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Voltammetric Studies on Some Arylhydrazones of α-Cyano Ketones and α-Cyano Esters

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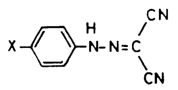
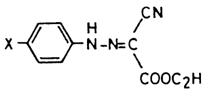
The redox characteristics of the title compounds are extensively studied using DC-, cyclic voltammetry, coulometry, and controlled potential electrolysis in benzonitrile at platinum electrodes. These compounds are oxidized in one-electron transfer process followed by deprotonation which leads to dimerization. The reduction process differs according to the nature of the compound and the electron-withdrawing power of the substituent in the α-position. They can be reduced in a single two electron or two one electron waves leading in both cases to saturation of the hydrazonic moiety.

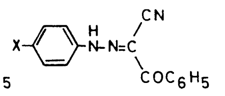
The electrochemical behavior of α-arylhydrazononitriles and their *N*-methylated derivatives has been recently reported in literature.[1–8] The increase of interest in the chemistry of this class of compounds arose from their reported biological activity.[9–13] It has been found that these compounds are more effective than cyanides in the uncoupling oxidative phosphorylation in mitoconderial systems.[14,15] In a previous investigation,[16] it has been shown that arylhydrazonomesoxalonitrile (**I**) are electrochemically active in proton-free benzonitrile. These compounds are oxidized in a single irreversible one-electron-transfer process forming the corresponding radical cation which undergoes dimerization reaction. The electrochemical reduction occurs through acceptance of two electrons in two successive irreversible one-electron waves following the well-known ECEC-mechanism. In connection with this work we report here the redox characteristics of different substituted ethyl α-cyano-α-(arylhydrazono)glyoxalates (**II**) and 2-arylhydrazono-3-oxo-3-phenylpropionitriles (**III**).



I



II



III

III, III	a	b	c	d	e	f	g	h
X	H	NO_2	Br	Cl	CH_3	OCH_3	NH_2	H·(N-CH_3)

Experimental

Organic Synthesis. All compounds involved in this investigation are prepared following the procedures described by Bennett[17] and Elnagdi.[18] The obtained products were purified by repeated crystallization from ethanol.

Reagents. Benzonitrile (BN) (Rotitainerm, West Germany) was purified by first distillation under vacuum from orthophosphoric acid, followed by repeated distillations from phosphorus pentaoxide and final fractional distillation from potassium metal. The supporting electrolyte tetrabutylammonium perchlorate (TBAP) (Fluka-Swiss) was crystallized several times from ethanol-water (9:1 v/v) mixture and dried in vacuum before use.

Apparatus and Instruments. The voltammetric measurements were carried out with the following apparatus:

Potential Source	: Potential Scan Generator VSG 72.
Potentiostat	: Potential Control Amplifier PCA 72C (Bank Electronic, Gottingen, W. Germany).
X-Y Recorder	: Servoger XY (Metrawatt, Nurnberg, West Germany).
Digital Multimeter	: T 2201 (Hartman & Braun, Frankfurt, West Germany).
Coulometer	: (Bank Electronic, Gottingen, W. Germany).

The rotating platinum disc electrode (RDE) is mounted to a rotating motor (750 rpm) (Metrohm, Swiss).

Measurements. The electrochemical measurements were carried out in dry benzonitrile (BN) containing 0.1 M TBAP (1 M=mol dm^{-3}). The voltammetric study involved direct current (DC) voltammetry at RDE and cyclic voltammetry at a stationary platinum disc electrode. The number of electrons participating in each electrode process was obtained by the controlled potential coulometry (CPC) at a platinum sheet electrode. The electrode potentials were measured against saturated Ag/AgCl/Cl$^-$ (BN) electrode, which was from time to time calibrated against the redox potential of cobaltocenium/cobaltocene system.[19] The standard potential of Ag/AgCl/Cl$^-$ (BN) electrode against the normal hydrogen electrode (NHE) is −176 mV.[20,21]

Controlled Potential Electrolysis (CPE). Electrolysis of ethyl α-cyano-α-(*p*-chlorophenylhydrazono)glyoxalate (**IId**). CPE was carried out twice with 300 mg of **IId** in both acetonitrile and benzonitrile. The potential was adjusted at a value on the limiting current plateau (+2.2 V in oxidation and −1.2 V in reduction). The electrolysis was stopped after the passage of a quantity of electricity corresponding to the uptake of 1 mole of electrons per mole of product for oxidation and 2 moles at reduction. In each case, after electrolysis, the resulting solution was evaporated in vacuo and the product was extracted with ethyl acetate solvent which was evaporated in turn. The obtained mixture was chromatographed on thin-layer silica-gel plates using chloroform solvent.

The Reduction Product of CPE. A quantitative yield of the original compound **IId** was obtained. Anal. Calcd: C, 52.49; H, 3.98; Cl, 14.12; N, 16.70%. Found: C, 52.33; H, 3.84; Cl, 13.98; N, 16.80%. IR (KBr) 3220 (NH), 2220 (CN), 1760 (ester CO), 1620 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$, TMS) δ=1.4 (t, 3H, $\underline{CH_3}$-CH_2-), 3.6 (q, 2H, CH_3-$\underline{CH_2}$-), 7.2—7.5 (m, 4H, aromatic protons), 10.0 (s, br, 1H, NH).

The Oxidation Product of CPE. Two main products were obtained:

i) The zone with R_f value 0.68 was scraped off the plate and extracted with acetonitrile, filtered and evaporated in vacuo. The resulting solid compound (yield 55 %) was identified as compound **IV**. Anal. Calcd: C, 41.38; H, 3.13; Cl, 22.26; N, 13.17%. Found: C, 41.20; H, 3.01; Cl, 22.40; N, 13.12%. IR (KBr) 3220—3300 (two NH), 2220 (CN), 1760, 1750 (ester CO), 1630 (C=N), 1220 cm^{-1} (ClO_4^-). ^{1}H NMR ($CDCl_3$, TMS) δ=1.4 (t, 6H, two $\underline{CH_3}$-CH_2-), 3.6 (q, 4H, two CH_3-$\underline{CH_2}$), 7.2—7.5 (m, 8H, aromatic protons), 10.0 (s, br, 2H, two NH).

ii) The zone with R_f value 0.79 was scraped and extracted as above. The obtained product (yield 30%) was identified as compound **V**. Anal. Calcd: C, 52.69; H, 3.59; Cl, 14.17; N, 16.77%. Found: C, 52.52, H, 3.53; Cl, 14.23; N, 16.59%. IR (KBr) 3200—3300 (two NH), 2220 (CN), 1760—1750 (ester CO), 1630 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$, TMS) δ=1.4 (t, 6H, two $\underline{CH_3}$-CH_2-), 3.6 (q, 4H, two CH_3-$\underline{CH_2}$-), 7.2—7.4 (m, 6H, aromatic protons), 10.0 (s, br, 2H, two NH).

Results and Discussion

The voltammetric redox data of compounds (**IIa—h** and **IIIa—h**) are summarized in Table 1. Figures 1 and 2 represent typical DC- and cyclic voltammograms of the investigated compounds respectively.

Ethyl (Arylhydrazono)glyoxalate (IIa—h). All the investigated compounds **IIa—h** behave similarly in shape in both oxidation and reduction. They are oxidized in a single irreversible one-electron process which is followed by a coupled chemical reaction (EC-mechanism). This mechanism is clearly indicated by the absence of the corresponding reduction peak in the

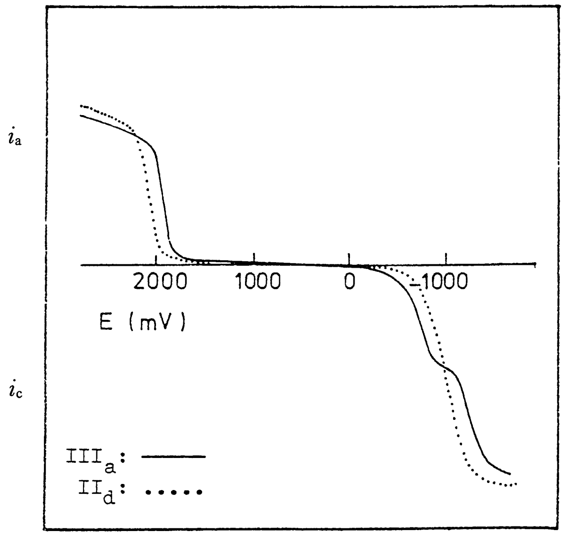


Fig. 1. DC-voltammograms of compounds **IId** and **IIIa** at RDE in benzonitrile.

Table 1. DC Voltametric Data of Ethyl (α-Cyano-α-hydrazono)glyoxalates (**IIa—h**) and 2-Arylhydrazono-3-oxo-3-phenylpropionitriles (**IIIa—h**) at RDE in Benzonitrile

Compd	Process	$E_{\frac{1}{2}}$/mV	$S^{a)}$	Compd	Process	$E_{\frac{1}{2}}$/mV	$S^{a)}$
IIa	O_I	1835	133	**IIIa**	O_I	1932	121
	R_I	−1075	114		R_I	−723	240
					R_{II}	−1170	199
IIb	O_I	2222	66	**IIIb**	O_I	2215	75
	R_I	−825	99		R_I	−428	178
	R_{II}	−1203	52		R_{II}	−1088	116
IIc	O_I	2002	196	**IIIc**	O_I	1902	84
	R_I	−1050	189		R_I	−573	215
					R_{II}	−1133	127
IId	O_I	2047	189	**IIId**	O_I	1912	92
	R_I	−980	190		R_I	−583	244
					R_{II}	−1003	86
IIe	O_I	2002	143	**IIIe**	O_I	1812	180
	R_I	−998	230		R_I	−473	176
					R_{II}	−965	62
IIf	O_I	1845	75	**IIIf**	O_I	1532	106
	R_I	−948	193		R_I	−488	181
					R_{II}	−1043	123
IIg	O_I	748	191	**IIIg**	O_I	760	183
	O_{II}	2072	176		O_{II}	2030	100
	R_I	−972	141		R_I	−505	180
					R_{II}	−1112	130
IIh	O_I	1932	130	**IIIh**	O_I	1902	97
	R_I	−1238	147		R_I	−1148	178

a) S=dE/d log[$(i_d-i)/i$].

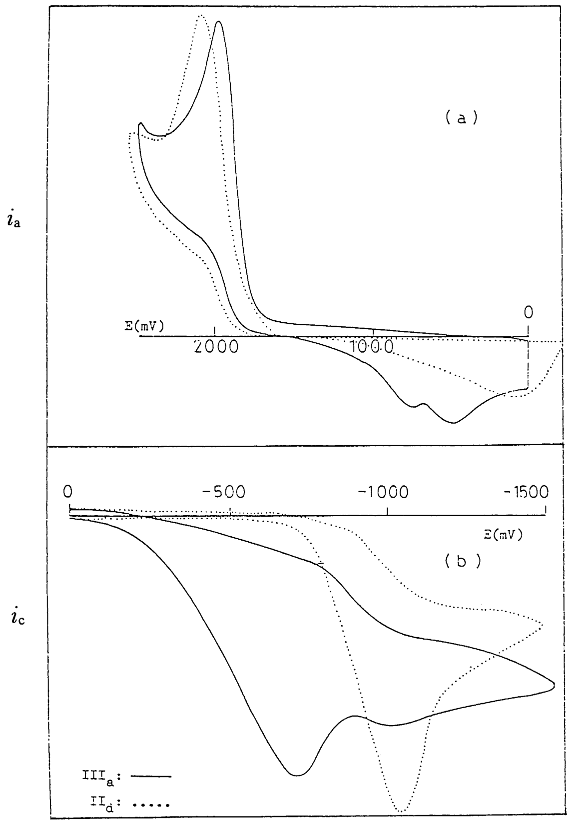


Fig. 2. Cyclic voltammograms of compounds **IId** and **IIIa** at a stationary platinum disc electrode in benzonitrile (a) Oxidation, (b) Reduction. Scan rate=100 mV s^{-1}.

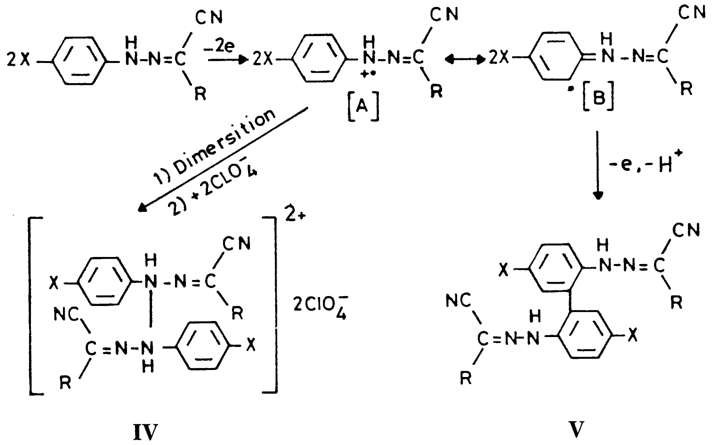
reverse cycle[22] of the cyclic voltammogram (Fig. 2). The reduction process occurs through the acceptance of two electrons in a single irreversible wave following also the EC-mechanism. The irreversibility of the electrode process is obtained also from the slope of the logarithmic analysis curves[23] as shown from Table 1. The amino group in the compound (**IIg**) can be also oxidized in a first oxidation wave and the nitro group in the compound (**IIb**) reduced in the well-known reduction wave of nitro aromatic compounds.

2-Arylhydrazono-3-oxo-3-phenylpropionitrile (IIIa—h). These compounds are oxidized in the same manner as compounds (**IIa—h**) in a single irreversible one-electron transfer process following the EC-mechanism. The reduction process is markedly different: Although the total number of electrons participating in the electrode reaction is two electrons per moelcule as for compounds (**IIa—h**), these two electrons appear not as a single wave but as a two successive irreversible one-electron waves. The *N*-methyl derivative **IIIh** behaves as its similar **IIh**; the reduction occurs in a single two-electron wave.

The polarographic behavior of this class of compounds was investigated.[24—29] They are reduced in a 4-electron wave in either acidic or basic media accompanied by N-N bond cleavage to the corresponding amines. Although this reduction process has been well-documented,[30] it cannot be generalized to account for the reduction of other substituted α-arylhydrazono nitriles since these compounds are tautomeric with the corresponding azo forms. The contribution of each form would depend on the nature of substituents in the molecule. Several articles suggested the existence of certain arylhydrazono nitriles in a charge separated azo form.[31,32] Recently the different substituted (*N*-methylarylhydrazono)-mesoxalonitriles were studied in both aqueous and nonaqueous media.[33,34]

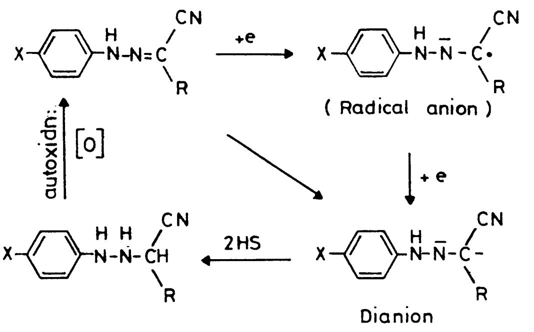
In this work, based on the careful analysis of the data obtained and the identification of the resulting product of CPE, Scheme 1 is suggested for the electrochemical oxidation of the investigated compounds.

The electrochemical oxidation (Scheme 1) proceeds through a one-electron transfer forming the radical cation with its canonical forms A and B. Mesomer A undergoes a dimerization process leading to the formation of the dication **IV** which can be stabilized through its combination with two perchlorate ions from the supporting electrolyte forming salt (**IV**). Also mesomer B may be dimerized with proton removal from the ortho-position in the phenyl ring leading



IV **V**

Scheme 1.



VI

Scheme 2.

to the formation of the neutral dimer **V**.

The difference in electron-withdrawing power of the -$COOC_2H_5$ and -CN or -COC_6H_5 groups plays a significant role in the mode of the reduction process. The high electron-withdrawing power of the -CN or -COC_6H_5 groups compared with that of -$COOC_2H_5$ group stabilized the firstly formed radical anion which appears in a well-defined separate one electron wave.

The reduced center in these compounds is the -N=C double bond which accepts two electrons to form the corresponding dianion. The formed dianion would be strong base enough to abstract protons from the solution (from the solvent-moisture or from the supporting electrolyte or even from the solvent itself)[35,36] forming compound **VI**. It is clear from the structure of **VI** (Scheme 2) that this compound is unstable especially in air, which can be oxidized with air oxygen to give the starting substance. This is in full agreement with the results obtained from CPE. Thus instead of the final product **VI**, a quantitative yield of the starting material was isolated.

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