

**POLAROGRAPHIC AND CYCLIC VOLTAMMETRIC BEHAVIOUR
OF SOME AZO COMPOUNDS DERIVED FROM SULFONAMIDE
IN DMF-AQUEOUS SOLUTIONS**

El-Sayed M. MABROUK*, Hamada M. KILLA, Abdel Fattah A. Abdel FATTAH
and Shalaby A. YASEN

Chemistry Department, Faculty of Science, Zagazig University Zagazig, Egypt

Received October 10, 1990

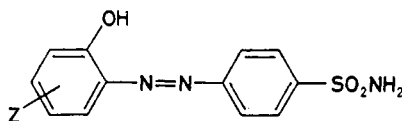
Accepted April 1, 1991

The polarographic and cyclic voltammetric behaviour of (2-hydroxyphenylazo)-4-benzene-sulfonamide and some of its derivatives have been studied in Britton-Robinson buffer series containing 30 vol. % of DMF. Over the entire pH range (2–12), the reduction pathway occurs through an irreversible 4-electron step corresponding to the reduction of N=N center to the amine stage. The voltammograms recorded in acidic and alkaline solution at different scan rates exhibit one or two cathodic peaks depending on the substituent and the pH of the medium. The electrode reaction mechanism was suggested, also the kinetic parameters were calculated.

Azo dyes and Schiff bases derived from sulfonamides have acquired wide interest in application to biological systems¹⁻³ and electrochemical studies⁴⁻⁶. Although the electroreduction of azo compounds drew the attention of many workers, yet it seems that little attention has been paid to the electrochemical behaviour at a mercury electrode of those derived from sulfanilamide. Accordingly, the present article is devoted to study the electroreduction of these compounds using DC-polarography and cyclic voltammetry techniques.

EXPERIMENTAL

The azo dyes of sulfonamide derivatives were prepared by coupling the diazotized amine with *m*- or *p*-substituted phenol derivatives in sodium hydroxide medium⁷. The crude products were then recrystallized from the proper solvent. Elemental and structural analysis confirmed the general formula shown below.



- | | |
|---|---------------|
| I, Z = 4-OH | IV, Z = 5-Br |
| II, Z = 5-OCH ₃ | V, Z = 5-COOH |
| III, Z = 4-N(CH ₃) ₂ | VI, Z = 5-CHO |

* Author to whom correspondence should be addressed.

A series of Britton–Robinson buffers (pH 2–12) was used as supporting electrolyte. The prepared solutions were checked using a digital pH-meter ORION RESEARCH model 601A. The calculated volume of stock solution ($5 \cdot 10^{-3} \text{ mol dm}^{-3}$) of the depolarizer was introduced into the electrolysis cell with a final concentration $1.25 \cdot 10^{-4} \text{ mol dm}^{-3}$ containing 30 vol. % of DMF. A stream of pure nitrogen gas was bubbled for 10 min through the mixture to remove oxygen traces.

The polarograms were recorded using a Metrohm polarograph model 663 VA stand with X–Y recorder model 626 and Ag/AgCl as a reference electrode. A polarographic Analyzer model 264A (PARC) and the electrode assembly model 303 A with hanging mercury drop electrode (HMDE) of area $2.6 \cdot 10^{-2} \text{ cm}^2$ as working electrode, a platinum wire as counter electrode and Ag/AgCl as a reference electrode were used for cyclic voltammetry measurements. X–Y recorder model RE0089 (Houston Instruments) was used for recording the voltammograms. A coulometric system model PARC-380 with a mercury pool cathode was used in determining the number of electrons consumed in the reduction process.

RESULTS AND DISCUSSION

DC-Polarography (*Tast Mode*)

The polarograms of $1.25 \cdot 10^{-4} \text{ mol dm}^{-3}$ of the azo compounds I–VI were recorded in Britton–Robinson buffer solutions of pH 2–12 containing 30 vol. % of DMF. For all compounds except VI, the polarograms exhibit a single wave with a limiting current corresponding to a four electron consumption as shown in Fig. 1 for the compound IV. On the other hand, the polarograms of compound VI are

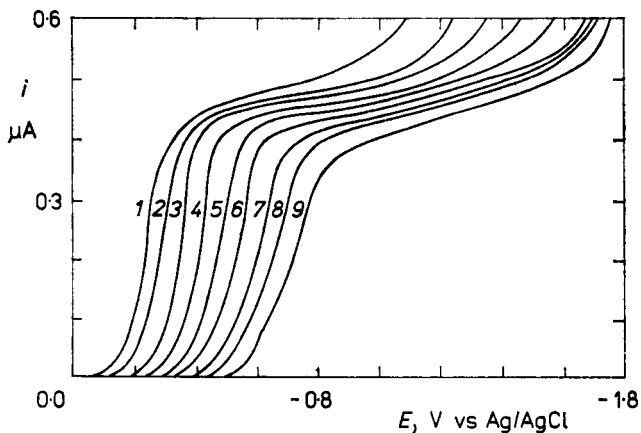


FIG. 1

DC polarograms of $1.25 \cdot 10^{-4} \text{ mol l}^{-1}$ of compound IV (5-Br) in 30 vol. % of DMF buffer solutions at different pH values 1 3.22, 2 4.0, 3 5.15, 4 6.06, 5 7.18, 6 8.05, 7 9.03, 8 10.00, 9 11.80

composed of two waves of unequal height. The height of the first wave is almost twice that of the second one. In comparing this compound with the other, it is concluded that the first wave represented the electroreduction of the N=N center, whereas the second wave is due to the reduction of the electroactive (-CHO) group⁸⁻¹⁰. However, in solution of pH > 7, the reduction wave of compound *I* splits into two waves of unequal heights, the i_d of the second wave increases while the i_d of the first wave decreases on increasing the pH of the electrolysis solution within the pH range 7–11 confirming an acid-base equilibrium¹¹.

The effect of mercury pressure on the limiting current denotes that the reduction process is mainly diffusion-controlled with a slight adsorption contribution, since the values of the exponent x in the relation $i_L = Kh^x$ at different pH values equal to 0.47–0.62 (ref.¹²). The analysis of the polarographic waves applying the fundamental equation¹³ indicates that the electrode process proceeds irreversibly, since the values of the transfer coefficient (α) are found to be less than 0.7 at $n_a = 2.0$ as illustrated in Table I, n_a is the number of electrons involved in the rate-determining step. The half-wave potentials ($E_{1/2}$) display a cathodic shift on increasing the pH of the medium. This behaviour means that hydrogen ions are consumed in the reduction process and the proton transfer precedes the electron uptake¹¹. The plots of $E_{1/2}$ values vs pH yield straight lines consisting of one or two segments. From the slopes of logarithmic analysis (S_1) and those of $E_{1/2}$ -pH plots (S_2), the number of protons (Z_H^+) participating in the rate-determining step was calculated¹³ and found to be unity (Table I). Thus, the rate-determining step should involve one proton and two electrons.

Cyclic Voltammetry

The voltammograms of all compounds (except *VI*) exhibit one or two peaks in the cathodic scan in acidic and alkaline solutions, respectively, which represent the reduction of the N=N center in one or two steps, depending on the acidity of electrolysis solution, Fig. 2 represents the C. V. of compound *IV* at pH 3.8. However, in case of the azo compound *VI* an additional cathodic peak is observed (Fig. 3) which represents the reduction of the electroactive (-CHO) center. These results are in a good agreement with those obtained from DC-polarography. The variation of the peak potential (E_p) with scan rate, reveals that the reduction process was irreversible. On the other hand, the plotting of peak current (i_p) vs square root of scan rate ($v^{1/2}$) applying the equation¹⁴.

$$i_p = 3.01 \cdot 10^5 n(\alpha n_a)^{1/2} AD^{1/2} C^0 v^{1/2} \quad (1)$$

gives straight line passing through origin confirming that the electrode reaction is mainly diffusion-controlled¹⁴. The anodic peak appearing in the reverse scan (anodic direction) may be attributed to the formation of hydrazo intermediate¹⁵.

Mechanism of the Electrode Reaction

In order to investigate the reduction pathway of the azo compounds (I–VI) at mercury electrode, the total number of electrons involved in the reduction process have been calculated using Ilkovich equation. The values of the diffusion coefficient

TABLE I
Data obtained from DC-polarography

Compound	pH	i_d μA	$-E_{1/2}$, V (Ag/AgCl)	$\frac{0.0591}{\alpha n_a}$ mV	$E_{1/2}/\text{pH}$ mV	Z_H^+	α
I	2.25	0.62	0.28	61	45	0.74	0.48
	6.09	0.60	0.36	87	70	0.80	0.34
	10.12	0.08 ^a	0.57 ^a	56 ^a	60 ^a	1.07 ^a	0.53 ^a
		0.54 ^b	1.09 ^b	61 ^b	75 ^b	1.23 ^b	0.48 ^b
II	2.03	0.60	0.14	72	53	0.74	0.41
	6.06	0.55	0.33	80	53	0.66	0.37
	10.00	0.51	0.56	70	53	0.76	0.43
III	2.03	0.58	0.19	72	61	0.85	0.41
	6.06	0.52	0.46	83	61	0.73	0.38
	10.00	0.45	0.64	83	52	0.63	0.35
IV	3.22	0.55	0.22	59	55	0.94	0.50
	6.06	0.50	0.38	72	55	0.78	0.41
	10.00	0.45	0.60	73	55	0.77	0.40
V	2.03	0.69	0.13	66	56	0.85	0.45
	6.06	0.64	0.33	81	56	0.69	0.36
	10.00	0.58	0.55	67	56	0.84	0.44
VI	3.10	0.59	0.24	73	53	0.73	0.41
	6.40	0.54 ^a	0.35 ^a	74 ^a	53 ^a	0.72 ^a	0.40 ^a
		0.30 ^b	1.38 ^b	63 ^b	65 ^b	1.05 ^b	0.47 ^b
	10.34	0.46 ^a	1.15 ^a	79 ^a	170 ^a	2.15 ^a	0.38 ^a
		0.30 ^b	1.64 ^b	65 ^b	127 ^b	1.95 ^b	0.46 ^b

^a First wave; ^b second wave.

coefficients of the depolarizers in units $\text{cm}^2 \text{s}^{-1}$ were calculated using the following equation¹⁶.

$$D^0 = 3.22 \cdot 10^{-5} / (V_m)^{1/3} \quad (2)$$

knowing the molar volume V_m of the depolarizer species. The obtained D^0 corresponded to the depolarizer values in aqueous solutions. In the present work, 30 vol. % of DMF was used. Thus, the viscosity of the medium should be taken into account. The corrected value of D^0 was calculated and found to be $2.6 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

By substituting the D^0 values in Ilkovich equation, it was found that four electrons were consumed in the reduction of $\text{N}=\text{N}$ centre of the present azo compounds in alkaline and acidic solutions. For compound *VI*, the number of electrons calculated for the second wave ($-\text{CHO}$ group) was found to be 2 electrons.

It should be noted that the above results were confirmed by controlled potential coulometry using a mercury pool cathode. The accumulated charge (Q) was taken directly from the digital coulometer at a potential corresponding to the limiting cur-

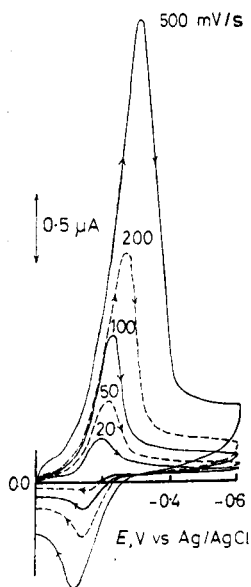


FIG. 2
Cyclic voltammograms of 0.1 mmol l^{-1} of compound *IV* in 30 vol. % of DMF buffer solutions at pH 3.8 for different scan rates

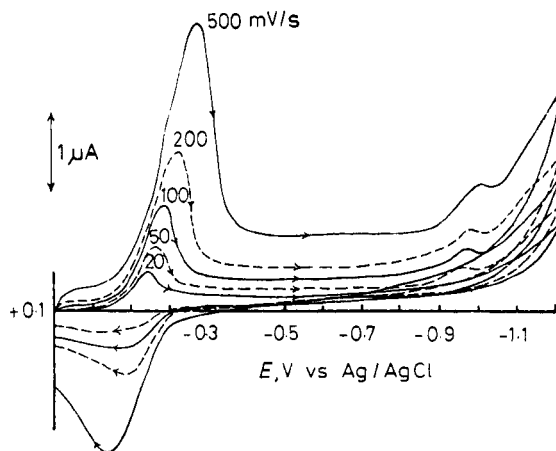


FIG. 3
Cyclic voltammograms of 0.1 mmol l^{-1} of compound *VI* in 30 vol. % of DMF buffer solutions at pH 3.8 for different scan rates

rent. Applying the following equation:

$$Q = \frac{nFW}{M}, \quad (3)$$

where W is the weight of the sample (grams) and M its molecular weight. The average number of electrons (n) was found to be four electrons in both acidic and alkaline

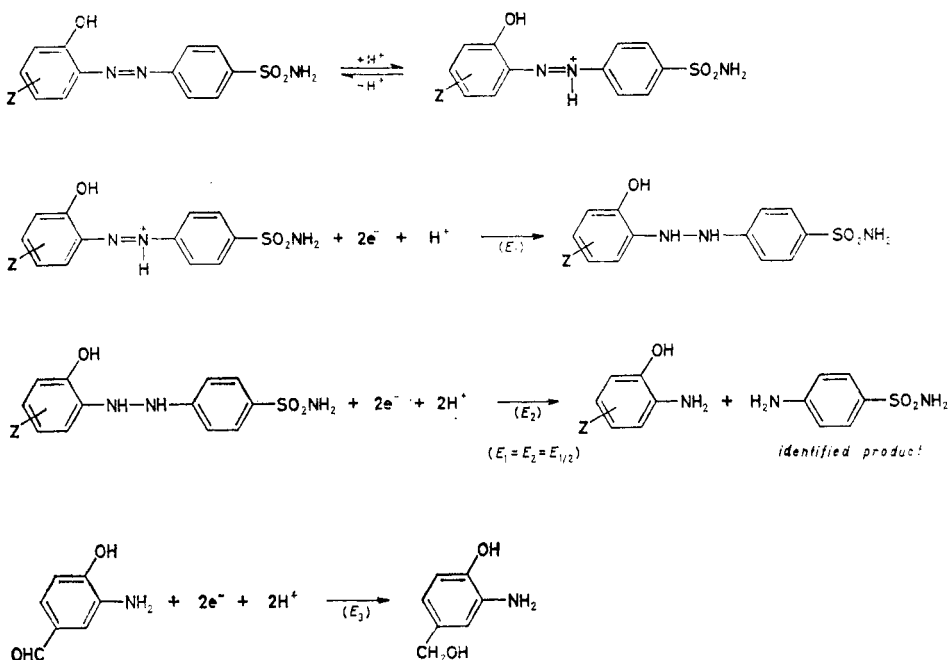
TABLE II
Kinetic parameters calculated using DC-polarography

Compound	pH	$K_{f,b}^0$ cm s^{-1}	ΔG^* kJ mol^{-1}
I	2.25	$2.05 \cdot 10^{-4}$	212.3
	6.09	$5.94 \cdot 10^{-5}$	225.3
	10.12	$4.99 \cdot 10^{-7a}$	275.5 ^a
		$4.25 \cdot 10^{-11b}$	373.7 ^b
II	2.03	$6.94 \cdot 10^{-3}$	175.1
	6.06	$4.96 \cdot 10^{-5}$	226.9
	10.00	$5.92 \cdot 10^{-9}$	321.9
III	2.03	$1.16 \cdot 10^{-3}$	193.9
	6.06	$6.47 \cdot 10^{-7}$	272.5
	10.00	$5.40 \cdot 10^{-9}$	322.7
IV	3.22	$4.05 \cdot 10^{-4}$	205.2
	6.06	$2.74 \cdot 10^{-6}$	257.5
	10.00	$2.30 \cdot 10^{-7}$	280.9
V	2.03	$1.02 \cdot 10^{-2}$	171.4
	6.00	$3.31 \cdot 10^{-5}$	235.3
	10.00	$5.06 \cdot 10^{-9}$	323.5
VI	3.10	$4.19 \cdot 10^{-4}$	204.8
	7.05	$1.55 \cdot 10^{-5a}$	239.5 ^a
		$2.21 \cdot 10^{-5b}$	477.4 ^b
	10.34	$5.06 \cdot 10^{-13a}$	420.1 ^a
		$1.96 \cdot 10^{-19b}$	575.2 ^b

^a First wave; ^b second wave.

solutions. But in case of compounds *VI*, 6 electrons (e.g. N=N and -CHO groups) were obtained at a potential corresponding to the total limiting current.

Thin layer chromatography was applied on the completely electrolyzed solutions of compounds *I* and *VI* to characterize the products of the reduction process. The solution was firstly concentrated and the buffer ingredients were removed by extracting the slurry with ether. On comparing the TLC of the ethereal extract in petroleum ether-ethylacetate mixture with authentic sulfanilamide sample, it was found that the sulfanilamide is one of the main electrolysis products. It is concluded that the reduction process involves the cleavage of the -N=N- bond through the uptake of four electrons. For compound *VI*, six electrons were consumed in the reduction process, four electrons for the cleavage of the N=N centre. This means that the remaining two electrons are consumed in the reduction of the (-CHO) group. Based on the foregoing results, the reduction mechanism can be suggested as represented in Scheme 1.



SCHEME 1

On the other hand, the heterogeneous rate constant ($K_{f,h}^0$) and energy of activation (ΔG^*) of the electrode reaction were calculated from DC-polarography wave (tast mode) using Koutecký¹⁷ and Heyrovský¹⁸ equations. The calculated values are

given in Table II, it is concluded that ($K_{r,n}^0$) decreases on increasing the pH of the electrolysis medium showing a more difficult electron transfer. This behaviour may be supported by the increasing of the (ΔG^*) as the pH increased.

The authors wish to thank Prof. M. M. Ghoniem, Tanta Univesity, for his kind assistance and Dr M. Gaber of the same University for his help in preparing and characterization the azo compounds.

REFERENCES

1. Yamashita S., Seyama Y., Ishikawa N.: *Experientia* **34**, 472 (1979).
2. Bult A., Uitterdijk J. A., Kalsen H. B.: *Pharm. Weekbl. Sci. Ed.* **3**, 191 (1979).
3. El-Ries M. A., Abu-El-Wafa S. M., El-Kousy S. M.: *J. Pharm. Belg.* **43**, 99 (1988).
4. Bittencourt C. F., Wisniewski K. C.: *Rev. Inst. Adolfo Lorentz*, **35—36**, 23 (1976).
5. Malik W. U., Dau P. N.: *J. Electroanal. Chem.* **132**, 211 (1982).
6. Seth C. K., Bannerjee N. R., Sharma V. K.: *Electrochim. Acta* **26**, 1915 (1981).
7. Grinberg I. V., Kushko G. M.: *Zap. L'vov. Palickh. Inst. Khim. Ukr. Zh.* **27**, 94 (1961).
8. Dur-Sun K., Dezelic M.: *Glas Hem. Technol. Bosne Hercegovine* **16**, 87 (1968).
9. Hornyl G.: *Electrochim. Acta* **31**, 1095 (1986).
10. Rodriguez-Mellado J. M., Ruiz J. J.: *J. Electronal. Chem.* **199**, 177 (1986).
11. Zuman P.: *The Elucidation of Organic Electrode Processes*, p. 28. Academic Press, New York 1969.
12. Heyrovský J., Kůta J.: *Principles of Polarography*, p. 61. Academia, Prague 1965.
13. Meites L.: *Polarographic Techniques*, 2nd ed., p. 240. Interscience Publishers, New York 1965.
14. Bard A. J., Faulkner L. R.: *Electrochemical Methods*, p. 218. Wiley, New York 1980.
15. Millefiori, Salvatore: *Ann. Chem.* **59**, 128 (1969).
16. Kolthoff I. M., Lingane J.: *Polarography. Theoretical Principles. Instrumentation and Technique*, Vol. 1, p. 58 (1965).
17. Koutecký J.: *Chem. Listy* **47**, 323 (1953); *Collect. Czech. Chem. Commun.* **18**, 597 (1955).
18. Heyrovský J.: *Polarographie*, p. 185. Springer, Wien 1941.