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Mechanistic Studies of the Cathodic Reduction of 1,8- Dinitronaphthalene

by

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Mechanistic Studies of the Cathodic Reduction of 1,8-Dinitronaphthalene

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ABSTRACT

The mechanistic studies of the cathodic reduction of 1.8-Dinitronaphthalene (DNN) at Pt cathode in an aceptonitrile solution were done, by cyclic voltammetry, specular reflectance spectroscopy and ESR techniques.

The radical anion was observed as an intermediate during the reduction of 1.8-DNN.

INTRODUCTION

In an early paper [1] preparative results of the electrochemical reduction of some dinitronaphtlenes was mentioned and it was found that although 1,4-dinitronaphthalene and 1,5-dinitronapthalene gave respectively 1-nitro, 4-aminonapthalene and 1,5-diaminonapthalene as a product, 1.8-DNN gave only some resinous material.

This result was in a good accord with the results of Boyd [2,3] who was found that polarographic reduction behaviour of 1,8-DNN was completely different from the other dinitronaphthalenes. According to his results initial reduction wave of 1.8-DNN corresponded to either an eight or ten electron change depending on the acidity of the solution.

In this work electrochemical behaviour of 1,8-DNN in acetonitrile was investigated in a mechanistical way and was tried to observe the reduction intermediate of this compound spectroscopicly.

EXPERIMENTAL

Chemicals: Acetonitrile was purified according to G.J.Edwards [4] and tetra-n-butylammoniumtetrafluoroborate was prepared

by tetra-n-butylammonium hydrogen sulphate and sodium tetrafluoroborate.. 1,8-DNN were obtained from Fluka.

Apparatus: Hi-Tek potentiostat, Chemical Electronics waveform generator and Servagor XY recorder were used for cyclic voltammetry.

Specular Reflectance Spectroscopy (SRS) studies were carried out with the same equipment in the same manner as described for the work done by A.Bewick and G.Robinson (6) Varian E4 ESR spectrometer were used for the ESR experiments. The electrochemical cell for ESR experiments is shown Fig. 1.

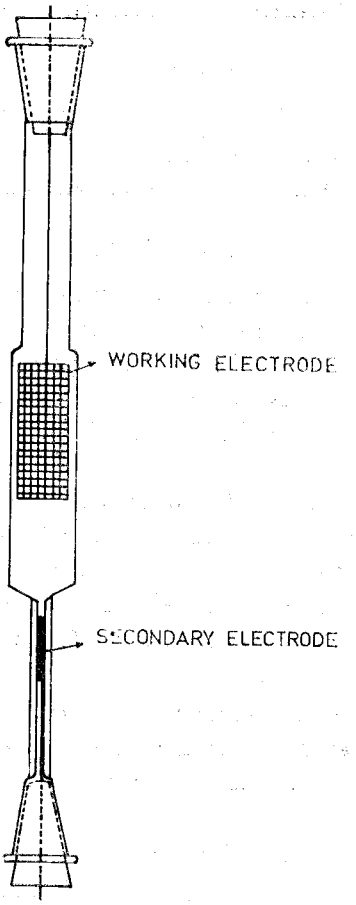

Fig 1

RESULT and DISCUSSION

The kinetic studies of the reduction of 1.8 DNN using cyclic voltammetry over a wide range of sweep speeds showed that the first (lowest potential) cathodic process was reversible in a high sweep speeds and corresponds to one electron change. Fig 2a shows a lineer sweep voltammogram for a 10^{-2}M solution of 1,8-DNN at Pt cathode in acentonitrile. As the sweep speeds decreased the resersiblity of the first wave disappeared gradually. (fig 2 b, c)

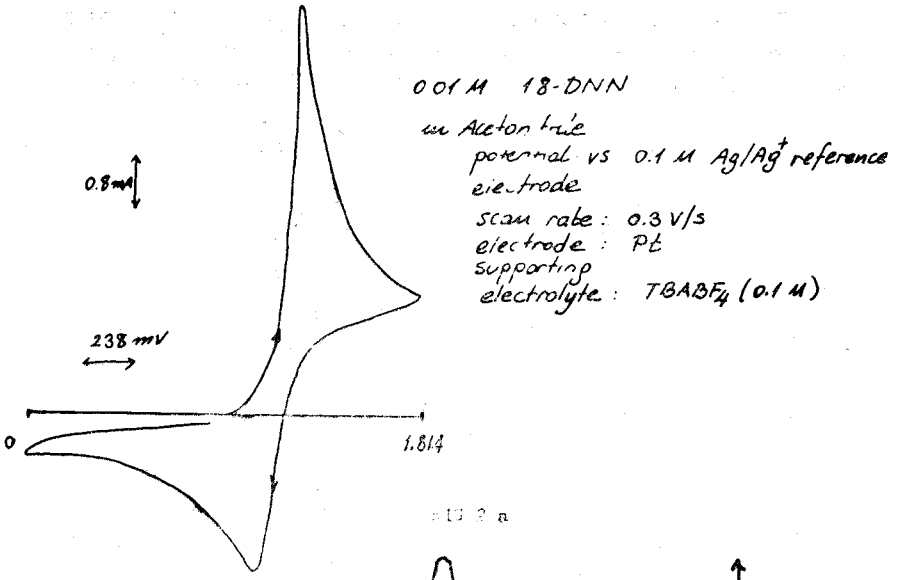

Fig 2 b

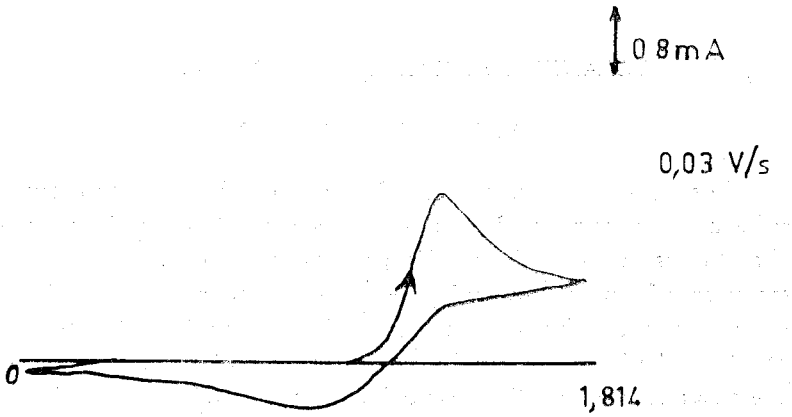

Fig 2 c

The effect of added water on the voltammetry of 1,8-DNN solution is shown in Fig 3. The voltammetry of the dry acetonitrile solution of 1,8-DNN showed one well defined resersible peak.

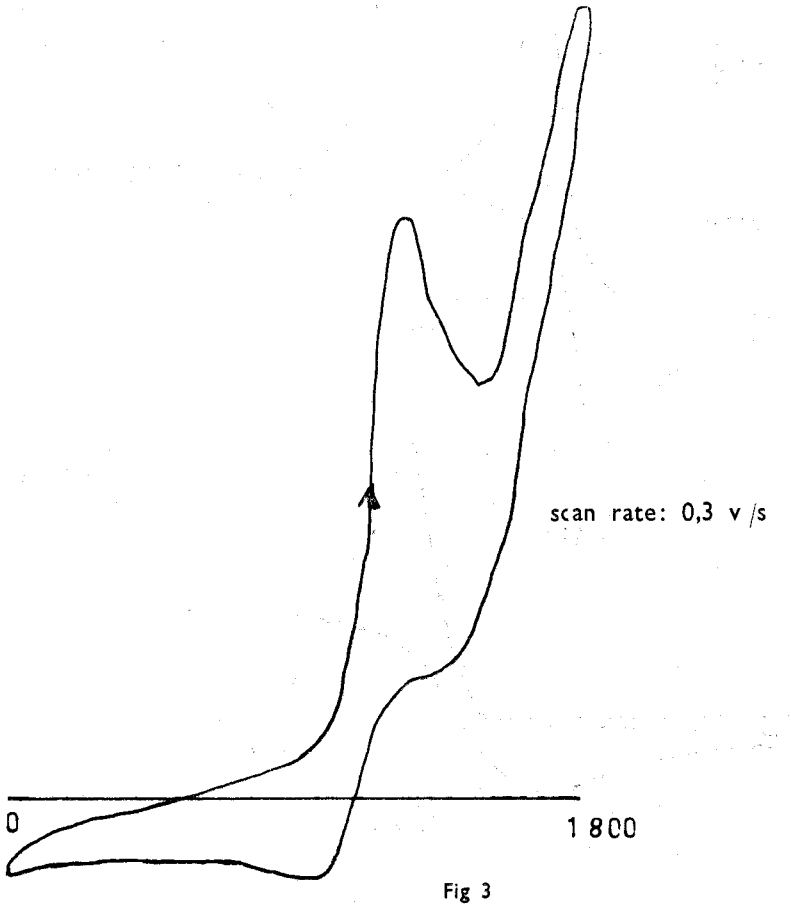

Fig 3

Upon addition of water to a dry acetonitrile solution containing 1,8-DNN the reduction peak was seen to broaden and shift to higher potential while a new second reduction peak at the potential of 1,8 V was appeared. At the same time the reversiblity of the first reduction peak disappeared.

The existence of radical anion as an intermediate during the electrochemical reduction of 1,8-DNN in acentonitrile at the first cathodic wave was observed using Specular Reflectance Spectroscopy. This in-situ technique enables the UV-Visible spectra of short lived intermediates to be obtained. In the case of 1,8-DNN the optical measurements showed the appearance of absorbsion peaks at 407 nm when reduction was carried out potential in the first reduction wave. These are in good accord with published spectral data [7] for ion radicals produced in γ-irradiated rigid solutions at 77K.

The SRS spectrum of 1,8-DNN radical anion at 13 Hz ossilation frequency is shown in Fig 4.

The ESR studies of 1,8-DNN was carried out in the cell shown Fig 1. and the spectrum was taken while electrolysis were carried out at the same time.

The ESR spectrum of 1,8-DNN radical anion in acetonitrile was similar to that reported by Gersan and Adams [8].

The coupling constants of 1.8-DNN radical anion was shown below:

a_N = 3,0 gauss belongs to two equivalent N nuclei.

a'_H = 3,71 gauss belongs to four equivalent protons,

a''_H = 1 gauss belongs to two equivalent protons.

CONCLUSION

All of these experimental results shows that the first wave cathodic reduction of 1,8-DNN in acetonitrile gave radical anion which is easly reacts further.

Therefore possible reduction products of 1,8-DNN are greatly depends on the solution media. As it is shows in Fig 3 in the

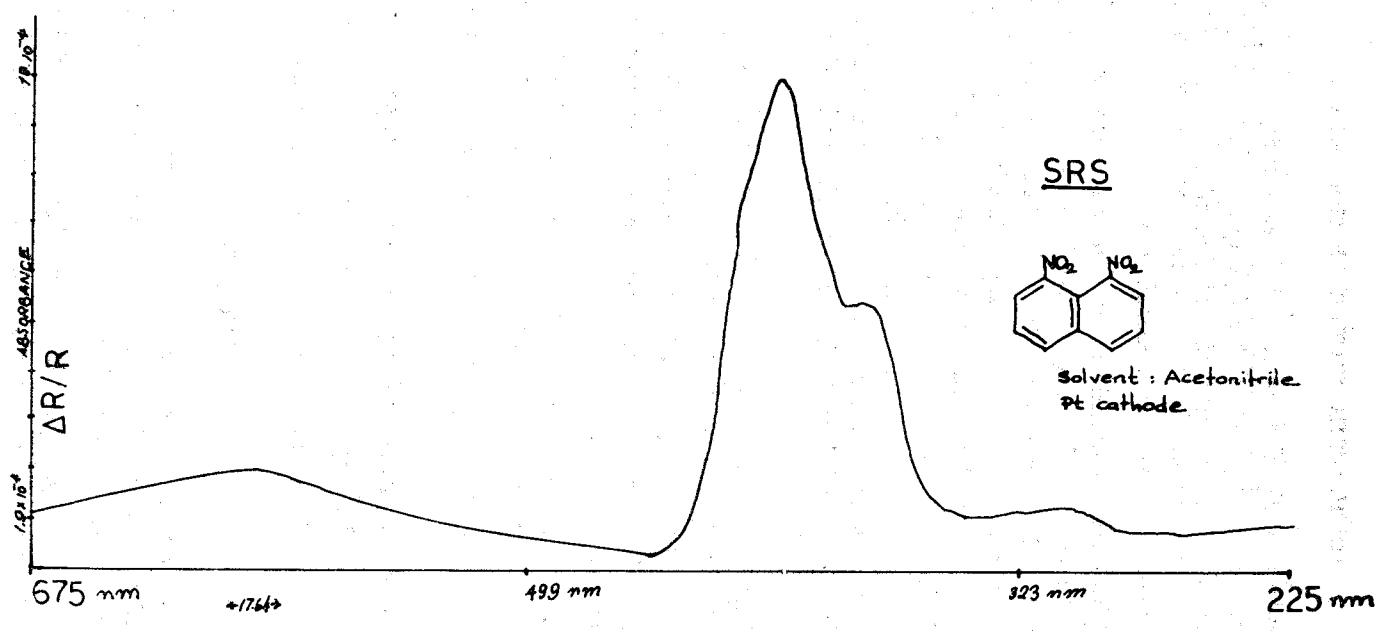
SRS
NO2
NO2
Solvent : Acetonitrile
Pt cathode
ΔR/R
675 nm
499 nm
323 nm
225 nm

Fig 4

presence of water the radical anion react further so that while a new reduction peak form at 1.8 volt due to the new intermediate, the peak belongs to the oxidation of radical anion disappeared.

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ÖZET

Bu çalışmada 1,8 DNN'nin asetonitril içinde ve pt elektrodda indirgenmesi mekanistik açıdan incelendi. Bu amaçla siklik voltametri, Görülür Yansima Spektroskopisi ve Elekron Spin Rezonans teknikleri kullanıldı. Bu çalışmalar sonucunda 1,8 DNN nin katodik indirgenmesinde anyon radikalinin ara ürün olarak oluştuğu bulundu.

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