

The Polarographic and Electrolytic Reduction of the Cyano-group in Substituted Benzonitriles

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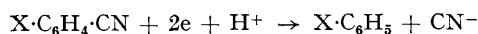
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THE polarographic reduction of benzonitrile in 75% dioxan containing 0.05M-tetraethylammonium bromide shows two waves at -2.26 and -2.37 v, whereas in *NN*-dimethylformamide containing 0.1M-tetrapropylammonium perchlorate one wave at -2.74 v (against silver/silver perchlorate electrode) was reported.² In the latter reaction the formation of a radical has been proved. Owing to the anomalous behaviour of the *p*-cyano-derivatives in linear free-energy relationships,³ in the reaction of *p*-cyanobenzoic acid with diphenyldiazomethane,⁴ and in the polarographic reduction of substituted benzophenones⁵ it was decided to study substituted benzonitriles in more detail.

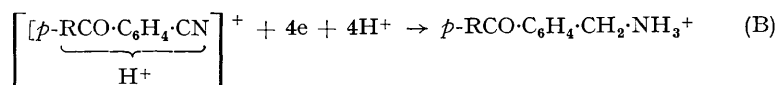
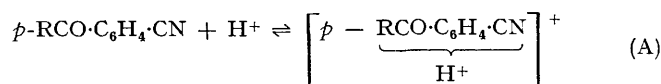
In acid solution benzonitriles of the type *p*-RCO·C₆H₄·CN (for R = H, Me) undergo reduction at -0.70 v (against s.c.e. in 0.1M-sulphuric acid) according to the scheme:

with reduction of the protonized carbonyl group occurring in a subsequent step. A four-electron exchange was proved from the wave-height and also coulometrically. The rate of protonation, which is expected to occur at the cyano-group, limits the height of the four-electron step, which decreases at pH values >1.5 . The formation of the benzylamine derivative was proved by controlled potential electrolysis with subsequent reaction with ninhydrin, polarography, and comparison of the u.v. spectra with that of the *p*-RCO·C₆H₄·CH₂·NH₂.

In neutral solution, compounds of the type X·C₆H₄·CN (where X = *p*-CO₂⁻, *p*-SO₂·NH₂ and *m*-SO₂·NH₂) are reduced according to the scheme:



The number of electrons transferred was determined as above, and the formation of cyanide



¹ M. v. Stackelberg and W. Strocke, *Z. Electrochem.*, 1949, **53**, 118.

² P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 1963, **85**, 683.

³ P. Zuman, *Coll. Czech. Chem. Comm.*, 1960, **25**, 3225.

⁴ A. Talvik, P. Zuman, and O. Exner, *Coll. Czech. Chem. Comm.*, 1964, **29**, 1266.

⁵ P. Zuman and V. Nauta, unpublished results.

ions was detected after controlled-potential electrolysis. The anodic polarographic waves of cyanides were used for detection, and also the reaction with barbituric acid after oxidation by chloramine T was used.

That the reduction of the cyano-group would occur more easily than that of the carbonyl group was entirely unexpected. The difference in the course of reduction in acid and in neutral media is analogous to that found for 2- and 4-cyanopyridines.⁶ The products obtained in acid solutions

were in accordance with the results obtained for electrolysis with lead electrodes⁷ and by chemical reductions.⁸ As the course of electrolysis at a mercury-pool electrode was the same as with a dropping-mercury electrode, then electrolysis in acid media can be used for the synthesis of amines $p\text{-RCO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}_2$, whereas in neutral solutions the cyano-group can be removed from $\text{X}\cdot\text{C}_6\text{H}_4\cdot\text{CN}$.

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⁶ J. M. S. Jarvie, R. A. Osteryoung, and G. J. Janz, *Analyt. Chem.*, 1956, **28**, 264; J. Volke, R. Kubíček, and F. Šantavý, *Coll. Czech. Chem. Comm.*, 1960, **25**, 1510; E. Laviron, *Compt. rend.*, 1960, **250**, 3671; J. Volke and J. Holubek, *Coll. Czech. Chem. Comm.*, 1963, **28**, 1597; H. Lund, *Acta Chem. Scand.*, 1963, **17**, 2325.

⁷ F. B. Ahrens, *Z. Elektrochem.*, 1896, **3**, 99; K. Ogura, *Mem. Coll. Sci. Kyoto Univ.*, 1929, [A]12, 339.

⁸ W. H. Carothers and R. Adams, *J. Amer. Chem. Soc.*, 1925, **47**, 3051; A. Albert and D. Magrath, *J. Chem. Soc.*, 1944, 678.