

THE CATHODIC CLEAVAGE OF THE 4-NITROBENZYLOXYCARBONYL GROUP
FROM AMINE DERIVATIVES IN APROTIC CONDITIONS

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Many deprotection reactions are known to occur
successfully by electrolysis¹⁻⁴.

The cathodic reduction of the 4-nitrobenzyloxycarbonyl
amides in DMF/Bu₄NBF₄ (0.1 mol dm⁻³) at a vitreous carbon
electrode occurs at about -1.2V vs SCE and on the timescale

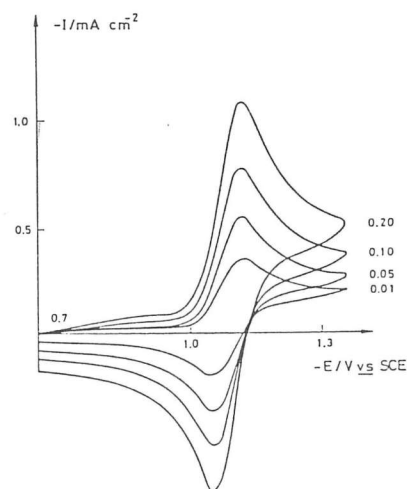


Figure 1 - Cyclic voltammograms run between -0.7 and -1.3 V for $Z(NO_2)NHC_4H_9$ (2.5 mmol dm^{-3}) in DMF/Bu_4NBF_4 (0.1 mol dm^{-3}). Vitreous carbon disc electrode. Potential scan rates in Vs^{-1} as shown in the figure.

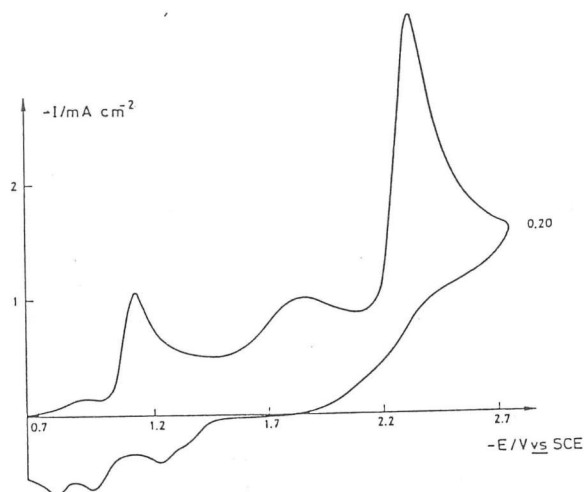



Figure 2 - Cyclic voltammogram of $Z(NO_2)NHC_4H_9$ over a wide range of potentials at a scan rate of 0.2 Vs^{-1} . Other conditions as Figure 1.

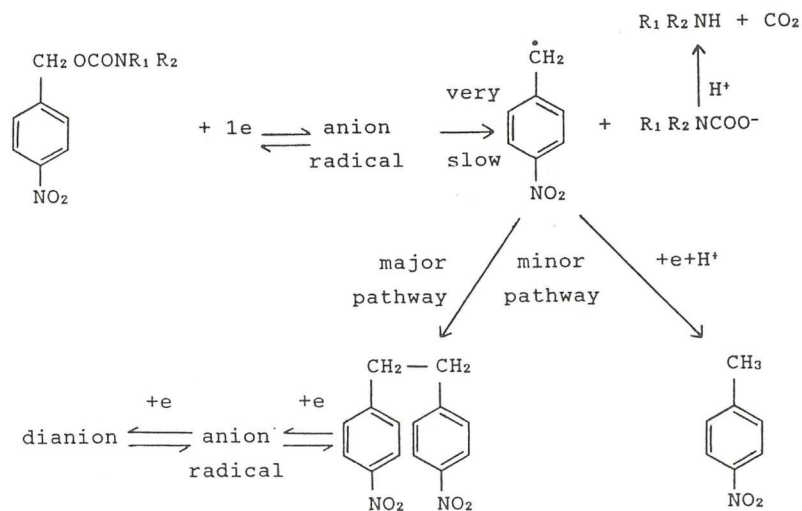
Table 1

Coulometry and yields in amine from the reduction of the urethanes presented (20 mmol dm^{-3}) in DMF/Bu_4NBF_4 (0.1 mol dm^{-3}) at -1.2 V vs SCE . For each case the yields are shown for duplicate experiments.

Urethane	n/F	Yield of amine/%
$Z(NO_2)NHC_4H_9$	1.9	91,86
$Z(NO_2)NHC_6H_{11}$	2.0	78,92
$Z(NO_2)N(C_2H_5)_2$	2.2	95,82
$Z(NO_2)N$ 	2.1	98,88

The influence of proton donors on the reduction of the urethane derivatives was also studied, since most cleavage reactions in peptides have to be carried out in the presence of protons. Methanol is an appropriate proton donor but acetic acid is too strong leading to chemical reactions within the NO_2 group instead of cleavage.

The proposed mechanism is:



References

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SIMULATION OF A NATURAL WATER INTERFACE

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For a better understanding of adsorption of organic matter on particles in natural waters in terms of kinetics and equilibrium, adsorption studies of single compounds and their mixtures on a mercury/aqueous solution interface are being done using alternating current voltammetry^{1,2}. This interface has been chosen since the behaviour of tensioactive compounds on natural hydrophobic interfaces is similar to the one shown on the mercury/water interface. The species adsorbed, the concentration below which there is no adsorption, the time required to attain equilibrium as a function of concentration, and adsorption constants are the major parameters to be determined.

In this context studies were carried out on the adsorption of :
a) some aminoacids existing in natural waters, with a relatively long aliphatic hydrocarbonated chain or π bonds, namely, lysine and phenyl-alanine, b) some aromatic organic ligands, chelating parts of humic and fulvic acids, namely, benzyloiminodiacetic, pyridine-2,6-dicarboxylic and pyridine-2 carboxylic acids, c) mixtures of polyethyleneglycol with a molecular weight of about 8000 and phthalic acid.