

Electrochemical Reduction of Some 3-Aryl-2-cyanothioacrylamide Derivatives at the DME

M. A. Aboutabl*, M. A. Abdel Aziz, A. A. Magd El Din, H. A. Elwy,
and H. M. Fahmy

Chemistry Department, Faculty of Science, Cairo University, Giza, A. R. Egypt

Summary. The polarographic behaviour of the title compounds is reported and discussed in acid media. The obtained data indicate that these compounds undergo a four-electron reduction. A mechanism for the electrode process at $pH < 7$ is proposed, discussed and clarified via identification of controlled potential electrolysis (CPE) product and application of cyclic voltammetry (CV).

Keywords. Electroreduction; 3-Aryl-2-cyanothioacrylamide derivatives.

Die elektrochemische Reduktion einiger 3-Aryl-2-cyanothioacrylamid-Derivate an der DME

Zusammenfassung. Es wurde das polarographische Verhalten der Titelverbindungen in saurem Medium untersucht. Die erhaltenen Daten zeigen, daß diese Verbindungen eine Vierelektronenreduktion eingehen. Es wird ein Mechanismus für den Elektrodenprozess bei $pH < 7$ vorgeschlagen und diskutiert. Zur Klärung der Verhältnisse wurden die mittels kontrollierter Potential-Elektrolyse (CPE) erhaltenen Produkte identifiziert und auch cyclische Voltammetrie eingesetzt.

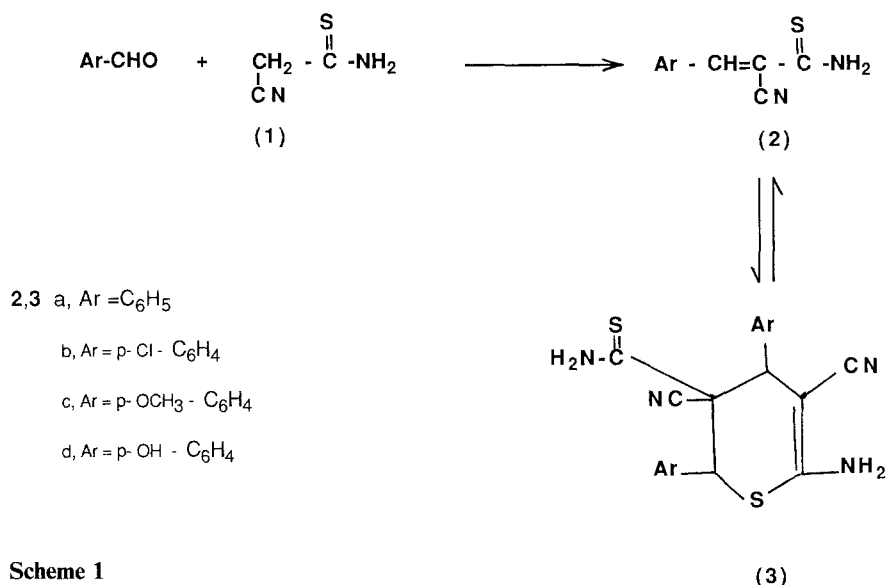
Introduction

α -Cyanothioacetamide (**1**) is a versatile compound of exceptional reactivity. From the structural point of view, the reactivity of this compound is due to the presence of different functional groups (cyano, amine and active methylene) thus constituting a multifunctional reagent. The unique reactivity of α -cyanothioacetamide makes it an excellent and very important candidate in the fields of chemical research, medicinal, industrial and agricultural chemistry.

Aromatic aldehydes condense with (**1**) in the presence of basic catalysts to afford the corresponding 3-aryl-2-cyanothioacrylamide derivatives (**2**). Several examples of (**2**) were reported in literature to be synthesised via this route [6, 7].

Brunskill et al. [8] reported that the products obtained by the action of aromatic aldehydes in (**1**) had the correct elemental composition and had appropriate melting points in agreement with those previously reported in literature. The thioacrylamide structure (**2**) was consistent with the $^1\text{H-NMR}$ spectra for compounds derived from heterocyclic aldehydes and 2-substituted benzaldehydes. However, for the reactions with benzaldehyde, p-methoxybenzaldehyde, 4-chlorobenzaldehyde and 4-hydroxy-

benzaldehyde, the reaction products had more complex spectra. These products proved to be an equilibrium mixture between (2) and the dimeric form 6-amino-2,4-diaryl-3,5-dicyano-3,4-dihydro-2H-thiopyran-3-thiocarboxamide (3). These latter were assumed to be formed via the Diels-Alder's self-condensation reaction of the corresponding thioacrylamide derivatives (2) (cf. Scheme 1).



Scheme 1

Experimental

Organic Syntheses

Synthesis of 3-aryl-2-cyanothioacrylamide derivatives (2 a–d). A mixture of the appropriate aromatic aldehyde (0.1 mole), cyanothioacetamide (0.1 mole) and 4 drops of triethylamine in absolute ethanol (200 ml) was stirred for 30 min at 40–50°C. The dark red solution was cooled at room temperature and the crude products (2 a–d) were collected after 1 h and recrystallised from ethanol. Compounds (2 a–d) were prepared according to literature procedure [8] in exception of p-hydroxy derivative (2 d) which is newly reported. Compound (2 d) was crystallized from ethanol as yellow crystals, m. p. 225°C: yield 78%. Analysis: C₁₀H₈N₂OS, calcd. C 58.82, H 3.92, N 13.72, S 15.68; found C 58.60, H 4.10, N 13.50, S 15.80. IR (KBr, ν cm⁻¹): 3 450–3 330 (OH, NH₂), 2 220 (CN), 1 200 (C=S). ¹H-NMR (δ ppm): 6.2 (s, 1 H, CH=C), 6.8 (s, br, 2 H, NH₂), 7.2–7.4 (m, 4 H, aromatic protons), 11.5 (s, 1 H, OH).

Polarography

(a) *Apparatus.* Polarographic curves were recorded with a 633 VA stand Metrohm in conjunction with a 626 polarecord Metrohm (Switzerland). The electrolysis cell was a conventional 50 ml type RMO 4 cell, with a platinum wire auxiliary electrode and a saturated calomel electrode (SCE). The dropping mercury electrode (DME) [working electrode] had the following characteristics in H₂O at zero applied potential; flow rate of 1.54 mg s⁻¹ and drop-time 3.9 s drop⁻¹. Voltammograms were recorded on an X-Y recorder type JJPL 3 in conjunction with a Wenking Potentiostat (POS 73) with a HMDE (663 VA Metrohm). The amount of electricity was calculated using the classical Lingane [9] method and checked electronically with a Wenking EVIH electronic integrator and the number of electrons was found to be 4 at pH 1.

(b) *Solutions.* $10^{-3} M$ stock solutions were prepared by dissolving an accurately weighed quantity of material in the appropriate volume of absolute ethanol (n_D^{25} 1.359). Britton-Robinson modified universal buffers [10] were used as supporting electrolyte.

(c) *Measurements.* All experiments were carried out at $15 \pm 1^\circ C$. The half-wave potentials were measured graphically and expressed versus saturated calomel electrode (SCE) with an accuracy $\pm 0.005 V$.

(d) *Polarographic procedure.* Ethanol and the appropriate buffer solution were introduced into the cell. The mixture was then deaerated with hydrogen for 10 min. 2 ml stock solution were introduced into the cell [final concentration $10^{-4} M$ in 20 ml of 40% (v/v) ethanolic buffer] and the solution was further deaerated for two minutes.

(e) *Controlled potential electrolysis (CPE) and identification of the electrolytic products.* A conventional three electrode system was used with a mercury pool cathode as working electrode. The electrolytic cell consisted of a 500 cm^3 conical flask in which the reference, auxiliary electrodes and the hydrogen gas inlet were fixed. The potential was controlled by a Wenking Potentiostat POS 73 at $-0.75 V$ vs. SCE (i.e. on the limiting current plateau of wave A). 250 mg of **2c** (p-methoxy-substituted derivative)¹ dissolved in 5 ml dimethylformamide (DMF) and completed to 100 ml with a [50% (v/v) ethanol – 0.1 M HCl] solution were introduced into the cell. The mercury surface was stirred with a magnetic stirrer during the electrolysis and the mixture was deoxygenated with a stream of hydrogen gas. The progress of electrolysis was followed by recording the decrease in current with time (starting current 140 mA; final current 0.2 mA).

After complete electrolysis, the cell was disconnected from the circuit and the pH measured to be 1.3. The solution was evaporated in vacuo to one third of its original volume, neutralized with ammonia to pH 6 and extracted by ether several times. The ethereal layer was then evaporated at room temperature and the remaining yellowish brown residue (yield 70%) was chromatographed on a silica gel column (Merck) using n-hexane-chloroform (1 : 1) as irrigant. The compound zone was removed (previously located by a TLC technique) using methanol. This product was identified as 6-amino-2,4-di-p-ansiyl-3,5-dicyano-3-fromyl-thiopyran (**6**) (60%), m.p. $72^\circ C$; found C 65.1, H 5.0, N 10.5, S 7.6; $C_{22}H_{21}N_3O_3S$ requires C 64.9, H 5.1, N 10.3, S 7.9%. IR (KBr, $\nu \text{ cm}^{-1}$): 3420, 3390 (NH_2), 2230, 2220 (2 CN), 1700 (CO) and 2730, 1480, 1270 (Thiopyran ring). $^1\text{H-NMR}$ (δ ppm): 3.3 (s, 2 H, NH_2), 3.7 (t, 1 H, H-5), 4.0 (s, 6 H, 2OCH_3), 4.3 (d, 1 H, H-6), 4.8 (s, 1 H, H-2), 5.3 (d, 1 H, H-4), 7.2–7.5 (8 H, aromatic protons) and 10.1 (s, 1 H, CHO).

Results and Discussion

The polarograms of each compound (**2a–d**) displayed a well-defined wave A in acid media of $\text{pH} < 6$ (Fig. 1). This wave proved to be irreversible in nature and corresponded to a four-electron process as revealed from coulometric analysis. At $\text{pH} \geq 7$ another wave B made its appearance and the polarograms consisted of two waves A and B respectively. Due to the hydrolysis and instability of these compounds in alkaline medium, this study was carried out in detail through the pH range 2–6 only as effect of time on the limiting current in a time interval of 3 hours showed that these compounds are stable in solutions of $\text{pH} < 7$. Logarithmic analysis on wave A at two pH values in acid media, namely 2.8 and 4.8 indicated that the process is irreversible in nature as revealed from the transition and transfer coefficient values tabulated in Table 1. From the identification of the main CPE product of **2c** in acid medium it is not unreasonable to assume that wave A is a

¹ Taken as typical representative example of the studied compounds

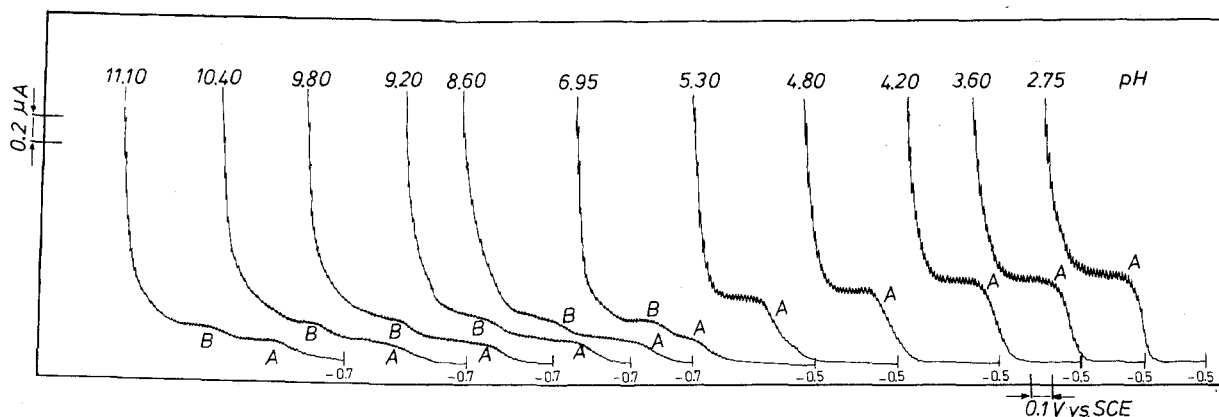


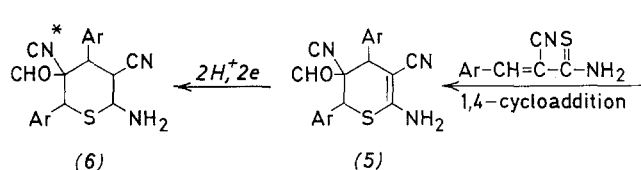
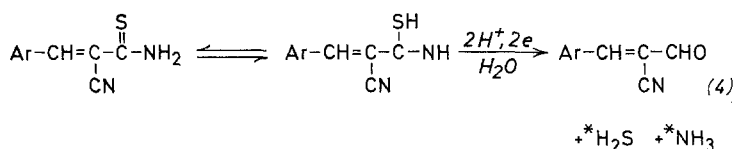
Fig. 1. Typical representative polarograms of $10^{-4} M$ of compound **2c** in 50% v/v ethanolic Britton-Robinson buffers; pH and starting potential is given on the curves

Table 1. $E_{1/2}$ -pH and logarithmic analysis data of compounds **2a–d**

Comp. no.	Ar	$E_{1/2}$ -pH linear equation ^a	pH ^b	Rt/anF	an
2a	C_6H_5	$E_{1/2} = -0.54 - 0.078 \text{ pH}$	2.75	0.053	1.110
			4.45	0.080	0.738
2b	$p\text{-ClC}_6\text{H}_4$	$E_{1/2} = -0.56 - 0.08 \text{ pH}$	2.75	0.075	0.788
			4.00	0.057	1.036
2c	$p\text{-OCH}_3C_6\text{H}_4$	$E_{1/2} = -0.54 - 0.096 \text{ pH}$	2.75	0.064	0.923
			4.20	0.079	0.748
2d	$p\text{-OHC}_6\text{H}_4$	$E_{1/2} = -0.75 - 0.060 \text{ pH}$	2.80	0.066	0.895
			4.20	0.047	1.257

^a pH Limits of validity **2–6**

^b Individual pH values at which logarithmic analysis was carried out



* Isolated and identified products

combined wave, i.e. the wave is a combination of two simultaneous processes involving a cleavage of a C-SH and the saturation of an olefinic bond (a total of 4e process). This overlap of two consecutive processes is often encountered in polarography [11, 12] when the $E_{1/2}$ of the two processes have very close values and thus the separation is not detectable in highly acidic media.

Cyclic voltammetry curves showed in the cathodic direction one peak due to wave A observed in the classical Dc i-E curves (Fig. 2). On the other hand, in the anodic direction no peaks were observed. It is important to draw attention to the fact that this peak indicate that the process is completely irreversible in nature in accordance with the logarithmic analysis.

From the above, Scheme 2 can be proposed for the elucidation of the mechanism of electrode process occurring in wave A in acid medium.

Compound (2) can be in the tautomeric thiol form as illustrated in Scheme 2. This form is reduced via an irreversible 2 electron process with the simultaneous hydrolysis of the imino $C=N$ to give (4) since H_2S has been identified by its characteristic smell and by lead acetate paper also ammonia was tested for in a sample of the electrolysis solution by Nessler's test [13]. Since (6) was the identified main electrolysis product (60%) one cannot overlook the fact that a 1,4 cycloaddition process will occur between two molecules (2) and (4) at the electrode solution interface with the simultaneous electrosaturation of the activated $C=C$. It is also important to mention that other side reactions could be neglected since the yield of the main product (6) is somewhat significant.

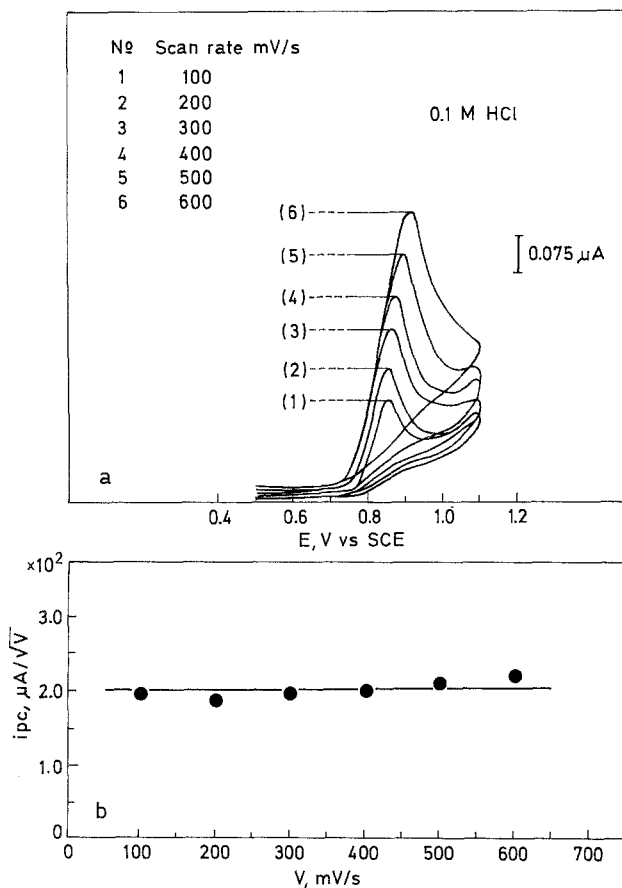


Fig. 2. a Cyclic voltammograms of compound 2c in acidic medium, scales and scan rates are given on the plot. **b** Plot of the ratio of cathodic peak currents to the square roots of the scan rate as a function of the scan rate (compound 2c)

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