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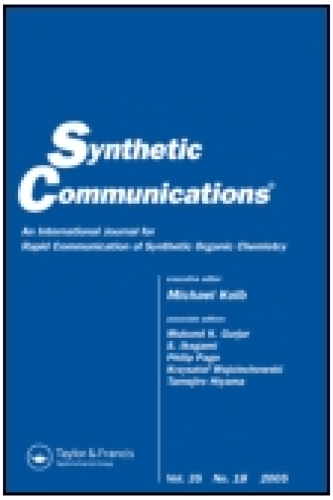

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ELECTROCHEMICAL BEHAVIOUR OF HYDRAZONATES IN PROTIC AND APROTIC MEDIUM

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ELECTROCHEMICAL BEHAVIOUR OF HYDRAZONATES IN PROTIC AND APROTIC MEDIUM

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ABSTRACT

Cathodic reduction of several hydrazonates of a typical structure (Scheme 1) has been investigated by cyclic voltammetry and controlled potential electrolysis at mercury electrode in aprotic solvent. Quantitative results for preparative electrolysis run in the presence of a protic donor show the occurrence of reductive cleavage of the median N–N bond leading to the formation of imines and iminoethers in good yields.

INTRODUCTION

The electrochemical reduction of compounds with carbon–nitrogen double bond of the type [$R_1(R_2)C{=}N\text{-}Y$] has gained considerable interest over the last years. The reduction of imines (Y : H),[1,2] oximes (Y : OH),[3,4] azines (Y : N=CRR′),[5,6] hydrazones (Y : NRR′),[7,8]... depends on their

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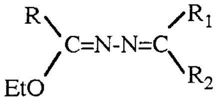
structure and the experimental conditions.[9,10] Cleavage of N–Y bond and saturation of the carbon–nitrogen double bond are the expected reactions.

The present work deals with the electrochemical behavior of compounds **1** (cf Scheme 1 for the investigated derivatives) in aprotic medium using a stationary mercury electrode. The effect of acid addition on their reduction and oxidation characteristics is also reported.



1

	1a	**1b**	**1c**	**1d**
R	Me	Me	Me	H
R_1	Me	Me	Me	Me
R_2	Ph	4-pyridinyl	2-thiophenyl	Ph

Scheme 1.

The electrochemical reduction mechanism and the structure of the final products are investigated.

RESULTS AND DISCUSSION

Typical cyclic voltammograms for reduction of compound **1b** is shown in Figure 1 and peak potentials from cyclic voltammetry measurements are summarized in Table 1.

All the hydrazonates **1** are reduced via two one-electron processes on mercury electrodes at a sweep rate of 0,1 V/s, except **1b** which shows a third reduction peak located at a very high negative potential ($E_p = -2{,}27$ V vs $Ag/AgI/I^-$ 0,1 M) and ascribed to the reduction of the pyridinyl group.

On the reverse scan, an anodic peak was observed assigned to the oxidation of the anion radical outlet of the first electron transfer. The cathodic peak potential E_{pc} and the current fraction $I_{pc}/v^{0,5}$ remain constant (Figure 2) with the increase of the scan rate in the range from 50 to 500 mV/s.

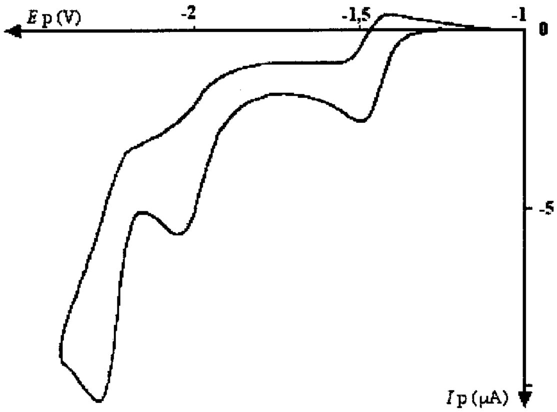


Figure 1. Cyclic voltammetry of hydrazonate **1b** in DMF-Bu_4NClO_4 0,1 M. Hanging mercury electrode. Reference electrode $Ag/AgI/I^-$ 0,1 M. Sweep rate: $v = 50$ mV/s. Substrate concentration: $c = 10^{-3}$ mol/l.

Table 1. Cyclic Voltammetry of Some Hydrazonates **1** in DMF-Bu_4NClO_4 0,1 M. Hanging Mercury Electrode. Reference Electrode $Ag/AgI/I^-$ 0,1 M. Sweep Rate: $v = 50$ mV/s. Substrate Concentration: $c = 10^{-3}$ mol/l

	First Step		Second Step		Third Step	
Compounds	E_p (V)	I_p (μA)	E_p (V)	I_p (μA)	E_p (V)	I_p (μA)
1a	−1,87	10,60	−2,34	4,10	–	–
1b	−1,47	5,50	−2,03	5,10	−2,27	6,20
1c	−1,40	2,10	−1,77	3,60	–	–
1d	−1,68	10,80	−2,09	2,10	–	–

On the other hand, the potential difference between E_{pc} and E_{pa} is about (59/n) mV. These criteria indicate that the first electrode process of hydrazonates **1** on mercury is reversible.

Nevertheless, the ratio I_{pa}/I_{pc} is less than one regardless of the scan rate (Table 2). So the first electron transfer may be coupled to a fast chemical reaction which is very likely a protonation reaction by the tetrabutyl ammonium cation via an Hofmann elimination[11] or by residual proton impurities.

When adding a proton donor as phenol, the current of the first reduction peak decreases slightly and a more anodic peak appears (Figure 3) ascribed to the reduction of the protonated chemical entitiy. Thus, a partial

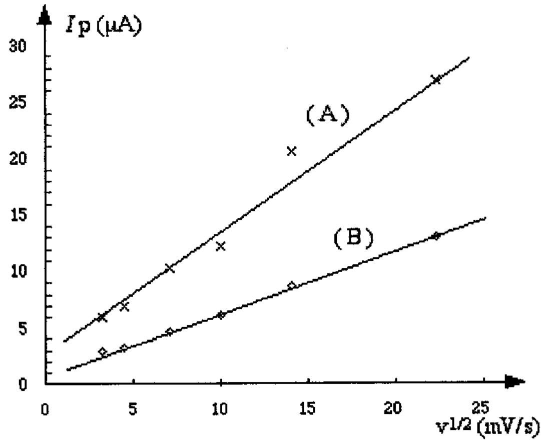


Figure 2. Influence of the sweep rate on the reduction current value for hydrazonates **1a** and **1b** in DMF-Bu_4NClO_4 0,1 M. Hanging mercury electrode. Reference electrode Ag/AgI/I^- 0,1 M. Substrate concentration: $c = 10^{-3}$ mol/l. -**A**: substrate **1a**; -**B**: substrate **1b**.

Table 2. Ratio I_{pa}/I_{pc} of Some Hydrazonates **1** in DMF-Bu_4NClO_4 0,1 M at Different Sweep Rates. Reference Electrode Ag/AgI/I^- 0,1 M. Hanging Mercury Electrode. Substrate Concentration: $c = 10^{-3}$ mol/l

Scan Rate	I_{pa}/I_{pc} Values			
Compounds	50 mV/s	100 mV/s	200 mV/s	500 mV/s
1a	0,63	0,63	0,63	0,63
1b	0,74	0,76	0,75	0,78
1c	0,81	0,68	0,72	0,71
1d	0,72	0,65	0,675	0,65

protonation of the starting material **1** cannot be excluded. The protonation reaction may be reasonably fast because of the basic nature of hydrazonates **1**. For a large excess of phenol the cyclic voltammogram exhibits only one reduction peak located at a more positive potential.

The controlled potential electrolysis performed on mercury pool electrode in DMF solution using tetrabutyl ammonium perchlorate 0,1 M, shows that the electrochemical behavior of hydrazonate **1** differs depending on whether the starting material is reduced in presence or in absence of a proton donor.

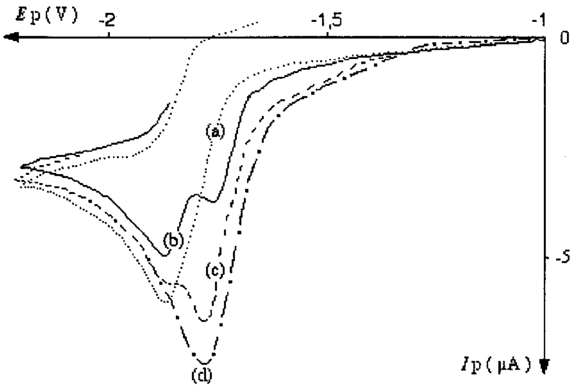
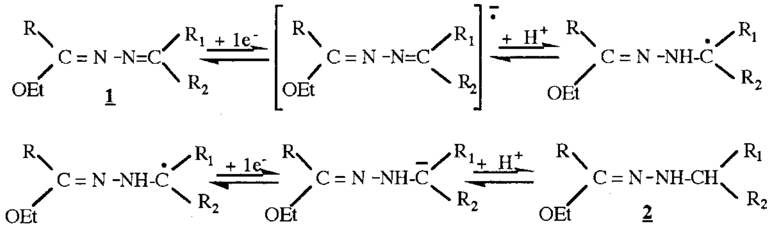


Figure 3. Cyclic voltammetry of hydrazonate $\underline{\mathbf{1a}}$ in DMF-Bu_4NClO_4 0,1 M. after addition of phenol ($\alpha = [\text{phenol}]/[\text{hydrazonate}]$). Hanging mercury electrode. Reference electrode $Ag/AgI/I^-$ 0,1 M. Sweep rate: $V = 50\,mV/s$. **a**: $\alpha = 0$; **b**: $\alpha = 0{,}4$; **c**: $\alpha = 0{,}6$; **d**: $\alpha = 1{,}2$.

In aprotic medium, the electrolysis of $\underline{1}$ at applied potential, corresponding to the value of E_{pc}, leads to the saturation of carbon–nitrogen double bond. The hydrazonates derived of benzylhydrazine $\underline{2}$ are the reduction products obtained in a good yield. After purification, their ir and nmr spectra are in good agreement with the assigned structure.

Thus the cathodic reduction process of $\underline{1}$ may be summarized as follows (Scheme 2).



	2a	2b	2c	2d
R	Me	Me	Me	H
R_1	Me	Me	Me	Me
R_2	Phe	4-pyridinyl	2-thiophenyl	Ph

Scheme 2.

Table 3. Macroelectrolyses of Some Hydrazonates **1**. DMF-Bu_4NClO_4 0,1 M. Cathode: Mercury Pool ($s = 12\,cm^2$). Reference Electrode $Ag/AgI/I^-$ 0,1 M

	Aprotic Medium			Protic Medium		
Compounds	Fixed Electrolysis Potential (V)	Electricity Consumption (F/mole)	Products Yield (%)	Fixed Electrolysis Potential (V)	Electricity Consumption (F/mole)	Products Yield (%)
1a	−1,85	2,15	**2a** (59)	−1,8	3,21	**3a** (71)
1b	−1,45	2,11	**2b** (49)	−1,37	3,09	**3b** (69)
1c	−1,75	2,12	**2c** (63)	1,68	3,12	**3c** (65)
1d	−1,65	2,2	**2d** (59)	−1,59	2,98	**3a** (53)

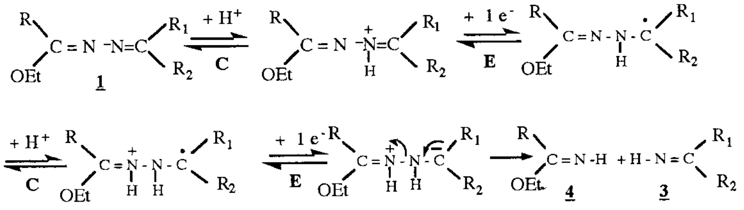
After the first charge transfer, the protonation of the radical anion leads to a neutral radical whose charge is more favorable for the second electron transfer to occur. Therefore, a second charge transfer occurred leading, after protonation, to the saturation of carbon nitrogen double bond. The reduction of **1** occurs according to an ECEC mechanism. In previous studies[12] we have reported that hydrazonates derived from hydrazines with similar structures to the final products are not reducible in aprotic medium. These results are in agreement with the electricity consumption for all the compounds (Table 3).

In the presence of a ready source of proton (phenol for example), coulometric measurements prove a consumption of 3 F/mole for all the investigated substrates **1** and the reaction leads up to the cleavage of the nitrogen–nitrogen bond.

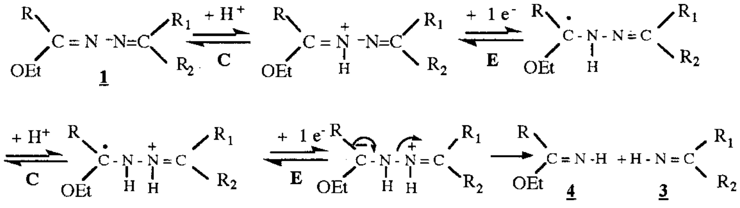
The cathodic reduction process of **1** displays a rather complex mechanism were a CECE mechanism is most dominant.

The protonation of the nitrogen nearest to the oxygen moiety in the neutral radical (Scheme 3a) or in the substrate (Scheme 3b) may be considered as the kinetic determining step to cleave the nitrogen–nitrogen bond.

Whatever the chemical route and the protonated form, the final products are the same. In the electrolysis conditions, imines **3** are not reduced,



Scheme 3a.



	3a	**3b**	**3c**
R₁	Me	Me	Me
R₂	Phe	4-pyridinyl	2-thiophenyl

Scheme 3b.

whereas in the post-electrolysis work-up iminoether **4** is hydrolysed.[13] This may explain why only the imines **3** are isolated.

EXPERIMENTAL SECTION

Materials and Reagent

The solvent, *N*,*N*-dimethyl formamide (DMF) was carefully dried and distilled under vacuum. Dried pure quality tetrabutylammonium perchlorate (TBAP) was used without further purification.

All hydrazonates **1** were prepared according to the described method.[13]

1a: Rdt: 60%; $Eb_{0,1mm\ Hg}$: 120°C; ir: $\nu_{C=N} = 1632$; nmr (^1H): 1.1 (t, 3H); 1.9 (s, 3H); 2.1 (s, 3H); 4 (q, 2H); 7.1 (mu, 5H).

1b: Rdt: 69%; $Eb_{0,1mm\ Hg}$: 130°C; ir: $\nu_{C=N} = 1633$; nmr (^1H): 1.2 (t, 3H); 2 (s, 3H); 2.2 (s, 3H); 4.1 (q, 2H); 8 (mu, 4H).

1c: Rdt: 49%; $Eb_{0,1mm\ Hg}$: 110°C; ir: $\nu_{C=N} = 1632$; nmr (^1H): 1.1 (t, 3H); 2.20 (s, 3H); 2.23 (s, 3H); 4 (q, 2H); 7 (mu, 3H).

1d: Rdt: 63%; $Eb_{0,1mm\ Hg}$: 110°C; ir: $\nu_{C=N} = 1635$; nmr (^1H): 1.2 (t, 3H); 2.1 (s, 3H); 4.4 (q, 2H); 7 (mu, 5H); 7.17 (s, 1H).

Apparatus and Procedures

The IR spectra ($CHCl_3$) were recorded on a Perkin-Elmer 1000 PC spectrophotometer and the ^1H NMR spectra were recorded on Brucker

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AC 300 MHz spectrometer using $CDCl_3$ containing tetramethylsilane as an internal standard.

The cyclic voltammetry measurements were performed using a PAR scanning potentiostat model 362. The cell was a three-electrode type with hanging mercury drop as a working electrode, the counter electrode was a platinium wire and $Ag/Ag/I/I^-$ system was used as a reference electrode.

Preparative electrolyses were carried out in a conventional H-cell with a medium porosity sintered glass separator between the anolyte and the catholyte. Mercury was used as a cathode and Pt as an anode. The potentiostat and coulometer were Tacussel radiometer PJT 35-2 and IG5-N respectively.

In a typical preparative electrolysis hydrazonate **1** (0.5 g) was reduced in the conditions described in Table 3 under nitrogen flow and magnetic stirring. At the end of electrolysis, the catholyte was poured into 200 ml of water.

The resulting mixture was extracted three times with 50 ml ether. The etheral phase was washed by small amounts of water and dried over magnesium sulfate. The ether was removed and the residue was purified by column chromatography on silica gel 60 (0,05–0,2 mm) using ethyl acetate/petrol ether ($v:v = 3:7$) as eluent. Pure compounds **2** were identified by IR and NMR spectra.

2a: ir: $\nu_{C=N} = 1633$; $\nu_{N\text{-}H} = 3520$. nmr (^1H): 1.2 (t, 3H); 1.5 (d, 3H); 2.1 (s, 3H); 4.1 (q, 2H); 4.8 (q, 1H); 7.3 (mu, 5H); 7.8 (ma;1H).

2b: ir: $\nu_{C=N} = 1634$; $\nu_{N\text{-}H} = 3522$. nmr (^1H): 1.2 (t, 3H); 1.6 (d, 3H); 2 (s, 3H); 4 (q, 2H); 4.5 (q, 1H); 5 (ma; 1H); 7.5 (mu, 4H).

2c: ir: $\nu_{C=N} = 1632$; $\nu_{N\text{-}H} = 3447$. nmr (^1H): 1.2 (t, 3H); 1.5 (d, 3H); 2.1 (s, 3H); 4.2 (q, 2H); 5 (q, 1H); 7 (mu, 3H); 7.8 (ma;1H).

2d: ir: $\nu_{C=N} = 1633$; $\nu_{N\text{-}H} = 3520$. nmr (^1H): 1.2 (t, 3H); 1.8 (d, 3H); 4.5 (q, 2H); 5.3 (q, 1H); 7 (mu, 5H); 7.5 (ma;1H); 7.8 (s, 1H).

For electrolysis run in protic medium, phenol ($m = 2$ g) was added to the catholyte in the begninning of the electrolysis. After electrolysis, the catholyte was separated and a Na_2CO_3 saturated solution was added. Electrolysis product was extracted with diethylic ether. The products of electrolysis **3** were identified by IR and NMR spectra.

3a: ir: $\nu_{C=N} = 1673$; $\nu_{N\text{-}H} = 3351$. nmr (^1H): 2.2 (s, 3H); 7.6 (mu, 5H); 9.3 (ma, 1H).

3b: ir: $\nu_{C=N} = 1681$; $\nu_{N\text{-}H} = 3348$. nmr (^1H): 2.2 (s, 3H); 8 (mu, 4H); 9.79 (ma, 1H).

3c: ir: $\nu_{C=N} = 1673$; $\nu_{N\text{-}H} = 3351$. nmr (^1H): 2.23 (s, 3H); 7.26 (mu, 3H); 8.8 (ma, 1H).

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