and thereafter recovering the aminated product.

2. The process of claim 1 wherein said alkyl halide is an alkyl chloride having 4 to 22 carbon atoms.

3. The process of claim 1 wherein the alkyl halide is an alkyl chloride, the secondary amine is a dialkyamine, the molar excess of the amine is about 2 to 1, and the alkaline material is an alkali metal hydroxide.

4. The process of claim 3 wherein the alkyl chloride has from 8 to 18 carbon atoms and the dialkyamine is dimethylamine.

5. The process of claim 1 wherein the alkaline material is an alkali metal hydroxide.

6. The process of claim 5 wherein the alkali metal hydroxide is sodium hydroxide.

7. The process of claim 1 wherein the alkyl halide is dodecyl chloride.

8. The process of claim 1 wherein said alkyl halide is an octyl chloride.

9. The process of claim 1 wherein said alkyl chloride is tridecyl chloride.

10. The process of claim 1 wherein said alkyl halide is a mixed alkyl chloride having from 11 to 15 carbon atoms.

References Cited

UNITED STATES PATENTS


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