

Baizer M M. Electrolytic reductive coupling. I. Acrylonitrile.
J. Electrochem. Soc. 111:215-22, 1964.
[Central Research Dept., Monsanto Chemical Co., St. Louis, MO]

The efficient conversion of acrylonitrile to adiponitrile by electrolytic reductive coupling is described. [The SCI⁹ indicates that this paper has been cited in over 140 publications.]

Manuel M. Baizer
School of Engineering and
Applied Science
University of California
Los Angeles, CA 90024
and
Department of Chemistry
University of California
Santa Barbara, CA 93106

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Although I did not become aware of the facts until after I had begun work on the project, O. Bayer had years earlier mentioned the desirability of converting acrylonitrile (AN) to adiponitrile (ADN). My immediate impetus late in 1959 to re-examine the AN→ADN process was a paper by Knunyants and Vyazankin¹ that had come to the attention of my supervisors, who assigned the project to me. After several months I made a first formulation of the technical problems.

I investigated the use of hydrotropic salts as both solvents and electrolytes. These alkali metal salts of aromatic sulfonic acids in concentrated aqueous solution had been found years earlier by McKee² to dissolve amazing quantities of ordinarily water-insoluble organic compounds. (I later named them McKee salts in his honor.) I found that a mixture of saturated sodium and potassium *p*-toluenesulfonates did indeed dissolve up to 20 percent of AN.

Using a divided cell and a mercury cathode, I began to get exciting yields of ADN. However, the ADN was accompanied by substantial quantities of by-products. It was easy to eliminate these by-products by controlling the pH of the catholyte. However, no manipulation of the electrochemical

parameters substantially reduced the yield of one of the by-products! Then I realized that all I might have achieved was an electrochemical equivalent of the Knunyants and Vyazankin amalgam procedure with perhaps some improvements.

It was time to rethink the technical problems. I succeeded in eliminating the amalgams being formed *in situ* by using a cation that is not discharged at the same potential at which AN is reduced and retaining the hydrotropic character of the solvent/supporting electrolyte. Tetraalkylammonium salts of aromatic sulfonic acids were even more hydrotropic than McKee's salts, so that by using these electrolytes even at mercury, formation of by-products could be eliminated. Yields and current efficiencies quickly went from 50 to 75 to 100 percent.

Only six months or so had elapsed from the initial experiments to this point. The vice president of our company then asked if I could do it without electricity! Yet the possible merit of a process that was 100 percent efficient and that met projected cost estimates could not be overlooked. So I, an organic chemist, set off to explore the scope of the reductive coupling process. There was no objection. The manpower quota was even increased 100 percent, i.e., it became a two-man project. After electrolyzing all the types of acrylic acid derivatives that Knunyants had hydrotropized, I postulated that reductive coupling, homo- and mixed, should be valid for all activated olefins.

This paper has been highly cited because it was the first of a large series of papers published by me and my colleagues that expanded electrolytic reductive coupling into a methodology of very wide scope. By 1964 patent applications had been filed and construction of a full-scale plant was at last well along. The installation using this process at Decatur, Alabama, went onstream in 1965 at an initial capacity of 32,000,000 lbs./yr. It has been operating continuously since then and has been expanded in several stages. A second plant, in Teeside, England, has been operating since about 1977.

As a result of this work, Monsanto Company received the Kirkpatrick Award in 1965 and I received the ACS Award for Creative Invention in 1976. Danly and I jointly delivered the Armstrong Memorial Lecture in England in April 1979. Danly also received the Vittorio deNora-Diamond Shamrock Award of the Electrochemical Society in May 1984 for his role in commercializing the process.

Some of the many more recent publications in this field are cited below.³⁻⁶

1. Knunyants I L & Vyazankin N S. Reduction dimerization of derivatives of alpha, beta-unsaturated acids. *Dokl. Akad. Nauk Otdel. Khim. Nauk* 113:112-15, 1957. (Cited 15 times.)
2. McKee R H. Use of hydrotropic solutions in industry. *Ind. Eng. Chem.* 38:382-9, 1946.
3. Roberts R, Ouellette R P & Cheremisinoff P N. *Industrial applications of electroorganic synthesis*. Ann Arbor: Ann Arbor Science, 1982. 205 p.
4. Pletcher D. *Industrial electrochemistry*. London: Chapman and Hall, 1982. 325 p.
5. Ebersson L. Electro-organic synthesis. (Scheffold R, ed.) *Modern synthetic methods*. Frankfurt am Main and Aarau: Otto Salle Verlag and Verlag Sauerländer, 1980. Vol. 2, p. 2-89.
6. Köster K & Wendt H. Electro-organic syntheses. (Bockris J O'M, Conway B E, Yeager E & White R E, eds.) *Comprehensive treatise of electrochemistry, Volume 2. Electrochemical processing*. New York: Plenum Press, 1981. p. 251-99.