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THE ELECTROCHEMICAL REDUCTION OF BENZOYL AZIDE IN ACETONITRILE

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The electrochemical reduction of benzoyl azide in acetonitrile was investigated. As the products, N-benzoyl benzamide, benzamide, and benzoic acid were obtained, and the presence of azide anion (N_3^-) was observed in the electrolytic solution. A tentative mechanism of the electrochemical reduction was advanced.

A large number of thermal and photochemical decompositions of azides have been carried out for studies of nitrene chemistry.[1] The electrochemical reduction of azides, however, has not been reported. In the present paper, we wish to report on the study of electrochemical reduction of benzoyl azide by cyclic voltammetry or by macro-scale controlled potential electrolysis.

At a glassy carbon electrode, the cyclic voltammetric behavior of benzoyl azide in acetonitrile (AN) containing tetraethylammonium perchlorate (TEAP) as the supporting electrolyte is shown in Fig. 1. The reduction wave was seen at around - 1.5 V (vs.SCE) on the first cathodic sweep. The reduction was confirmed to proceed by one electron process in comparison with the reduction of nitrobenzene in AN.[2] When the reduction of benzoyl azide was reversed after scan of the cathodic peak, a small reoxidation peak was observed at + 0.75 V (vs. SCE).

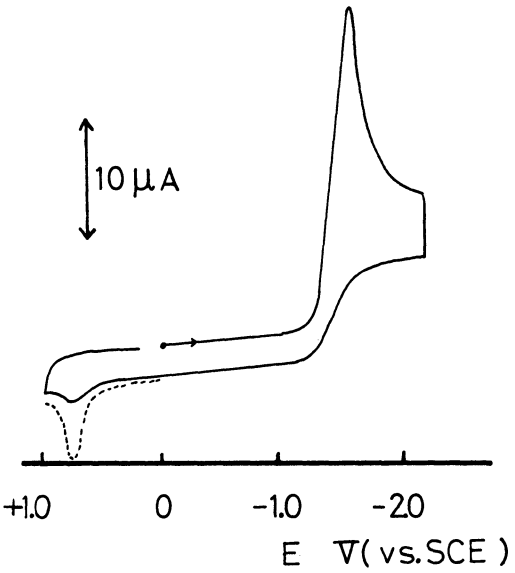


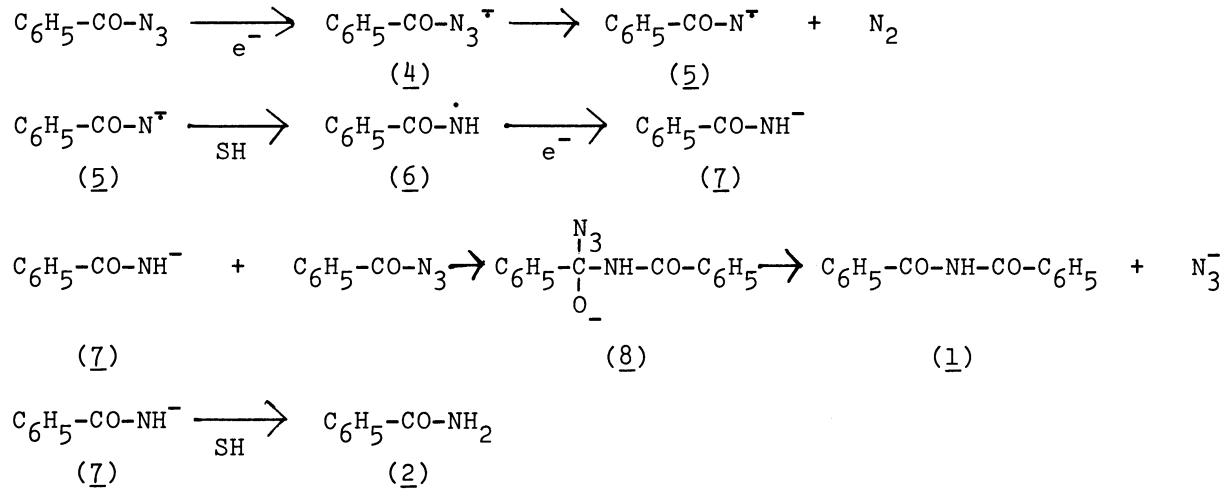
Fig. 1. Voltammogram of 1.0 mM benzoyl azide in 0.1 M TEAP-AN. Scan rate, 0.1 V/sec.
----- Voltammogram of sodium azide.

Benzoyl azide (1 mmol) in AN (35 ml) containing TEAP was electrolyzed, at room temperature under an atmosphere of nitrogen, by using a glassy carbon cathode at a potential slightly more cathodic than the reduction wave. Complete electrolysis involved transfer of close to 1 mF/mmol. The completely electrolyzed solution gave an oxidation wave at + 0.75 V (vs. SCE) by cyclic

voltammetry, and the cathodic wave of benzoyl azide disappeared. The peak potential of the oxidation wave coincided with that of sodium azide (azide anion). A comparison of the anodic peak height with that of sodium azide showed the formation of about 0.5 mmol azide anion.

Liquid chromatographic analysis of the reduction products revealed the presence of N-benzoyl benzamide (1), benzamide (2), and benzoic acid (3). The products were seperated and collected liquid chromatographically. IR and NMR spectra of each product were identical with those of authentic samples. The yield of each product was determined by the chromatograph, naphthalene being used as the internal standard. Thus, 1, 2, and 3 were obtained in a yield of 48, 17, and 19 %, respectively.

A tentative mechanism is shown in the following scheme.



The anion radical of benzoyl azide (4) is decomposed to the anion radical of benzoylnitrene (5). 5 is rapidly protonated to give benzamide radical (6),[3] followed by one electron reduction to afford 7. A nucleophilic attack of the anion, 7, on the carbonyl carbon atom of benzoyl azide leads to an intermediate (8), which loses an azide anion to give N-benzoyl benzamide (1).[4] On the other hand, 7 can be transformed into benzamide (2) by protonation. The formation of benzoic acid may originate in a C-N bond cleavage of 4, but the mechanism is not clear. Further mechanistic study is now in progress.

References and Note

1) W. Lwowski, Ed., "Nitrenes", Interscience Publishers, New York (1970) ; R.A. Abramovitch, "Nitrenes", in "Organic Reactive Intermediates", ed. by S.P. McManus, Academic Press, New York (1973).
2) E.R. Brown, H.L. Hung, T.G. McCord, D.E. Smith, and G.L. Booman, Anal. Chem., 40, 1424 (1968).
3) In our AN there is a possible source of protons, namely, water as impurity.
4) T. Shingaki, Nippon Kagaku Zasshi, 80, 55 (1959).

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