Voltammetric Reduction of 2-(4'-N,N-Dimethylaminostyryl)-1-ethyl Pyridinium Iodide in *DMF*

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Abstract. The voltammetric reduction mechanism of 2-(4'-dimethylaminostyryl)-1-ethyl pyridinium iodide at the hanging dropping mercury electrode has been studied in N,N-dimethylformamide solution containing $0.1\ mol\,dm^{-3}$ tetraethylammonium perchlorate. The depolarizer is reduced via a single diffusion-controlled irreversible two-electron cyclic voltammetric wave. The wave is attributed to the reduction of the azomethine bond of the pyridinium nucleus. Cyclic voltammetric studies indicate that the cv wave follows an ECE mechanism. The chemical reaction is proposed to be a protonation.

Keywords. Dimethylformamide; Electrochemical reduction; Cyclic voltammetry; ECE mechanism.

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Zusammenfassung. Es wurde der voltammetrische Reduktionsmechanismus von 2-(4'-N,N-Dimethylaminostyryl)-1-ethyl-pyridiniumjodid in Dimethylformamid-Lösung mit einem Tetraethylammoniumperchlorat-Gehalt von $0.1\ mol\,dm^{-3}$ an der tropfenden Quecksilberelektrode untersucht. Der Depolarisator wird über eine einzige diffusionskontrollierte irreversible Zweielektronenwelle reduziert. Diese Welle wird der Reduktion der Azomethinbindung des Pyridinium-Kerns zugeordnet. Cyclische voltammetrische Untersuchungen zeigen, daß die CV-Welle einem ECE-Mechanismus folgt. Als chemische Reaktion tritt Protonierung ein.

Introduction

The electrochemical behaviour of 4-styrylpyridine [1], 4-styrylpyrazole [2], 4-(chlorostyryl)pyridine [3], and 4-styrylpyridinium-N-methyl iodide [4] has been studied. For 4-styrylpyridines a two-electron reduction of the styryl (-CH = CH-) group was proposed, while for the quaternized 2-styrylpyridine a two electron hydrogenation of the azomethine (-C = N-) bond of the pyridinium nucleus was suggested. Zuman and Szyper [4] proposed a mechanism in which 4-styryrlpyridine was reduced in the protonated form at lower *pH*'s in two one-electronic steps.

The present investigation is an attempt to study in detail the voltammetric reduction behaviour of 2-(4'-N,N-dimethylaminostyryl)-1-ethyl pyridinium iodide in N,N-dimethylformamide at the hanging dropping mercury electrode.

Experimental Part

2-(4'-N,N-dimethylaminostyryl)-1-ethyl pyridinium iodide was synthesized by the condensation of 4-N,N-dimethylaminobenzaldehyde with 1-ethyl-2-picolinium iodide in 1 : 1 ratio in an ethanolic solution [5]. The solid product obtained was recrystallized from ethanol. Tetraethylammonium perchlorate (Fluka) was recrystallized from ethanol and dried in a vacuum oven at 60°C. N,N-dimethylformamide (A. R. grade BDH) was purified and dried using the method described previously [6] and stored over Linde type 4 Å molecular sieves under nitrogen atmosphere.

A fresh stock solution of tetraethylammonium perchlorate, *TEAP* (0.1 mol dm^{-3}), was prepared in N,N-dimethylformamide. A fresh stock solution of 2-(4'-N,N-dimethylaminostyryl)-1-ethyl pyridinium iodide (10 mM) was prepared from a fresh electrolyte solution on the same day as measurements were carried out.

All experiments were performed at 20°C in *DMF* containing 0.1 mol dm^{-3} *TEAP* as supporting electrolyte. Solutions were purged with pure nitrogen before each experiment and an atmosphere of nitrogen was maintained above the working solution.

Cyclic voltammetric experiments were carried out with an EG & G PARC model 173 potentiostat/galvanostat and EG & G model 175 universal programmer. Internal resistance ohmic drop distortions
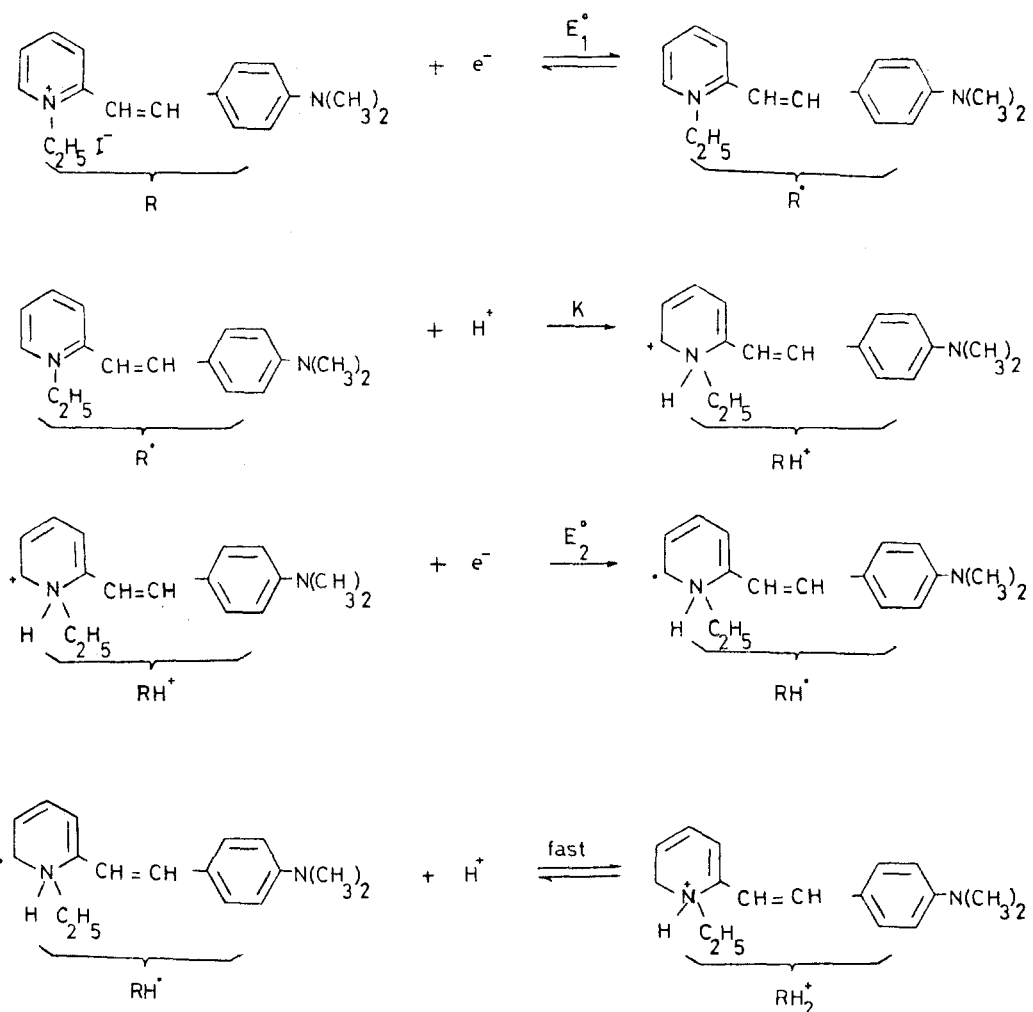
were minimized by applying positive feedback compensation via EG & G model 276 Interface. The maximum value of correction due to IR drop is 0.5 mV. The measurements were made using a conventional three electrodes cell configuration. An EG & G PARC model 303 A SMDE mercury-drop system in the small hanging-drop mode was used as working electrode. The electrode area was 1.84×10^{-3} cm². The reference electrode used was Ag/AgNO₃ (0.1 mol dm^{-3}) in 0.1 mol dm^{-3} *TEAP/ DMF*. A platinum wire auxiliary electrode was used throughout.

Results and Discussion

Cyclic voltammograms were recorded for nonaqueous solutions (N,N-dimethyl-formamide containing 0.1 mol dm^{-3} tetraethylammonium perchlorate, *TEAP/ DMF*) of 2-(4'-N,N-dimethylaminostyryl)-1-ethyl pyridinium iodide at the hanging dropping mercury electrode in the voltage range of -1.30 to -1.70 V vs. Ag/ (0.001 mol dm^{-3}) AgNO₃ reference electrode. Typical cyclic voltammograms are shown in Fig. 1. The voltammograms display cathodic wave at E_p -1.55 Volt. A closer inspection of the cyclic voltammograms reveals that the cv wave is unidirectional, i. e. irreversible. The relevant cyclic voltammetric data for the cv wave are given in Table 1. Examination of these data reveals that the anodic partner of the wave is lacking on the reverse sweep (c. f. Fig. 1). The cathodic peak current, i_{pc}, of the cv wave correlates significantly with the square root of scan rate, $v^{\frac{1}{2}}$.
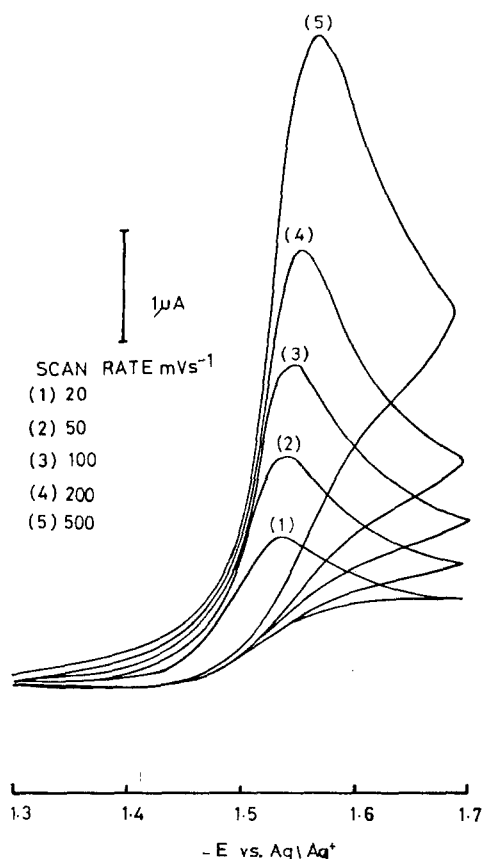

Fig. 1. Cyclic voltammograms of 0.5 mmol dm^{-3} 2-(4'-N,N-dimethylaminostyryl)-1-ethyl pyridinium iodide in 0.1 mol dm^{-3} *TEAP/DMF* solution

The best linear least-square line obtained is formulated as follows

$$i_p = 7.64 \cdot 10^{-6} v^{\frac{1}{2}} \quad r = 0.999 . \tag{1}$$

Furthermore, it correlates with the depolarizer concentration as well ($r = 0.979$). This indicates that the cv wave is diffusion-controlled [7].

In order to establish the nature of the cv reduction wave obtained in the electroreduction of the subject compound under investigation, the following electrochemical criteria will be applied.

(i) Potential width of the wave

The asymmetry of the cathodic peak potential of the wave of the styryl compound is indicated by the potential width, measured as $E_p - E_p/2$ (E_p is the cathodic peak potential and $E_p/2$ is the half peak potential, respectively), values are listed in Table 1. The width values, obtained over the entire range of scan rates ($20 - 500 \, mV \, s^{-1}$), are greater than 27.77 mV at 20°C [7] which is expected for a two-electron reversible cv wave. This indicates that the cv wave is irreversible in nature and involves transfer of two electrons.

(ii) Peak current potential versus scan rate

The relationship between peak current potential, E_p, and the scan rate, $\log v$, is a general test for electrochemical reversibility, depending on the magnitude of the slope of this relation [7-9]. Slopes between zero and 30 mV per decade are indicative of reversible electron transfer and provide information about the order of the following-up chemical reactions. Values greater than 30 mV for the tenfold increase are predicted for totally irreversible waves on the basis of the following equation [7]:

$$E_p = \ln(10) \, (RT/2 \, anaF) \log v + const. \tag{2}$$

The cyclic voltammetric results obtained for the cv reduction wave of the title compound show that the peak current potential E_p does shift towards negative potentials to the extent of 26.2 mV per $\log v$ unit. The best estimate linear least-square equation obtained is as follows

$$E_p = -1.576 - 26.2 \cdot 10^{-3} \log v \quad r = 0.977 . \tag{3}$$

Table 1. Cyclic voltammetric data of $5 \cdot 10^{-4} \, mol \, dm^{-3}$ 2-(4'-N,N-dimethyl-amminostyryl)-1-ethyl pyridinium iodide in $0.1 \, mol \, dm^{-3}$ *TEAP/DMF* solution at 293 K

Scan rate $mV s^{-1}$	i_p μA	$-E_p$ V	E_p-$E_p/2$ mV	$i_p/v^{-1/2}$ $\mu A V^{-1/2} s^{1/2}$
20	1.23	1.535 ± 0.002	39 ± 0.5	8.70
50	1.92	1.541 ± 0.001	40 ± 0.5	8.59
100	2.70	1.547 ± 0.003	41 ± 1.0	8.54
200	3.72	1.556 ± 0.002	43 ± 1.0	8.32
500	5.56	1.572 ± 0.003	46 ± 1.5	7.86

This reveals that the electron-transfer process in the cv reduction wave is coupled with a chemical reaction.

The variation of current function $i_p/v^{1/2}$, with the scan rate, v, is an important diagnostic criterion for establishing the type of mechanism by voltammetry. In case of an irreversible chemical reaction coupled between two charge-transfer processes, the current function should slightly decrease on increasing the scan rate [7]. The ECE systems are classified according to the number of cathodic and anodic waves and to the reversibility of the two charge-transfer [10]. When ΔE^0 ($\Delta E^0 = E_1^0 - E_2^0$ for the two charge-transfer process) has a positive value, only a single wave will be observed.

Examination of the results obtained (c. f. Table 1) reveals that the current function slightly varies with the scan rate, the peak current potential E_p does shift towards negative potentials to the extent of -26.2 mV per decade (Eq. 3) of the scan rate and the anodic partner of the cv wave is lacking (Fig. 1). Thus, according to Nicholson and Shain [7, 10], the substrate 2-styryl pyridinium iodide is electrochemically reduced via an $E_{rev}C_{irr}E_{irr}$ mechanism with an irreversible chemical reaction coupled between mono-electronic reversible and irreversible charge transfer steps. The current expression as a function of time was derived previously (Ref. [10], Eq. 49):

$$i(t) = n_1 FA(\pi D_a)^{1/2} C_A^* \chi(at) + n_2 FA(\pi D_b)^{1/2} C_A^* \varphi(bt) \tag{4}$$

where $a = n_1 Fv/RT$, n_1 and n_2 are the electrons involved in the two charge-transfers, C_A^* is the bulk concentration of the depolarizer, D is its diffusion-coefficient, v is the rate of the potential scan and $\chi(at)$ and $\varphi(bt)$ are functions, given in numerical form, which are related to the surface fluxes of the substrate and the intermediate, respectively. The other terms have their usual significance. The above equation was applied to the reduction of the styryl compound using $n_1 = n_2 = 1$ and $\alpha = 0.5$. The current function $[\chi(at) + \varphi(bt)]$ and hence the current maximum (for 298 K) reached 0.87 [10]. Thus, from Eq. 4, the peak current is

$$i_p = 0.87 FA(F/RT)^{1/2} D^{1/2} C_A^* v^{1/2} \tag{5}$$

or

$$i_p = const. v^{1/2} . \tag{6}$$

From the variation of i_p with the square root of the scan rate (Eq. 1), the value of the diffusion coefficient of the substrate is estimated as $2.51 \cdot 10^{-8}$ sq cm s^{-1}.

On the basis of these results the electrochemical reduction mechanism of 2-(4'-N,N-dimethylaminostyryl)-1-ethyl pyridinium iodide in N,N-dimethylformamide can be formulated as shown in Scheme 1.

The irreversible two electron cv wave is attributed to the reduction of the azomethine bond of the pyridine nucleus via an ECE kinetics. A similar interpretation has been proposed earlier by Zuman and Szyper [4].

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