CHEMISTRY LETTERS, pp. 1241-1244, 1974. Published by the Chemical Society of Japan

HYDRODIMERIZATION OF ACRYLONITRILE BY CATHODIC REDUCTION IN LIQUID AMMONIA

Toshiro CHIBA, Yoshiyuki TAKATA, and Akira SUZUKI
Faculty of Engineering, Hokkaido University, Sapporo 060

The electrolytic reduction of acrylonitrile using a mercury cathode in liquid ammonia employing ammonium perchlorate as a supporting salt was examined. It was found that acrylonitrile was dimerized to adiponitrile in an excellent yield without significant formation of by-products under such reaction conditions, compared with the usual cathodic reduction in an aqueous solution.

The cathodic dimerization of acrylonitrile is known to produce adiponitrile,[1)] and this method has been actually industrialized.[2)] Such electrochemical procedures are generally carried out in aqueous solutions, and one of the major problems is that they form propionitrile and oligomers[3)] as by-products. In order to depress these side reactions, it has been pointed out that control of acrylonitrile concentration and pH of the catholyte is necessary. For example, Baizer[4)] described that when the acrylonitrile concentration is higher than 10%, adiponitrile is mainly formed, whereas propionitrile is preferentially prepared in a low acrylonitrile concentration, less than 10%. On the other hand, since the solubility of acrylonitrile in water is only about 7% at 25°C, it is necessary to use a special kind of supporting salt which has an enhancing effect on the maintenance of a high acrylonitrile concentration. One of the typical compositions in the catholyte, is 40% acrylonitrile, 34% tetraethylammonium p-toluenesulfonate and 26% water, and acetic acid should be added continuously to keep the catholyte weak alkaline.

We wish to report here a cathodic dimerization of acrylonitrile to adiponitrile in liquid ammonia using ammonium perchlorate as the supporting salt. Liquid ammonia seems to be appropriate for this reaction in the following points. In liquid ammonia, (a) conductivity of electrolyte is high even at low temperatures; (b) compared with water, solubilities of organic compounds are high, and some of the inorganic salts, especially ammonium salts, are highly soluble; (c) separation of products from the reaction mixture is easy; and (d) pH control to eliminate side reactions such as formation of propionitrile is unnecessary.

Electrolysis was carried out in a 100 ml-beaker shielded from the anode compartment by using a porous cup. A mercury pool was used as the cathode and the anode was a coil of platinum wire. The cell was cooled with dry ice in methanol at -78°C during electrolysis. A representative procedure is as follows. Acrylonitrile (10.6 g) was reduced in a solution containing 12 g of ammonium perchlorate dissolved in 40 g of liquid ammonia at a constant current of 0.55 A. After completion of the reaction, ammonia was removed under reduced pressure, and the residue was extracted with 30 ml of ether. Then, 10 ml of water was added to the residue, followed by dual extractions with 10 ml of ether. The combined extracts were analyzed by glpc Analytical samples were obtained by distillation: fraction 1, b.p. 92-94°C; fraction 2, b.p. 154-156°C/ 15 mmHg. The products were identified by direct comparison with those of authentic samples, indicating that fractions 1 and 2 are propionitrile and adiponitrile, respectively.

The relationship between current density and product yield is summarized in Table I. The current density does not seem to have any influence on the adiponitrile yield in the range of 2.5 to 15 A/dm^2. Although when the electrolysis was carried out at a high current, over 15 A/dm^2, the anolyte was occasionally boiled and a slight contamination of the electrode surface was observed, the yield of adiponitrile was not greatly affected.

Table I. The Effect of Current Density on Product Yield

Constant current (A/dm^2)	Product yield, (%) ADN	PN	Current efficiency for ADN (%)
15	76	6	93
10	77	6	94
5.5	76	3.5	93
2.5	76	2.5	93

Catholyte: AN, 10.6 g; NH_4ClO_4, 12.0 g; NH_3, 40 g. Consumed current, 0.11 F. ADN, Adiponitrile. PN, Propionitrile. AN, acrylonitrile.

In Table II, the effect of the supporting salt concentration on adiponitrile yield is shown. The conductivity of electrolyte was increased by the rise in concentration, although the use of a large amount of supporting salt rendered the solution heterogeneous. The yield of adiponitrile did not vary significantly by changing the concentration of the supporting salt, but the yield of propionitrile gradually increased

Table II. The Effect of Supporting Salt Concentration on Product Yield

NH_4ClO_4 (g)	Product yield, (%) ADN	PN	Current efficiency for ADN (%)
4	74	1.5	93
8	77	2	95
12	76	3.5	95
20	80	5	88

Catholyte: AN, 10.6 g; NH_4ClO_4; NH_3, 40 g. Consumed current, 0.11 F. Constant current, 0.55 A.

Table III. The Relationship among Acrylonitrile Concentration, Consumed Current and Product Yield.

AN (g)	Consumed current (F)	Product yield, (%) ADN	PN	Current efficiency for ADN (%)
5.3	0.055	68	3	81
5.3	0.11	63	19	47
10.6	0.11	76	3.5	93
10.6	0.165	70	4.5	69
10.6	0.22	77	11	63
15.9	0.11	71	2	97
15.9	0.165	74	2.5	91
15.9	0.22	83	7	83

Catholyte: AN; NH_4ClO_4, 12.0 g; NH_3, 40 g. Constant current, 0.55 A.

The relationship between the consumed current and product yield in each acrylonitrile concentration is indicated in Table III. A high selectivity of adiponitrile formation was observed until the acrylonitrile concentration decreased to about a half of its initial value, but thereafter propionitrile was formed remarkably. Since the formation of the by-product is markedly dependent upon the initial acrylonitrile concentration, it is necessary to maintain a certain level of concentration of the catholyte in order to obtain adiponitrile selectively.

When water was added to the catholyte system described above, gas evolution from the cathode surface was observed, and both the yield of adiponitrile and current efficiency showed a remarkable decrease.

Although it is known that acrylonitrile reacts with ammonium hydroxide to give α-aminopropionitrile and bis(α-cyanoethyl)amine under low pressure,5) both reactions were hardly detected in the present experiments. Consequently, the present procedure is considered to be a convenient synthetic method of adiponitrile from acrylonitrile under mild conditions.

References

1) Monsanto, US-Pat. 3193481 (1963).

2) See, for example, F. Beck, Angew. Chem., 84, 798 (1972).

3) Asahi Chem. Ind., Jap. Pat. 26489 (1965).

4) M. M. Baizer, J. Electrochem. Soc., 111, 215 (1964).

5) S Buc, " Organic Syntheses ", Coll. Vol. III, p. 93 (1955).

(Received August 26, 1974)