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Electroreduction of the Activated Olefinic Double Bond in Some 2-Aryl-1(2-acetylamino-1,3,4-thiadiazol-5-yl)-propionitrile Derivatives

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The electrochemical reduction of a series of the title compounds has been investigated in alcoholic buffered media at the DME. A mechanism for the reduction process has been proposed and confirmed through spectrophotometric and potentiometric *pKa* determinations and identification of CPE products. A trial to calculate the kinetic parameter $k^{\circ}_{f,h}$ by different methods is included.

(Keywords: Electrochemistry; Thiadiazol derivatives; Polarography)

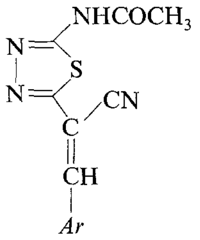
Elektroreduktion der aktivierten olefinischen Doppelbindung in einigen 2-Aryl-1(2-acetylamino-1,3,4-thiadiazol-5-yl)-propionitril-Derivaten

Es wurde die elektrochemische Reduktion einer Serie der Titelverbindungen in alkoholischer, gepufferter Lösung an der tropfenden Quecksilberelektrode untersucht. Ein Mechanismus für den Reduktionsprozeß wird vorgeschlagen, der auf Befunde spektrophotometrischer und potentiometrischer *pKa*-Messungen und die Identifizierung von Produkten der kontrollierten Potentialelektrolyse (CPE) gestützt ist. Ein Versuch zur Ermittlung der kinetischen Parameter $k^{\circ}_{f,h}$ mit verschiedenen Methoden wurde unternommen.

Introduction

Activated olefins are compounds containing a double bond which is attached to an electroactive substituent capable of conjugation. The electroreduction is generally initiated by the uptake of an electron into the lowest unfilled molecular orbital. The fate of the resulting anion depends usually on the reduction medium. In acid media the main product is the dimer, on the other hand in neutral and alkaline media hydrodimerization occurs [1–5].

In this paper we report the polarographic behaviour of a series of 2-aryl-1(2-acetylamino-1,3,4-thiadiazol-5-yl)-propionitrile derivatives (**1 a–d**), in which the C=C is activated with both the cyano and the thiadiazol ring, in a wide range of *pH* with the purpose of elucidating the mechanism of the electrode process and to obtain kinetic parameters. It is also known that structurally related molecules have pronounced medical and pharmalogical applications [6, 7]. For the sake of comparison a model compound, namely 2-acetylamino-5-cyanomethyl-1,3,4-thiadiazol (**2**) has been studied under the same experimental conditions.



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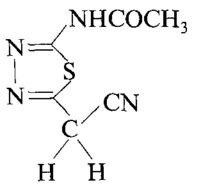
1 a, *Ar* = —C_6H_5

1 b, *Ar* = —C_6H_4-*p*-CH_3

1 c, *Ar* = —C_6H_4-*p*-Cl

1 d, *Ar* = —C_6H_4-*m*-NO_2



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Experimental

2-Aryl-1(2-acetylamino-1,3,4-thiadiazol-5-yl)-propionitrile derivatives (**1 a–d**) were prepared according to the following procedure. The solution of 2-acetylamino-5-cyanomethyl-1,3,4-thiadiazole [8] (10 mmol) in ethanol (50 ml) was treated with the appropriate aromatic aldehyde (12 mmol) and a catalytic amount of piperidine. The reaction mixture was refluxed for 3 hours and the precipitated product was filtered off and crystallized from the appropriate solvent (cf. Table 1).

Table 1. *Data for compounds* **1 a–d**

Compound No.	Molecular Formula	m.p., °C	Solvent of Crystallization	Yield %		Analysis %	
						Calcd.	Found
1 a	$C_{13}H_{10}N_4OS$	294	Ethanol/*DMF*	65	C	57.76	57.80
					H	3.72	3.80
					N	20.73	20.60
					S	11.86	11.70
1 b	$C_{14}H_{12}N_4O_2S$	>295	Ethanol/*DMF*	85	C	55.99	55.70
					H	4.03	4.00
					N	18.66	18.50
					S	10.76	10.50
1 c	$C_{13}H_9N_4OSCl$	>295	Acetic acid	85	C	51.23	51.00
					H	2.98	3.00
					N	18.39	18.10
					S	10.52	10.40
					Cl	11.63	11.50
	$C_{13}H_9N_5O_3S$	265	Ethanol/Dioxan	75	C	49.52	49.30
					H	2.88	2.70
					N	22.21	22.10
					S	10.17	10.00

Polarography

Polarographic curves were recorded on an LP 7 polarograph (Laboratorni Pristrojé, Prague). The capillary possessed the following characteristics in H_2O open circuit: $t = 3.75\,S$ drop^{-1}, $m = 2.15\,mg\,S^{-1}$ for $h = 57$ cm.

Preparation of solutions and detailed procedures for the polarographic analysis are as previously reported [9].

Controlled Potential Electrolysis (CPE) and Identification of the Resulting Products

Electrolysis at pH 2.5

CPE of about 50 mg of **1 a** at a fixed potential —800 mV vs. SCE in 50% ethanol/10^{-2} *M* HCl (*v*/*v*) solution was carried out. Coulometric analysis showed that one electron per molecule of **1 a** was consumed in the reduction process. After complete electrolysis, the cell was disconnected from the circuit and the mixture was partially evaporated on a water bath to half of its volume, allowed to cool and extracted with ether. The ether was left to evaporate at room temperature and the remaining pale yellow residue was recrystallized from ethanol (yield 65%). The obtained compound had the following characteristics: m.p. 308 °C. Analysis for $C_{26}H_{20}N_8S_2O_2$: Calc.: C 57.8, H 3.7, N 20.7, S 11.9%. Found: C 57.6, H 3.8, N 20.8, S 11.7%. IR (KBr) νcm^{-1} 1 605 (C=C), 1 705 (CO), 2 225 (CN), 3 150–2 800 (chelated NH and CH stretch). ^{1}H NMR (*DMSO-d*$_6$) δ/ppm: 2.2 (s, 3 H, CH_3), 2.3 (s, 3 H, CH_3), 7.6–8.1 (m, 12 H, 2 *Ph* and 2 NH protons).

Electrolysis at pH 8.6

The same method was followed in a buffered ethanolic solution of *pH* 8.6 and the potential was controlled on the limiting current plateau of wave A. The same procedure of extraction was also followed and the obtained product (~ 10% yield) was recrystallized from ethanol and had the following characteristics: m.p. > 300 °C. Analysis for $C_{13}H_{12}N_4OS$: Calc.: C 57.3, H 4.4, N 20.6, S 11.8%. Found: C 57.5, H 4.5, N 20.5, 11.6%. IR (KBr) νcm^{-1}, the same bands as the starting compound with additional bands characteristic for $-CH_2$ at 2 860 cm^{-1} and 2 930 cm^{-1}, and the absence of the band at ~ 1 605 cm^{-1}.

Determination of the Apparent Acid Dissociation Constants

Spectrophotometric Measurements

Spectrophotometric measurements were carried out using a PYE Unicam SP 1800 spectrophotometer supplemented with a program controller automatic linear recording unit. The runs in the visible and UV range were carried out for $4 \cdot 10^{-5}$ *M* solutions in 50% ethanolic *Britton-Robinson* buffer. The *pKa* was then calculated using the equation [10]

$$pH = pKa + \log(A - A_{min})/(A_{max} - A)$$

The intercept of the straight line of *pH* vs. log $(A - A_{min})/(A_{max} - A)$ with the *pH* axis at $\log(A - A_{min})/(A_{max} - A) = 0$ gave the *pKa* value directly.

pH-Titration

A freshly prepared stock solution of 10^{-3} *M* of each of the studied compounds in 25 ml absolute ethanol (20% *DMF*) was transferred into a 100 ml beaker and filled up to 50 ml with twice-distilled H_2O to a final concentration of $5 \cdot 10^{-4}\,M$ (in 50% aqueous solution). The latter solution was titrated against $2 \cdot 10^{-2}\,M$ aqueous NaOH with continuous stirring using a magnetic stirrer. Values of *pKa* were calculated using the *Henderson-Hasselbach* equation [11].

Results and Discussion

Polarography of Compounds **1 a–d**

Fig. 1 represents the polarograms obtained with $10^{-4}\,M$ of compound **1 a** as typical example for the series **1 a–c**. At $pH < 3.5$ one well defined cathodic wave A_1 with a height corresponding to a one electron transfer is observed. At $pH > 3.5$ another wave A_2 appears with the same height. These two waves amalgamate to give wave A with a height equal $i_{A_1} + i_{A_2}$ at $pH \geqslant 8.5$. As the pH of the solution increases, the i_l of wave A starts to decrease till it reaches a value corresponding to the uptake of one electron ($\sim 0.2\,\mu A$). The i_l and $E_{1/2}$—pH dependences of these waves are illustrated graphically in Fig. 2 for compound **1 c** and the shifts of $E_{1/2}$ with pH for all other members are compiled in Table 2. As is clear from Fig. 2, $E_{1/2}$—pH plots of waves A_1 and A show mainly two segments in which $E_{1/2}$ is sensitive to pH and two others in which $E_{1/2}$ is practically pH-independent. The values compiled in Table 2 show that d $E_{1/2}$/dpH of segment 1 varies from 65 to 94 mV while in segment 3 from 84 to 94 mV. On the other hand, wave A_2 shows only two segments in which the first one is practically pH-independent while the second depends on pH and the $E_{1/2}$ shift takes a value ranging from 36 to 73 mV. The intersection of the segments are given in Table 3. Also it is important to mention that waves A_1 and A_2 amalgamate at $pH \simeq pKa$ obtained potentiometrically (cf. further discussion).

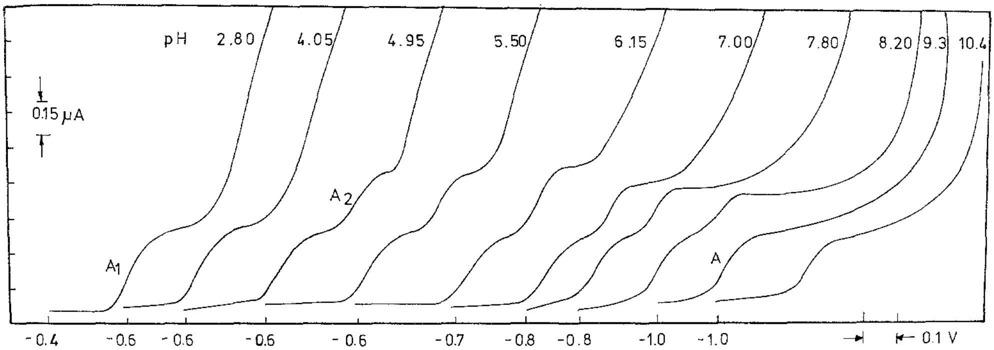


Fig. 1. Schematic representation of the polarograms of $10^{-4}\,M$ of **1 a** in 50% (*v*/*v*) ethanolic *Britton-Robinson* buffers

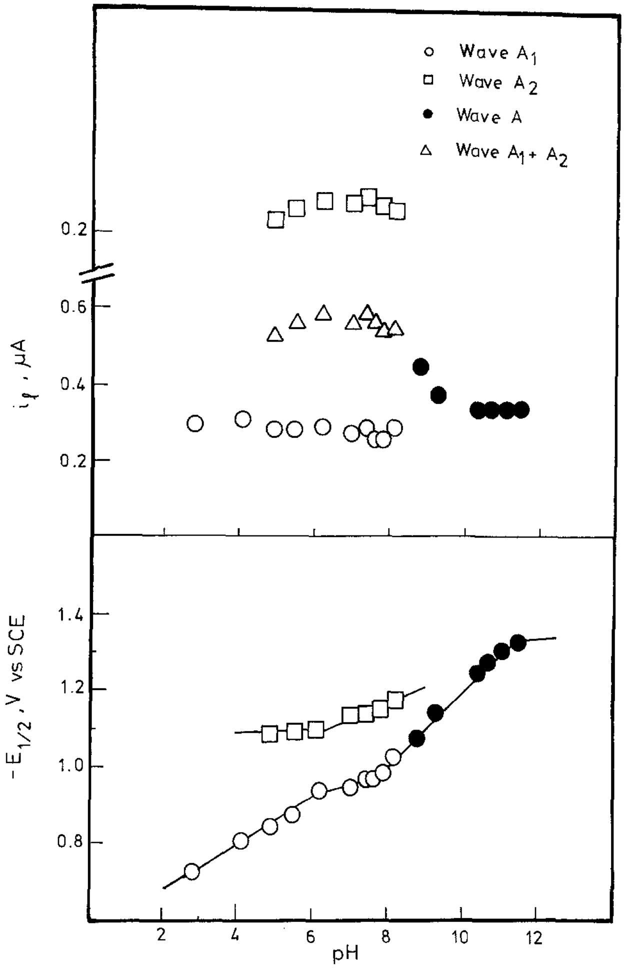


Fig. 2. $E_{1/2}$, i_l–*pH* plots for 10^{-4} *M* **1 a** 50% (*v*/*v*) ethanolic *Britton-Robinson* buffers

The plots of *E* vs. log $(i/i_d - i)$ were found to be linear for each wave, but with different slopes as tabulated in Table 4. These values indicate that the A_1 and A_2 process are reversible individually while the overall process given by wave *A* is irreversible in nature. The reversibility of both waves A_1 and A_2 was also confirmed through *Tom*'s criterion[12].

In addition to wave *A* displayed in polarograms of **1 a–c**, compound **1 d** showed another two additional four and two electrons irreversible diffusion-controlled waves *B* and *C* respectively. The behaviour of the

Table 2. *Linear representation of $E_{1/2}$—pH dependence of waves A_1, A_2 and A of compounds* **1 a–d** *(1 denotes the first segment, 2 the second, and 3 the third)*

Compound No.	Wave A_1	Wave A_2	Wave A
1 a	$E_{1/2}^{1} = -0.490-0.086\,pH$ $E_{1/2}^{3} = -0.390-0.084\,pH$	$E_{1/2}^{2} = -0.790-0.042\,pH$	$E_{1/2}^{1} = -0.390-0.084\,pH$
1 b	$E_{1/2}^{1} = -0.550-0.073\,pH$ $E_{1/2}^{3} = -0.360-0.090\,pH$	$E_{1/2}^{2} = -0.650-0.036\,pH$	$E_{1/2}^{1} = -0.360-0.090\,pH$
1 c	$E_{1/2}^{1} = -0.540-0.065\,pH$ $E_{1/2}^{3} = -0.180-0.094\,pH$	$E_{1/2}^{2} = -0.660-0.073\,pH$	$E_{1/2}^{1} = -0.180-0.940\,pH$
1 d			$E_{1/2}^{1} = -0.150-0.119\,pH$ $E_{1/2}^{3} = +0.100-0.166\,pH$

additional wave *B* can be described by the following linear equation $E_{1/2} = +0.060 - 0.063\,pH$. Since the behaviour of this wave is comparable to the well known aromatic *m*-nitro group [13–15], it is not unreasonable to attribute this extra wave to the reduction of the nitro group to the hydroxylamine stage [14]. At $pH < 4$, the further 2 e wave *C* is attributed to the reduction of the hydroxylamine to the amino stage [15].

Absorption Spectra of Compounds **1 a–d**

The absorption spectra of $4 \cdot 10^{-5}\,M$ of compounds **1 a–d** in solutions of *pH* values 2.0–6.2 are characterised by a broad band with λmax ranging from 338 to 336 nm. This band decreases sharply at $pH \geqslant 7.2$ with the appearance of two broad bands at λmax varying between 282 to 290 and 370 to 400 nm, respectively. The spectra are characterised by the presence of 2 isobestic points (cf. Table 3). The absorption spectra of compounds **1 a** are recorded in Fig. 3 as a typical representative example of the studied series. The absorbance—*pH* curves (Fig. 4) at different wavelengths are characterised by two branches accordingly indicating two ionization processes. The obtained *pKa* values are listed in Table 3. On the other hand, the absorption spectra of $4 \cdot 10^{-5}\,M$ of **2** at *pH* values 2.0–6.2 showed no characteristic bands while at *pH* 7.2 a broad shoulder appeared. Above *pH* 7.2, the spectra are characterised by a band at λmax 286 nm. As the *pH* is further increased the absorbance tends to attain gradually constant values in the *pH* range 9–12. The spectra are illustrated in Fig. 5. The absorbance—*pH* curve (Fig. 6) obtained at wavelength

Table 3. *Spectrophotometric, potentiometric and polarographic data of compounds* **1 a–d** *and model* **2**

Compound No.	Spectrophotometric Data		Potentiometric data			Polarographic Data		
	Maxima/nm	Isobestic Points/nm	*pKa 1*	*pKa 2*	*pKa*	Intersection 1 *pH*	Intersection 2 *pH*	Intersection 3 *pH*
1 a	282 338 370	304 356	5.1	7.55	8.55	4.80	6.00	10.70
1 b	290 366 382	318 378	4.3	7.60	8.60	5.90	7.30	10.40
1 c	286 342 374	306 366	4.6	7.45	8.50	6.20	7.80	11.20
1 d	290 350 400	310 380	5.1	7.50	8.50	7.00	7.90	8.60
2	286 — —	270 —	—	7.60	8.50	—	—	—

Table 4. *Logarithmic analysis data of compounds* **1 a–d**

Compound No.	pH[a]	$RT/\alpha nF$[b]			αn[c]		
		Wave A_1	Wave A_2	Wave A	Wave A_1	Wave A_2	Wave A
1 a	2.90	0.038			1.555		
	5.25	0.037	0.039		1.597	1.515	
	7.70	0.042	0.042		1.407	1.407	
	8.90			0.073			0.810
	10.70			0.060			0.985
1 b	2.50	0.046			1.285		
	5.90	0.051	0.048		1.159	1.231	
	7.20	0.045	0.038		1.313	1.555	
	8.70			0.073			0.810
	10.20			0.061			0.969
1 c	2.80	0.049			1.206		
	5.50	0.052	0.052		1.137	1.137	
	7.35	0.052	0.046		1.137	1.285	
	9.30			0.076			0.778
	10.70			0.060			0.985
1 d	2.80			0.074			0.799
	5.50			0.065			0.909
	7.35			0.069			0.857
	8.20			0.074			0.799
	9.30			0.071			0.832
	11.05			0.067			0.882

[a] Individual *pH* value at which logarithmic analysis was carried out
[b] Slope of logarithmic analysis
[c] Transition coefficient

286 nm displayed one neutralization step analogous to that of a monobasic acid. The inflection of the S shaped plot is comparable to the second inflection in the absorbance—*pH* plots of the spectra of compounds **1 a–d**. Comparing *pKa 2* values with the *pKa* value of model **2** (cf. Table 3) it may be assumed that the ionization is due to the —NH of the acetylamino group. On the other hand, the first *pKa 1* can be assumed to the protonation-deprotonation of the molecule as a whole, since this latter contains different basic sites.

It is also important to mention that the *pKa* values of compounds **1 a–d** and **2** were obtained potentiometrically and only one *pKa* value was observed. These values are found to be practically constant and equal to that of model **2** which is a further indication that the ionization process arises from the —NH site since the activated olefinic (—CH=C—CN) moiety is absent in **2**.

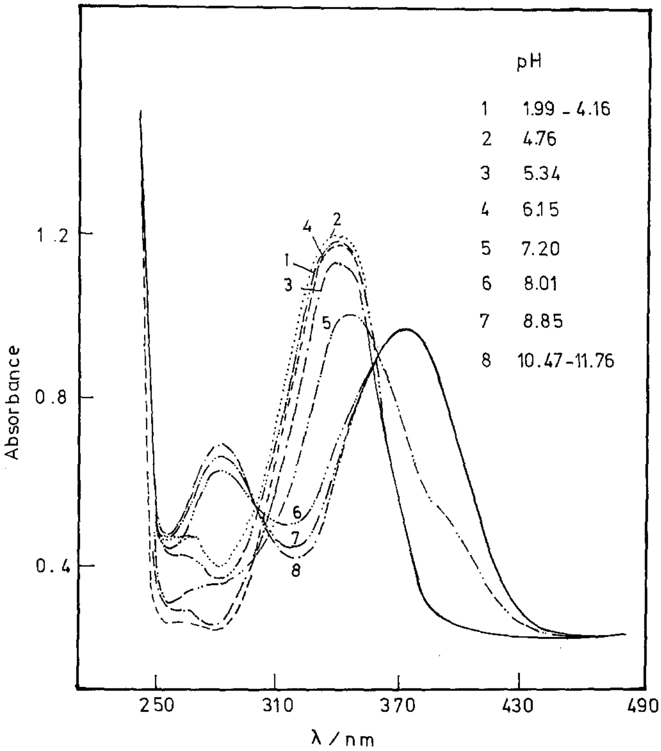


Fig. 3. Electronic absorption spectra of $4 \cdot 10^{-5} M$ **1a** in 50% (*v*/*v*) ethanolic *Britton-Robinson* buffers

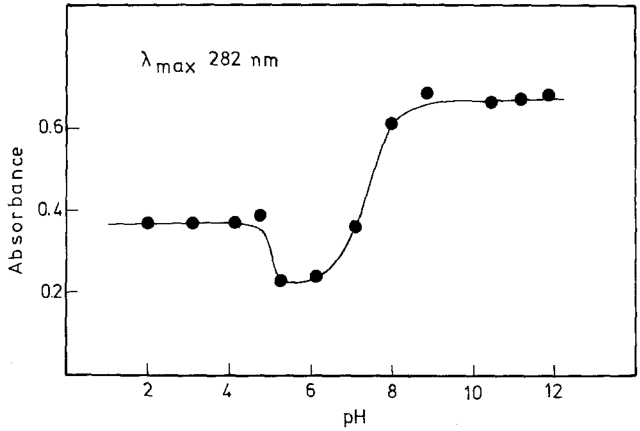


Fig. 4. Absorbance—*pH* curve of **1a**

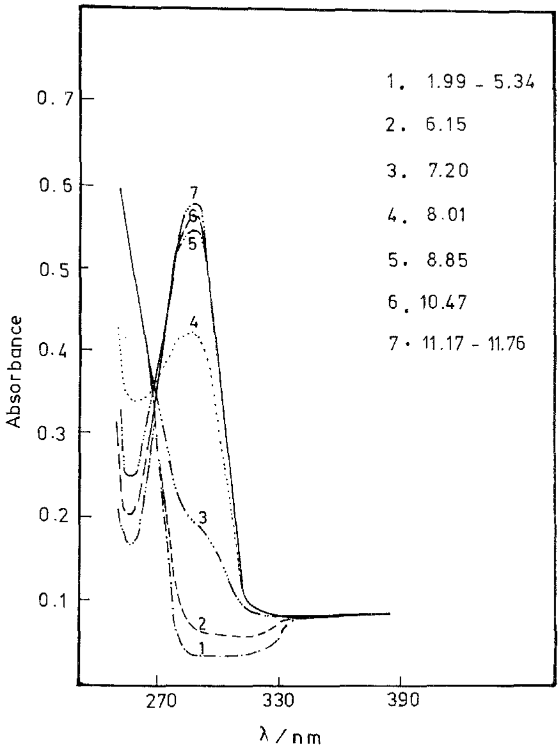


Fig. 5. Electronic absorption spectra of $4 \cdot 10^{-5}$ *M* of model compound **2** in 50% (*v*/*v*) ethanolic *Britton-Robinson* buffers

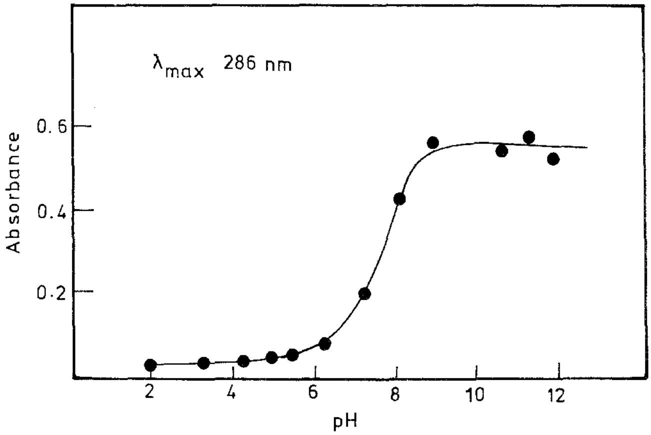


Fig. 6. Absorbance—*pH* curve of model compound **2**

Determination of the Heterogeneous Rate Constant of the Forward Reaction $k^{\circ}_{f,h}$

For an irreversible electrode process the $E_{1/2}$ value is given by Eq. (1) as derived by *Meites* and *Israel* [16, 17]

$$E_{1/2} = [0.0592/\alpha n] \log \frac{1.349\, k^{\circ}_{f,} h^{t^{1/2}}}{D^{1/2}} \tag{1}$$

When potentials are measured against SCE and referred to the NHE a value of —0.2412 is introduced in the RHS of (1).

The same authors used another Eq. (2) in which the constant $E^{\circ}_{1/2}$ is given by (3).

$$E = E^{\circ}_{1/2} - \frac{0.0592}{\alpha n} \left[\log \frac{i}{i_d - i} - 0.0546 \log t \right] \tag{2}$$

$$E^{\circ}_{1/2} = \frac{0.0592}{\alpha n} \log \frac{1.349\, k^{\circ}_{f,h}}{D^{1/2}} \tag{3}$$

Thus a plot of E vs. log $(i/i_d - i) - 0.546 \log t$ will give a straight line and $E^{\circ}_{1/2}$ is equal to the value of E at $\log(i/i_d - i) - 0.546 \log t$ equals zero. Where α, n, t are known parameters and D is calculated from the *Ilkovic* equation using i_{max} and hence the constant 708 [18] and not 604. The values of $k^{\circ}_{f,h}$ for wave A calculated from Eqs. (1) and (2) respectively are tabulated in Table 5. The values are more or less equal. These values decrease with *pH* increase and thus the rate of the forward reaction is directly related to the variation of the H^+ concentration [19].

Mechanism of the Electrode Process

At this stage it was of interest to see whether the heterocyclic portion of the molecule is an electroactive site or not, thus the polarograms of model **2** were run under the same experimental conditions (*pH* 2–12). No wave was displayed, indicating that under these conditions the ring is electroinactive. From the foregoing results one may conclude that waves A_1, A_2 and A are due to the electroreduction of the —C=C— linkage as illustrated in Scheme 1. Thus in acid media of $pH < 3.5$ the compound is reduced along a one electron reversible *pH*-dependent diffusion-controlled wave A_1. Since the ^{1}H NMR spectra did not fit the dimer structure proposed for the activated double bonds [1–5] and after the discussion of the onbtained data (C, H, N, S, analyses, IR and ^{1}H NMR) we found that they fit structure **3** (cf. Scheme 1). It is important to mention that we failed to isolate compound **2** which is easily oxidized to **3** during the extraction process [20]. This latter structure (**3**) is formed through a

Table 5. *Polarographic characteristics of compounds* **1 a–d**

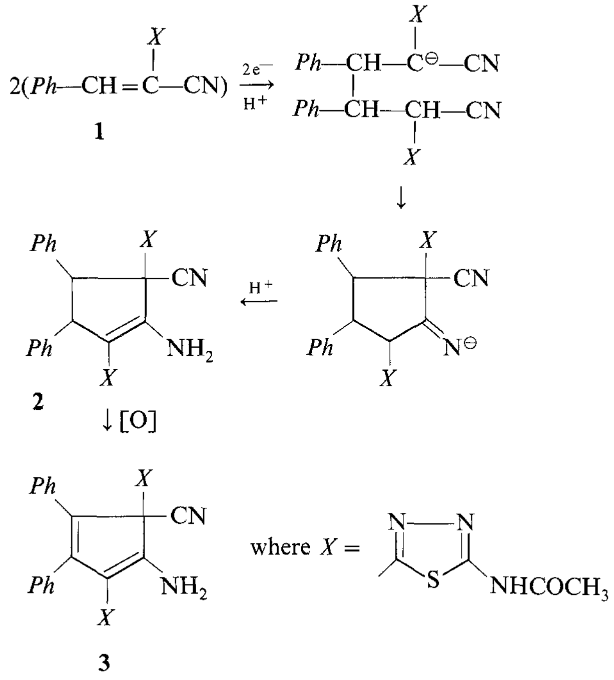
Compound No.	*pH*	$-E_{1/2}$/V vs. SCE	i_d, μA	$\frac{0.0592}{\alpha n}$	*n*	$D \cdot 10^{-6}$ cm^2/s	$k^\circ_{f,h}$/cm^{-1} [a]	$k^\circ_{f,h}$/cm^{-1} [b]
1 a	8.5	1.17	0.45	0.073	2	2.3	$1.110 \cdot 10^{-16}$	$1.131 \cdot 10^{-16}$
	10.7	1.30	0.26	0.060	1	3.0	$1.530 \cdot 10^{-21}$	$1.345 \cdot 10^{-20}$
1 b	8.5	1.19	0.48	0.073	2	2.6	$6.310 \cdot 10^{-17}$	$4.670 \cdot 10^{-17}$
	10.4	1.33	0.24	0.061	1	2.6	$8.874 \cdot 10^{-22}$	$1.401 \cdot 10^{-21}$
1 c	8.8	1.08	0.45	0.076	2	2.3	$1.546 \cdot 10^{-15}$	$1.187 \cdot 10^{-15}$
	9.3	1.18	0.38	0.076	2	1.6	$2.436 \cdot 10^{-16}$	$9.152 \cdot 10^{-17}$
	10.4	1.32	0.34	0.060	2	1.3	$4.400 \cdot 10^{-22}$	$3.893 \cdot 10^{-22}$
1 d	8.2	1.13	0.33	0.074	2	1.2	$1.146 \cdot 10^{-16}$	$1.172 \cdot 10^{-16}$
	9.3	1.23	0.27	0.071	1	3.3	$1.317 \cdot 10^{-18}$	$1.574 \cdot 10^{-18}$
	11.05	1.27	0.26	0.067	1	3.0	$6.034 \cdot 10^{-20}$	$2.624 \cdot 10^{-21}$

[a] According to Eq. (1)
[b] According to Eq. (2)

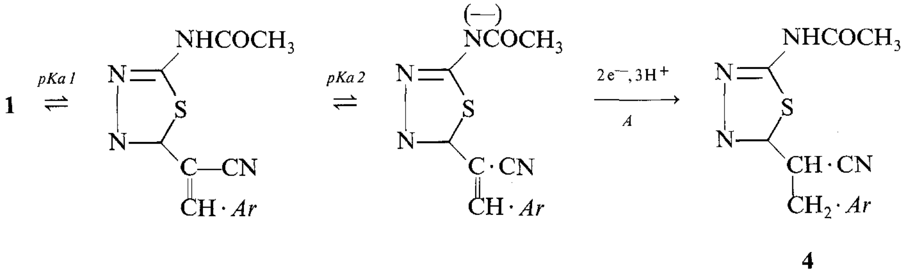
Ziegler-Throp reaction and a similar mechanism has been reported by *Wawzonek* et al. [21]. At $pH \geqslant 4$, two waves A_1 and A_2 are displayed. While A_1 is pH-dependent in $E_{1/2}$ wave A_2 is practically independent. With increasing pH the two waves amalgamate to give wave A, because the shift of $E^2_{1/2}$ is smaller than that of $E^1_{1/2}$ the two waves merge, which is irreversible

Scheme 1

At $pH < pKa\,1$



At $pH \geqslant pKa\,2$



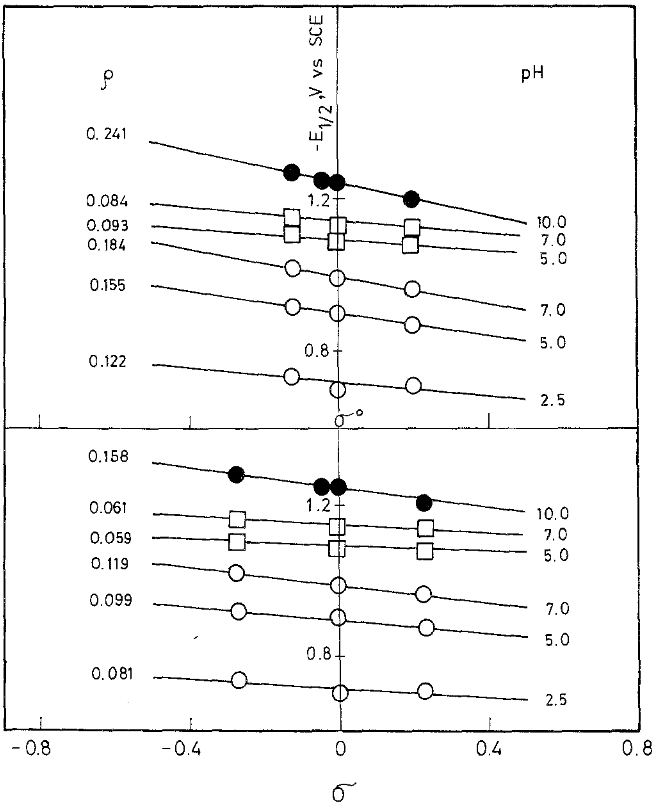


Fig. 7. *Hammett*'s correlation: ○ wave A_1, □ wave A_2, and ● wave A

in nature and the irreversibility of this wave increases towards higher *pH* values as revealed by the values of $k^{\circ}_{f,h}$ tabulated in Table 8. In highly alkaline media ($pH \geqslant pKa2$) the wave height of A decreases to a value corresponding to a one electron transfer to form most probably the hydrodimer as previously reported [4, 5]. The formation of compound **4** (cf. Scheme 1) has been proved by CPE at *pH* 8.6 in which the saturated olefin was separated and identified as a product of electrolysis.

For further confirmation of the suggested mechanism *Hammett*'s correlations were undertaken on waves A_1, A_2, and A. As is clear from Fig. 7, wave A_1 and A gave good linearity indicating that the reduction center is in a direct conjugation with the benzene ring (aryl group). The lower σ value of A_2 may be explained by the fact that two mechanism can participate at the same time (an CEEC or a CECE mechanism). The points fitted the straight line when σ_{NHOH} were used instead of $\sigma_{m\text{-}\mathrm{NO}_2}$ for **1d** indicating that the nitro group is reduced prior to C=C.

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