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3,842,081

**PREPARATION OF AMINOCARBOXYLIC ACIDS
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11 Claims

ABSTRACT OF THE DISCLOSURE

A novel process is provided for preparing aminocarboxylic acids and their salts from certain aminoalcohols in the presence of alkali metal hydroxides and cadmium salts that is characterized by employing high temperatures and very short reaction times.

This invention relates to a novel process for preparing aminocarboxylic acids and their salts.

The preparation of aminocarboxylic acids for aminoalcohols in the presence of alkali metal hydroxides has heretofore been described. Further, the use of metal catalysts, such as cadmium, copper, nickel, zinc, silver, and the like, in the reaction has also been suggested. U.S. Pat. Nos. 2,384,816, 2,384,817 and 2,384,818 are representative of such knowledge.

Several patents have recently issued that demonstrate further efforts to improve upon this general process. U.S. Pat. Nos. 3,535,373, 3,535,374 and 3,535,375, hereinafter 3,535,373 et al., are exemplary and describe the use of alcohol, paraffin and aryl carbinol compounds as promoters for the preparation of aminocarboxylic acid salts from aminoalcohols. In like manner, U.S. Pat. No. 3,578,709 describes a process for preparing nitrilotriacetic acid alkali metal salts from triethanolamine in the presence of alkali metal hydroxides and cadmium catalyst wherein mixtures of alkali metal hydroxides are employed.

These recent methods for preparing aminocarboxylic acids have been extolled, such as in the above-identified patents, for their ability to provide improved yields of the alkali metal salts of the carboxylic acids. In this regard, the basic process art, such as represented by U.S. Pat. Nos. 2,384,816, 2,384,817 and 2,384,818, has been the subject of substantial criticism.

The recent art, as exemplified above, correctly points out the fact that although U.S. Pat. No. 2,384,817 describes the use of cadmium catalysts for the preparation of aminocarboxylic acids in the presence of alkali metal hydroxides the techniques employed and the methods used to determine the yields of desired product were not reproducible and were misleading. Accordingly, the examples presented in this patent series have based their reported yields upon the amount of reaction gas developed during the reaction and/or the chelating effect of the reaction product.

The danger in using chelating effects and gas development as the criteria for yield determination was amply demonstrated and reported in U.S. Pat. No. 3,535,373 et al., at column 2, lines 41 to 45. German Pat. No. 1,809,263 also reports that yields based on gas development are misleading. Further, the German patent states that the data presented in U.S. Pat. No. 2,384,817 are too vague of be useful. Our work, as will be hereinafter described, further confirmed these facts. It is noteworthy that in U.S. Pat. Nos. 3,535,373 et al. there was described an unsuccessful effort to duplicate the teachings of U.S. Pat. No. 2,384,817. Likewise, in Example IV of U.S. Pat. No. 3,578,709 similar difficulty was demonstrated in obtaining acceptable yields using the cadmium catalysts according to the teachings of U.S. Pat. No. 2,384,817.

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Although recent improvements in the art of aminocarboxylic acid production have been made, such as represented by the art herein described, it is also apparent that although increased yields have, in some instances, been obtained, the described processes do not provide a comparatively simple process such as one that would facilitate a commercially feasible operation.

For example, the reaction times required, even with the use of the alcohol, paraffin, aryl carbinol promoters of U.S. Pat. Nos. 3,535,373 et al. the process is unduly long and is described therein as an extended reaction requiring about 8 to 70 hours.

Likewise, reaction times on the order of 6 hours, or more, are employed in U.S. Pat. No. 3,578,709.

It is evident from the recent art, as corroborated by our work, that the yields of aminocarboxylic acid as reported in U.S. Pat. Nos. 2,384,816 et al. are suspect and represent unduly long reaction times on the order of several hours.

It is a clear fact, therefore, that artisans in this field believe that reaction times on the order of several hours to several days are necessary for the cadmium catalyzed conversion of aminoalcohols to aminocarboxylic acids.

Another fact prevalent throughout the pertinent art and of general importance to this background discussion is the belief that high reaction temperatures are to be avoided because of the thermal instability of the aminocarboxylic acids and their salts.

For example, in U.S. Pat. No. 2,384,816 the practitioner is cautioned against the use of high temperatures when oxidizing aminoalcohols by heating in the presence of caustic alkalis because of the general thermal instability of the aminocarboxylic acids and their salts under such conditions.

Adherence to this fact is also evidenced by Dwyer & Mellor *Chelating Agents and Metal Chelates*, Academic Press, New York, 1964, where at page 287 it is stated:

“ . . . The main difficulty in the reaction (of aminoalcohols to yield aminocarboxylic acids) is in preventing the oxidation of the strongly reactive amino groups which are susceptible to attack by alkalis and oxidizing agents . . . ”

The avoidance of high temperatures is likewise taught and practiced in U.S. Pat. No. 3,578,709 and in U.S. Pat. Nos. 3,535,373 et al.

For example, although U.S. Pat. Nos. 3,535,373 et al. generally state that temperatures of about 150° C. to 260° C. can be employed, they state that temperatures from 190° C. to 240° C. are preferred. Reference to any of their examples clearly shows that temperatures higher than 240° C. were strictly avoided.

In like fashion, broad temperatures of 150° C. to 300° C. are generally described in U.S. Pat. No. 3,578,709, but all of the representative examples were conducted essentially within the preferred temperature range described above, i.e., 160° C. to 248° C.

In summary, the prior art recognizes and practices, without known exception, two important beliefs:

(a) The avoidance of high temperatures such as those greater than about 240° C., and

(b) The necessity of long reaction times on the order of hours or more.

In spite of the above knowledge and beliefs, we have surprisingly discovered that we can prepare aminocarboxylic acids from certain aminoalcohols in high yields in the presence of alkali metal hydroxides and cadmium salts at high temperatures, and at times, seemingly impossible according to prior art standards.

Accordingly, an important aspect of our process was the discovery that certain aminocarboxylic acid salts have an unexpectedly high temperature stability in the presence of aqueous alkali metal hydroxides and cadmium salts.