Monatshefte für Chemie 118, 1335—1343 (1987)

**Monatshefte für Chemie**
**Chemical Monthly**

# Polarographic Behaviour of 2,2′-Dipyridyl-2-pyridylhydrazone (*DPPH*) and Pyridine-2-aldehyde-2-quinolylhydrazone (*PAQH*) at the Dropping Mercury Electrode

**Ali Z. Abu Zuhri*** and **Jamal S. Shalabi**

Chemistry Department, Faculty of Science, An-Najah National University
Nablus, West Bank, Via Israel

*(Received 14 October 1985. Revised 20 June 1986. Accepted 25 June 1986)*

The polarographic behaviour of 2,2′-dipyridyl-2-pyridylhydrazone (*DPPH*) and pyridine-2-aldehyde-2-quinolylhydrazone (*PAQH*) at *dme* were studied in aqueous *Britton-Robinson* buffers containing 50% ethanol. The polarograms consist of one irreversible wave in the acidic and alkaline medium. Two electrons are consumed in the splitting of the N—N bond. The effect of *pH* on the limiting current and $E$ as well as the reduction mechanism are discussed and compared with similar compounds. The values of the kinetic parameters for the electrode reaction at different *pH* values are also computed from the polarographic results.

*(Keywords: Electrochemistry; Reduction mechanism; Kinetic parameters)*

*Das polarographische Verhalten von 2,2′-Dipyridyl-2-pyridylhydrazon (DPPH) und Pyridin-2-aldehyd-2-chinolylhydrazon (PAQH) an der tropfenden Quecksilberelektrode*

Das polarographische Verhalten der Titelverbindungen *DPPH* und *PAQH* wurde in wäßrigen *Britton-Robinson*-Puffern mit 50% Ethanolgehalt an der tropfenden Quecksilberlelektrode untersucht. Die Polarogramme zeigen eine irreversible Welle im basischen und alkalischen Medium. Zwei Elektronen werden bei der Spaltung der N—N-Bindung verbraucht. Der *pH*-Effekt auf den Grenzstrom und $E_{1/2}$ und auch auf den Reduktionsmechanismus wird diskutiert und mit ähnlichen Verbindungen verglichen. Die kinetischen Parameter für die Elektrodenreaktion werden für verschiedene *pH*-Werte aus den polarographischen Daten berechnet.

## Introduction

Hydrazones (particularly hydrazones of nitrogen-containing heterocycles) have attracted much attention as analytical reagents. *Lions* et al.

[1, 2] first reported the analytical properties of these compounds. Their analytical applications have been reviewed by *Katyal* et al. [3]. Various substituted hydrazones, especially 2,2′-dipyridyl-2-pyridylhydrazone (*DPPH*) and pyridine-2-aldehyde-2-quinolylhydrazone (*PAQH*) have been used for the spectrophotometric determination of different metal ions [4–10]. On the other hand, the polarographic behaviour of hydrazone compounds have been the subject of many investigations [11–16], but those related to nitrogen-containing heterocyclic hydrazones are scarce. However, a literature survey revealed the absence of polarographic data on *DPPH* and *PAQH.*

In this paper, the polarographic behaviour of *DPPH* and *PAQH* has been investigated to throw some light on their reduction mechanism and to compare their behaviour with that of pyridine-2-aldehyde-2-pyridylhydrazone (*PAPH*) which previously were reported by us [16].

## Experimental

2,2′-Dipyridyl-2-pyridylhydrazone (*DPPH*) and pyridine-2-aldehyde-2-quinolylhydrazone (*PAQH*) were prepared as reported by *Vasilikiotis* [4] and *Ryan* [9], respectively. $10^{-2}$ *M DPPH* and *PAQH* solutions were prepared by dissolution of an appropriate amount of solid in hot ethanol. As supporting electrolytes the universal buffer series of *Britton* and *Robinson* [17] was used.

The average current-voltage curves were recorded by a polarograph model A 3001 (Sargent Welch). The electrode characteristics of the dropping mercury electrode were $m = 1.53\,\mathrm{mg\,s^{-1}}$ and $t = 4.9$ s at a mercury height of 57 cm. The *pH* values of the solution were measured with an corning model 12 *pH* meter using a glass and SCE electrodes.

### *Controlled Potential Electrolysis and Identification of the Products*

In order to clarify the reaction mechanism, 200 mg of *DPPH* in two buffers (*pH* 1.89 and 11.80), containing 50% ethanol, was electrolysed. The potential was controlled at —1.50 V and —1.90 V vs. SCE at *pH*'s 1.89 and 11.80 respectively (i.e. on the limiting current plateau of the wave). The electrolysis cell was a 250 ml conical flask in which the reference (SCE), auxiliary electrode (Pt electrode), and the gas inlet were inserted through a cork. The progress of electrolysis was followed by recording the decrease in current with time and the number of electrons involved in the electrode process was computed from the *i-t* curves following the procedure outlined by *Lingane* [18]. For the reduction of *DPPH* the number of electrons was calculated and found to be $\cong 2$ in both buffers. After disconnecting the electrolysis cell from the circuit 2,2′-dipyridylketone was identified among the products of electrolysis by evaporating the ethanol and adding about 5 ml of 4% HCl solution, followed by extraction with ether several times; the ether layer was then evaporated and the i.r. spectra of the remaining residue was recorded. On the other hand, the aqueous layer was treated with NaOH solution and after workup as above, 2-aminopyridine was obtained.

## Results and Discussion

### *Effect of pH on the Polarogram*

The polarograms of $5 \cdot 10^{-4}$ *M DPPH* and *PAQH* in 50% ethanolic buffer covering the *pH* range 1.15–11.80 display a defined irreversible wave. The height of wave was practically constant within the whole *pH* range (Figs. 1 and 2). In all buffer solutions, the waves are accompanied by a maximum which can be eliminated by the addition of Triton X-100.

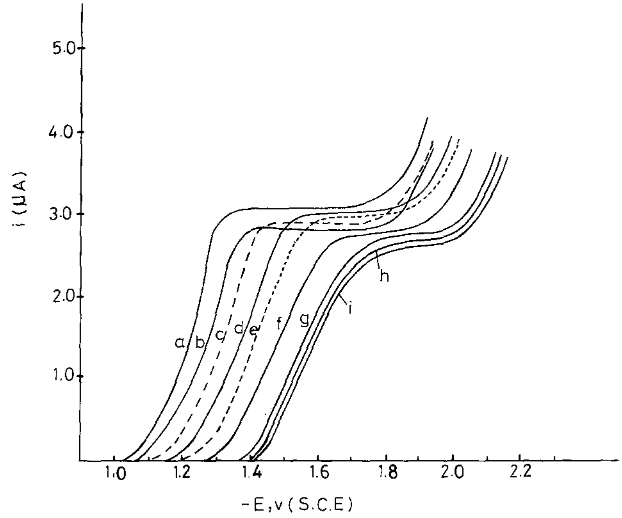


Fig. 1. Effect of *pH* on $5 \cdot 10^{-4}$ *M DPPH* in 50% ethanol in presence of $4.0 \cdot 10^{-3}$ *M* Triton X-100: *a pH* 1.89; *b ph* 2.56; *c pH* 3.41; *d pH* 4.68; *e pH* 5.44; *f pH* 6.20; *g pH* 8.25; *h pH* 10.70; *i ph* 11.80

The $\Delta E/\Delta pH$ relations are straight lines with slopes equal to 0.055 and 0.060 in the *pH* range 1.15–8.25 and 1.15–7.34 for *DPPH* and *PAQH*, respectively (Fig. 3). These slopes indicate that 1 $\mathrm{H}^+$ ion per electron was consumed in the rate-determining step, because $\Delta E/\Delta pH = X_{\mathrm{H}^+}(0.59/\alpha n_a)$ in which $X_{\mathrm{H}^+}$ and $n_a$ represent the number of $\mathrm{H}^+$ ions and electrons involved in the rate-determining step. Above *pH* 8.25 and 7.34 for *DPPH* and *PAQH*, respectively, *E* is practically *pH* independent, as shown in Fig. 2. This behaviour may be attributed to the fact that in the alkaline buffer solutions electrons are added directly to the molecule without preliminary pre-protonation reaction [19].

On comparing the values of *E* of the reduction waves for *DPPH*, *PAQH* and pyridine-2-aldehyde-2-pyridylhydrazone (*PAPH*) [16] at the

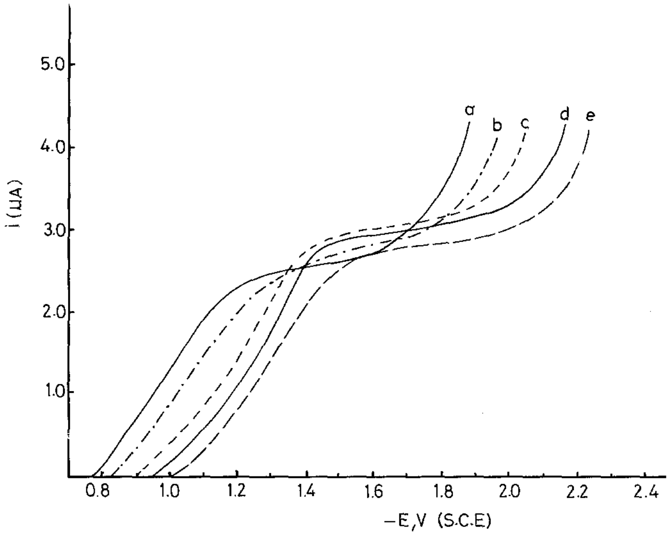


Fig. 2. Effect of *pH* on $5 \cdot 10^{-4}$ *M PAQH* in 50% ethanol in presence of $4.0 \cdot 10^{-3}$ *M Triton X*-100: *a pH* 1.89; *b pH* 3.41; *c pH* 5.44; *d pH* 7.53; *e pH* 10.75

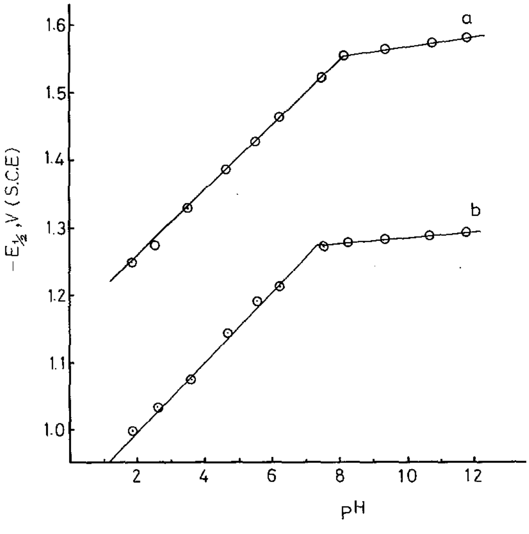


Fig. 3. *E—pH* plot: *a DPPH*, *b PAQH*

same *pH*, it becomes evident that *E* of *PAQH* has a less negative value than for the other two compounds. This may be due to the electron attracting character of the quinolyl group of *PAQH* which decreases the electron density of the nitrogen atoms causing the reduction of *PAQH* to take place at somewhat less negative potential in comparison to *PAPH* and *DPPH*, as shown in Table 1.

### *Investigation of the Waves*

The plot of log $i_1$ as a function of log $h$ for the reduction waves at *pH*'s 2.56, 7.34 and 11.80 indicates that the exponent $X$ in the relation ($i_1 = Kh^X$) varies between 0.44 and 0.66. These data indicate that the process of reduction is mainly under diffusion control with some adsorption contribution. Analysis of the waves was carried out by applying the fundamental equation for polarographic waves viz.

$$E = 0.059/\alpha n_a (\log i/i_d - i) \text{ at } 25\,^\circ\mathrm{C}$$

The slopes of $E$ vs. $\log i/i_d - i$ plots indicate that the electroreduction of *DPPH* and *PAQH* is irreversible (Table 1) since the overall electrode reaction involves the uptake of two electrons in the whole *pH* range (see below). The values of the transfer coefficient ($\alpha$) obtained are less than unity, confirming the irreversible nature of the wave (Table 1).

### *Reduction Mechanism*

In order to elucidate the mechanism for the electrode reduction process, the number of electrons involved along the reduction waves at various *pH*'s has been calculated. This can be done by the aid of the *Ilkovic* equation, provided that $D$, the diffusion coefficients of the two compounds, are known. The values of $D$ for *DPPH* and *PAQH* may be calculated using the method previously reported for *PAPH* [16]. The values of $D$ thus obtained correspond to that in aqueous solutions. For use in 50% ethanol solutions, the effect of viscosity of the medium must be accounted for. The corrected values of $D_{\mathrm{alc}}$ can be obtained from Eq. (1) and equals $8.32 \cdot 10^{-6}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ and $7.25 \cdot 10^{-6}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ for *DPPH* and *PAQH*, respectively.

$$\frac{\eta_{\mathrm{alc}}}{\eta_{\mathrm{aq}}} = \frac{D_{\mathrm{aq}}}{D_{\mathrm{alc}}} \qquad (1)$$

Thus, by substituting the values of $i_d$, $D_{\mathrm{alc}}$ (for *DPPH* and *PAQH*), $t$, $c$, and $m$ in the *Ilkovic* equation, it is evident that 2 electrons are consumed in the process of reduction of *DPPH* and *PAQH* in the whole *pH* range. The controlled potential electrolysis applied at potentials on the plateau of the

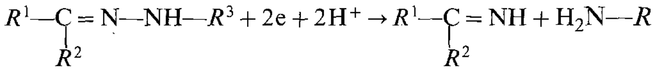
Table 1. *Polarographic data obtained for the reduction of DPPH and PAQH at dme in different buffer solutions containing 50% ethanol*

| *pH* | $-E/V$ | $0.059/\alpha n_a$ | $\alpha n_a$ | $\alpha$ ($n_a = 1$) | $\alpha$ ($n_a = 2$) | $\Delta E/\Delta pH$ |  | slope of $\log i - \log h$ plot |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | *pH* range | slope |  |
|  |  |  | 2,2′-Dipyridyl-2-pyridylhydrazone (*DPPH*) |  |  |  |  |  |
| 2.56 | 1.27 | 0.30 | 0.20 | 0.20 | 0.10 | 1.15–8.25 | 0.055 | 0.58 |
| 7.34 | 1.52 | 0.24 | 0.25 | 0.25 | 0.13 |  |  | 0.58 |
| 11.80 | 1.58 | 0.22 | 0.27 | 0.27 | 0.14 |  |  | 0.66 |
|  |  |  | Pyridine-2-aldehyde-2-quinolylhydrazone (*PAQH*) |  |  |  |  |  |
| 2.56 | 1.03 | 0.18 | 0.32 | 0.32 | 0.16 | 1.15–7.34 | 0.060 | 0.44 |
| 7.34 | 1.27 | 0.16 | 0.37 | 0.37 | 0.19 |  |  | 0.54 |
| 11.80 | 1.29 | 0.12 | 0.49 | 0.49 | 0.25 |  |  | 0.61 |

polarographic wave of *DPPH* verified a consumption of two electrons per molecule.

It is evident that the reduction mechanism involves cleavage of the N—N bond similar to the one proposed by *Lund* et al. [13, 20] for other hydrazones, by *Gomez* et al. [11] and recently by us [16]. The reduction of *DPPH* and *PAQH* is carried out by two electrons in the whole *pH* range. On the other hand, the compound 2-hydrazinopyridine (*Py*-NH—$NH_2$) is reduced polarographically in the available potential range confirming the splitting of the N—N bond.

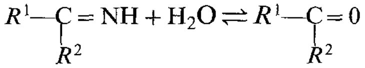
The process of reduction of *DPPH* and *PAQH* can be represented as:



$$\underset{R^2}{\underset{|}{R^1\text{—}C}}=N\text{—}NH\text{—}R^3 + 2e + 2H^+ \rightarrow \underset{R^2}{\underset{|}{R^1\text{—}C}}=NH + H_2N\text{—}R^3$$

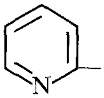
(I) (II) (III)

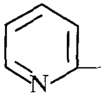
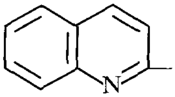
followed by hydrolysis of compound II to the corresponding aldehyde or ketone.



$$\underset{R^2}{\underset{|}{R^1\text{—}C}}=NH + H_2O \rightleftharpoons \underset{R^2}{\underset{|}{R^1\text{—}C}}=0$$

(IV)

where $R^1 = R^2 = R^3 =$  for *DPPH*

and $R^1 = H$, $R^2 =$ , and $R^3 =$  for *PAQH*.

This process of hydrolysis is in accordance to that obtained by *Lund* [21] and by us [16] for similar compounds.

### *Effect of Surface Active Substances*

The three *SAS*, Octylphenoxypolyethylene oxide (*Triton X*-100, non-ionic *SAS*), Sodium dodecylsulphate (*SLS*, anionic *SAS*), and Hexadecyltrimethylammonium bromide (*CTAB*, cationic *SAS*) have almost the same effect on the polarograms: (i) the elimination of the maximum, (ii) the shift of *E* to more negative values, and (iii) a decrease of the limiting current. From the results obtained the three *SAS* can be arranged according to their inhibiting power in the order, *T·X*-100 > *SLS* > *CTAB* at low *pH* and *T·X*-100 > *CTAB* > *SLA* at higher *pH*. The variable effects of *CTAB* and *SLS* in accordance of *pH* may be explained on the basis of the dissociation of the depolarizer to a cationic form at low *pH* and at the same time transformation of *CTAB* to the acid form, which appears to possess a lower surface activity than the anionic species. At higher *pH*, *SLS* is converted to the free base and the depolarizer exists as an anion; thus the effect of *SLS* is lowered.

### *Kinetic Parameters of the Electrode Reaction*

In order to confirm the irreversibility of the reduction process the kinetic parameters $n_a$, $\alpha$, $K_0$, $K_0 D^{-\frac{1}{2}}$ and $\Delta G^*$ for the electrode reaction at $E = 0$ were calculated using the *Koutecky* [22] equation and by plotting $\log(i/i_d - i)$ vs $E$.

Table 2. *Kinetic parameters of* $5 \cdot 10^{-4}$ *M DPPH and PAQH at dme in different buffer solutions containing 50% ethanol*

| $pH$ | $K_0$ cm s$^{-1}$ | $K_0 D^{-\frac{1}{2}}$ $(K = K_0)$ | $\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| | 2,2′-Dipyridyl-2-pyridylhydrazone (*DPPH*) | | |
| 2.56 | $4.18 \cdot 10^{-7}$ | $8.13 \cdot 10^{-5}$ | 69.50 |
| 7.34 | $2.35 \cdot 10^{-9}$ | $1.63 \cdot 10^{-6}$ | 79.32 |
| 11.80 | $2.58 \cdot 10^{-11}$ | $1.78 \cdot 10^{-8}$ | 90.65 |
| | Pyridine-2-aldehyde-2-quinolylhydrazone (*PAQH*) | | |
| 2.56 | $1.14 \cdot 10^{-6}$ | $7.42 \cdot 10^{-4}$ | 63.70 |
| 7.34 | $5.44 \cdot 10^{-9}$ | $3.55 \cdot 10^{-6}$ | 77.08 |
| 11.80 | $3.22 \cdot 10^{-10}$ | $2.14 \cdot 10^{-7}$ | 83.12 |

From Table 2 it is evident that $\Delta G^*$ increases and $K_0$ decreases with increasing *pH*, confirming the increase of irreversibility of the electrode reaction. On the other hand, the value of $\alpha$ is less than unity when the rate determining step involves the uptake of one or two electrons, confirming the irreversible nature of the wave.

## References

[1] *Lions F, Martin K* (1958) J Am Chem Soc 80: 3858

[2] *Geldard JF, Lions F* (1962) J Am Chem Soc 84: 2262; *Geldard JF, Lions J* (1963) Inorg Chem 2: 270

[3] *Katyal M, Dutt Y* (1975) Talanta 22: 151

[4] *Alexaki-Tzivanidou H, Vasilikiotis GS* (1981) Microchem J 26: 1

[5] *Alexaki-Tzivanidou H, Kounenis G, Elezoglou B* (1978) Microchem J 23: 329

[6] *Vasilikiotis GS, Alexaki-Tzivanidou H* (1981) Microchem J 26: 519

[7] *Vasilikiotis GS, Kouimtzis Th, Apostolopoulou C, Voulgaropoulos A* (1974) Anal Chim Acta 70: 319

[8] *Alexaki-Tzivanidou H* (1975) Anal Chim Acta 75: 231
[9] *Heit ML, Ryan DE* (1966) Anal Chim Acta 34: 407
[10] *Singhal SP, Ryan DE* (1967) Anal Chim Acta 37: 91
[11] *Gomez Nieto MA, Lugue De Castro MD, Valcarcel M* (1983) Electrochim Acta 28: 1725
[12] *Elnagdi MA, Fahmy HM, Morsi MA* (1976) J Electroanal Chem 68: 237
[13] *Lund H* (1959) Acta Chem Scand 13: 249
[14] *Cardinali ME, Carelli I, Andruzzi R* (1973) J Electroanal Chem 47: 335
[15] *Kitaev YuP, Skrekova IM, Maslova LI* (1970) Izv Akad Nauk SSSR Ser Khim 10: 2194
[16] *Abu Zuhri AZ, Shalabi J* (1985) J Chem Soc Perkin Trans II/4: 499
[17] *Britton HIS* (1952) Hydrogen ions, 4th edn. Chapman and Hall, London
[18] *Lingane JJ* (1945) J Am Chem Soc 67: 1916
[19] *Mairanovskii SG* (1965) Talanta 12: 1299
[20] *Gardner HJ, Georgans WP* (1956) J Chem Soc 0: 4148
[21] *Lund H* (1983) Electrochim Acta 28: 395
[22] *Koutecky J* (1953) Coll Czech Chem Commun 8: 597; Chem Listy 47: 323