Reversible Two-electron Cathodic Reduction of Nitropyridines

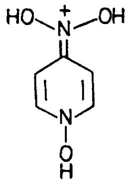
By ANDRÉ DARCHEN* and CLAUDE MOINET
(*Laboratoire d'Electrochimie, Université de Rennes, Avenue du Général Leclerc,* 35031 *Rennes Cédex, France*)

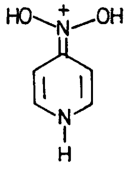
Summary In acidic aqueous ethanolic media, at −7 °C, the reversible two-electron cathodic reduction of nitropyridines ($PyNO_2$) leads to the corresponding dihydroxyamines [$PyN(OH)_2$] which produce nitrosopyridines (PyNO) by elimination of water.

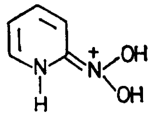
WE report here the two-electron reversible reduction (1) of 4-nitropyridine *N*-oxide (I), 2-nitropyridine (II), 3-nitropyridine (III), and 4-nitropyridine (IV), thus reconsidering the well known irreversible four-electron process for the reduction of nitro-compounds.[1]

$$PyNO_2 + 2e + 2H^+ \rightleftharpoons PyN(OH)_2 \quad (Py = Pyridine) \qquad (1)$$

Up to now, only a few papers[2,4] refer to reduction processes involving less than four electrons and showing some reversibility. The characteristics of the new reversible system (1) described here are consistent with the structure for dihydroxyamines suggested for the two-electron product[5] and recently observed.[3,4] Moreover we have established that the four-electron reduction of these nitro-compounds takes place by an *E.C.E.* mechanism.


(V)


(VI)


(VII)

At −7 °C, polarograms of compounds (I)-(IV) show a first wave whose height, depending upon pH and the period of the mercury drop, corresponds to a process involving less than four electrons (Figure). For (II), (III), and (IV) second and third waves are observed at −1·2 to −1·5 V† the total heights of which correspond to processes involving four and six electrons respectively. The three waves observed correspond to the successive formation of $PyN(OH)_2$, PyNHOH, and $PyNH_2$. As the temperature is raised the first wave increases in height while the second wave decreases. At 25 °C, the height of the first wave corresponds to four electrons except for (IV) as already reported.[6] For (I), the first wave behaves similarly but the reduction of the N → O group complicates interpretation of the succeeding waves. Cyclic voltammetry shows the anodic oxidation of dihydroxyamines taking place at potentials corresponding to reduction of nitro-groups. The degree of reversibility depends upon pH and the position of the nitro-group in the pyridine ring (Table).

TABLE. Cyclic parameters for the first wave [5 × 10^{-4} M nitropyridines in ethanol-N-H_2SO_4 (1 : 1); sweep rate 1 V s^{-1}; −7 °C; all potentials expressed in V *vs.* S.C.E.].

	Ep_c	$Ep_{c/2}$	$Ep_{a/2}$	$\lvert Ep_{c/2} - Ep_{a/2}\rvert$	ip_a/ip_c
(IV)	+0·084	+0·112	+0·092	0·020	1
(I)	−0·008	+0·024	+0·016	0·008	1
(II)	−0·044	+0·008	+0·060	0·052	0·84
(III)	−0·112	−0·068	+0·108	0·176	0·40

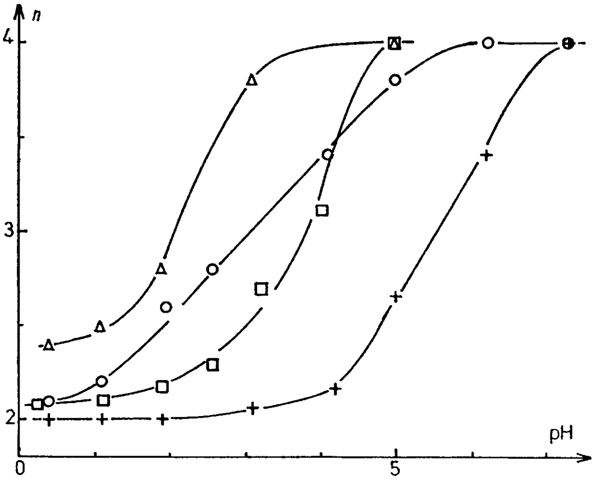


FIGURE. The heights of the first polarographic waves are expressed by the number of electrons transferred [5 × 10^{-4} M nitropyridines in ethanol-diluted H_2SO_4 Britton–Robinson buffers (1 : 1); − 7°C; drop period 1 s; □ : (I); ○ : (II); △ : (III); + : (IV)]. pH values are measured at 25 °C only for the buffer fractions.

At 0 °C, and pH 0—2, nitroso-compounds are observed during the course of electrolysis at a controlled potential corresponding to the first wave, as a result of the irreversible elimination of water from the dihydroxyamines [reaction (2)]. At the potential used, the nitroso-compounds are

$$PyN(OH)_2 \rightarrow PyNO + H_2O \qquad (2)$$

reduced [reaction (3)] to stable hydroxylamines.

$$PyNO + 2e + 2H^+ \rightleftharpoons PyNHOH \qquad (3)$$

For the *E.C.E.* mechanism described by the sequence of reactions (1)—(3) the rate of the chemical reaction (2) controls the overall four-electron process. At −7 °C, step (2) is relatively slow and permits reversible two-electron reduction. The chemical stability of the reduction product, deduced from the wave-heights (Figure) and the degree of electrochemical reversibility (Table) suggest that the protonated dihydroxyamines [structures (V), (VI), and (VII)] are stabilized by conjugation.

(*Received*, 21*st April* 1976; *Com.* 435.)

---

† All potentials refer to the saturated calomel electrode (S.C.E.).

‡ For (IV), at a sweep rate of 1 V s^{-1}, $Ep_c - Ep_{c/2}$ increases from 0·028 to 0·056 V when the pH varies from 0 to 5. However ip_a/ip_c remains unity.

[1] S. G. Mairanovskii, 'Catalytic and Kinetic Waves in Polarography,' Plenum Press, New York, 1968, p. 124.

[2] P. Zuman, O. Manousek, and S. K. Vig, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1968, **19**, 147; M. Heyrovsky, S. Vavricka, and L. Holleck, *Coll. Czech. Chem. Comm.*, 1971, **36**, 971.

[3] A. Darchen and C. Moinet, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1975, **61**, 373.

[4] A. Darchen and C. Moinet, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1976, **68**, 173.

[5] H. Lund, in M. M. Baizer, 'Organic Electrochemistry,' Marcel Dekker, New York, 1973, p. 326; A. P. Tomilov, 'The Electrochemistry of Organic Compounds,' I.P.S.T., Halsted Press, New York, 1972, p. 248.

[6] J. Holubek and J. Volke, *Coll. Czech. Chem. Comm.*, 1960, **25**, 3286.

Printed by Heffers Printers Ltd Cambridge England