ELECTROCHEMICAL STUDY OF FOLLOW-UP REACTIONS IN ELECTROOXIDATION OF p-PHENYLENEDIAMINE AND ITS N,N-DIETHYL DERIVATIVE IN NONAQUEOUS MEDIUM*

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The rate constants of deprotonation of the cation radical formed in the reversible one-electron oxidation of 1,4-phenylenediamine and N,N-diethyl-1,4-phenylenediamine in acetonitrile and dimethylformamide were determined by cyclic voltammetry and by the galvanostatic method with current reversal. The influence of the electrode material (Pt, Hg) and solvent was explained qualitatively in terms of the basicity of the medium and sorption of the substances on the electrode.

The oxidation of p-phenylenediamine (PPD) in nonaqueous media proceeds by two one-electron steps[1]. It was checked by several methods[2] that the first oxidation stage on a mercury or platinum electrode is reversible. The electrode reaction proper is somewhat more rapid on mercury than on platinum, an evidence that the electrode material influences the charge transfer. The primary product of the electrooxidation of PPD in acetonitrile, a cation radical, was identified by electron paramagnetic resonance[3]. The reactions following the electrooxidation of aromatic diamines have been hitherto studied only qualitatively[4].

The kinetic data of such reactions of PPD and its N-derivatives have not been reported in the literature. The present work deals with the determination of the rate constants of primary chemical reactions of cation radicals formed by electrooxidation of PPD and its N-diethyl derivative in acetonitrile and dimethylformamide.

EXPERIMENTAL

Apparatus and Chemicals

Galvanostatic, voltammetric, and coulometric measurements were performed in a cell with a mantle according to Hanzlík[5]. A screened platinum working electrode, sealed in glass, had a geometric surface area of 0.263 cm^2. During idling it was stored in a pure solvent and before the measurement it was cycled in a base electrolyte solution for about 1 min in the potential range from $+1$ to -1 V *vs* S.C.E. at a sweep rate of 1 V/s. Measurements on a mercury electrode were carried out in a modified vessel with a ring (an amalgamated platinum wire partly sealed in glass[6]).

The geometrical surface area of the mercury was $0.278 \, cm^2$. A reference aqueous saturated calomel electrode was joined with the cell by a nonaqueous salt bridge. A Luggin capillary on its end was placed so close to the working electrode as to minimize the iR drop in the solution and to prevent screening of the electrode surface[7]. A platinum counter-electrode with a large surface area was separated by a glass frit.

Galvanostatic pulses were generated by an electronic equipment of own construction enabling to use currents from 10^{-6} to 10^{-2} A with a pulse duration from $3 \cdot 10^{-4}$ to 60 s. Chronopotentiometric curves were recorded with an OPD 250 oscillograph with a slow time base (Tesla, ČSSR) and an X–Y recorder of the type ZSK Rohde-Schwarz (West Germany). During other measurements the voltage was applied to the working electrode through a potentiostat of the type VPZ (State Research Institute of Material Protection, Prague). The voltage program was obtained from a voltage pulse generator of the type TWG 500 Feedback (England). Coulometric measurements were carried out on a platinum electrode of a large surface area with an OH-104 type coulometer (Radelkis, Hungary). The measurements of EPR spectra were done with an ER 9 type apparatus (Carl Zeiss, Jena, East Germany) operating in the X band (about 9 GHz) with a 100 kHz modulation.

1,4-Phenylenediamine was of reagent grade (Laborchemie Apolda, East Germany) and was resublimed in vacuum. N,N-diethyl-1,4-phenylenediamine (DEPPD) (Lachema, Brno) was recrystallized in the form of its hydrochloride. Acetonitrile of reagent grade was redistilled several times with phosphorus pentoxide; it contained less than 10^{-3}M-H_2O (titrated by the Fischer reagent). Dimethylformamide was purified by azeotropic distillation with water and benzene, rectified on a column under reduced pressure, and dehydrated by a one-week contact with a molecular sieve of the type Nalzit A 4. Tetraethylammonium perchlorate (TEAP) was prepared from ammonia and perchloric acid, recrystallized several times and dried in vacuum. Other salts of reagent grade were also dried in vacuum. Nitrogen for deaeration of solutions was deoxygenated by passing through a column with a copper catalyst of the type BTS (BASF, Ludwigshafen) at a temperature of $150°C$ and dried in two molecular sieve columns. The temperature of the measured solutions was kept at $25 \pm 0.2°C$ by a water thermostat.

RESULTS

Primary Oxidation Product

Coulometric analysis of solutions of 10^{-3}M-PPD and DEPPD in 0.1M-TEAP in acetonitrile revealed that in both cases one electron per one molecule was transferred in the first oxidation step (calculated 1.09 for PPD). EPR measurements proved in accord with ref.[3] that cation radicals are formed also in DMF stable enough for their spectrum to be measurable during their generation directly in the resonator cavity[8]. Analysis of the spectrum enabled the evaluation of splitting constants (in gauss units): a_1^H (on the nucleus) $= 2.12$, a_2^H (on nitrogen) $= 5.97$, $a^N = 5.27$ with the Lorentz form of the line $\frac{1}{2}\Delta H_{\frac{1}{2}} = 0.26$. These values are very close to those in ref.[3], an evidence that the influence of the medium on the behaviour of the cation radical is small. From a satisfactory agreement between simulated and observed spectra it follows that they correspond to only one radical.

TABLE I

Rate Constants for the Reaction of PPD Cation Radical in Acetonitrile Determined by Cyclic Voltammetry

Platinum electrode of $0.264\ cm^2$ surface area, $5\ .\ 10^{-3}$M-PPD and 0.1M-NaClO$_4$; 25°C.

v $V\ s^{-1}$	$10^6\ i_p^a/v^{1/2}$ $A\ cm^{-2}\ V^{-1/2}\ s^{1/2}$	i_p^k/i_p^a	Δt s	k_1 s^{-1}
0·038	200	0·57	3·73	0·20
0·057	199	0·60	3·0	0·21
0·076	196	0·71	2·25	0·18
0·095	195	0·72	1·63	0·23
0·114	204	0·74	1·46	0·21
0·152	185	0·75	1·05	0·25
0·200	184	0·82	0·79	0·26
0·358	180	0·84	0·55	0·26
0·760	191	0·90	0·33	0·25

Cyclic Voltammetry

We usually chose the reversion potential, E_λ, of the triangular voltage sweep so that only the most negative peaks, a_1 and k_1, were formed (Fig. 1). The reversible behaviour[9] of both depolarizers and the independence of the value of $i_p^a/\sqrt{v}$ on $\sqrt{v}$ in the sweep rate interval $0.03 - 0.8$ V/s were substantiated (Table I). In solutions of PPD the ratio of the cathodic (after reversion of the slope dE/dt) to the anodic peak
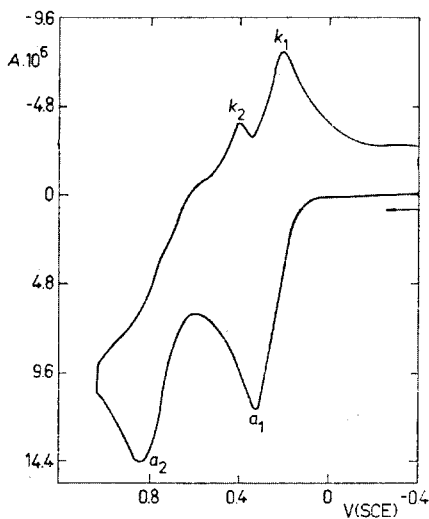

FIG. 1

Cyclic Voltammetric Curve for Oxidation of PPD in DMF on Platinum Electrode

$v = 0.3$ V/s; $5\ .\ 10^{-3}$M-PPD and 0.05M- -KClO$_4$; 25°C.

height was always smaller than unity. The cathodic peak height, i_p^k, was determined from the so-called decay curves according to Adams[10]. As follows from the elaborated criteria[9], the dependences of i_p^k/i_p^a on v are in accord with the assumption of a reversible follow-up chemical reaction of the first order. Its rate constant was determined with the aid of the calculated dependence[9] of the dimensionless product $k_1 \Delta t$ on the ratio of i_p^k/i_p^a. The half-wave potential, $E_{1/2}$, necessary for the calculation of the time, Δt, which elapsed between $E_{1/2}$ and the reversion of the slope $\left(\text{at } E_\lambda\right)$ is not known. We therefore used the method of successive approximations according to the scheme

(first approximation) $\qquad E_p \approx E_{1/2}$

(second approximation) $\quad k_1 \Delta t = f(i_p^k/i_p^a)$

$$E_p^A = E_{1/2} + 0.059[0.339 - \tfrac{1}{2} \log{(k_1/a)}] \; ; \quad a = v/25.6$$

In this case the rate constant in acetonitrile was calculated as $k_1 = (0.23 \pm 0.01) \text{ s}^{-1}$ on the platinum electrode and $(0.16 \pm 0.03) \text{ s}^{-1}$ on mercury. The accuracy of the results depends to a large extent on the perfectness of the iR compensation in the solution. In the case of DEPPD, we were unable to detect conclusively a follow-up reaction by cyclic voltammetry.

Galvanostatic Measurement

In the electrolysis without current reversal, the "galvanostatic product" $j \sqrt{\tau}$ is in the range of experimental errors independent of the current density as far as the concentration of PPD is less than $5 . 10^{-4}\text{M}$. At higher concentrations the term $j \sqrt{\tau}$ increases with the current density j, which is characteristic for adsorption of the depolarizer. Assuming a rapid adsorption with a linear isotherm[11], we evaluated the adsorbed amount on mercury from the extrapolated linear dependence of $j\tau$ on $\sqrt{\tau}$ (which was experimentally well established) as $\Gamma = (1/nF) \lim_{\sqrt{\tau} \to 0} j\tau$. Hence $\Gamma =$ $= 1.04 . 10^{-10} \text{ mol/cm}^2$ on mercury (and similarly on platinum) for 10^{-3}M-PPD in acetonitrile. A blue dye which was formed at the electrode and adsorbed on its surface did not influence these results as long as the electrode surface was renewed before every experiment.

When the current was reversed, two delays appeared on the cathodic branches of the chronopotentiometric curves in the acetonitrile as well as in the DMF medium: The first one at the potential of the first oxidation step and the second by more than

1 V more negative. The transition time of the first delay is decisive for the judgement of the follow-up reactions of the formed cation radical. According to the previously elaborated criteria[12,13], the relations between the depolarizer concentration, the transition time after the reversal, τ', the time of the reversal, t_1, the current density before the reversal, j, and the ratio of the currents, $i/j = u$, were in accord with an ir-reversible follow-up first-order reaction (in agreement with the results of cyclic voltammetry). The rate constants calculated from the nonabbreviated equation[12]

$$\text{erf}\,(k_1\tau)^{1/2} = \frac{1}{u+1}\,\text{erf}\,\left[k_1\tau'(1 + t_1/\tau')\right]^{1/2}$$

showed a moderate increase with decreasing time of the reversal t_1 and with increasing concentration of the depolarizer. Their values on mercury and platinum are in the ratio of cca 1 : 2 under equal conditions. If acetonitrile is replaced by DMF, the value of k_1 increases by about 50% (Table II). The rate constants for the reaction of the cation radical of DEPPD are about one fifth as large. Hence, with the half-time of $10 - 20$ s, this reaction is not detectable by cyclic voltammetry. Owing to the slowness of the follow-up reactions of PPD and DEPPD it was not possible to use the previous results[14] and to introduce a correction of the rate constants for adsorption of the electrode reaction product, *i.e.*, the cation radical.

DISCUSSION

The hitherto assumed mechanism[1] of electrooxidation of PPD in nonaqueous media can be supplemented by our results as follows: After a one -electron, reversible electro-oxidation comes a slow deprotonation of the cation radical with the participation of the solvent molecules or of the depolarizer. (If the latter adds a proton, it is not

TABLE II

Influence of Solvent and Electrode Material on Rate Constants for the Cation Radical Reaction in Galvanostatic Oxidation of PPD and DEPPD

Depolarizer concentration $5 . 10^{-3}$M; 0.1M-TEAP; $25°$C.

Substance	Electrode	Solvent	t_1, s	k_1, s^{-1}
PPD	Pt	MeCN	10·5	0·252 ± 0·005
	Pt	DMF	12·8	0·39 ± 0·02
	Hg	MeCN	33·8	0·122 ± 0·010
DEPPD	Pt	MeCN	15·9	0·043 ± 0·002

excluded from the electrode reaction.) This chemical reaction appears irreversible since the deprotonated radical undergoes rapidly a practically irreversible dimerization. An evidence for this is that during generation of the cation radical its EPR spectrum is not influenced and is perfectly symmetrical. The influence of the solvent on the rate constant k_1 can be qualitatively explained in terms of its different basicity. The slower deprotonation after alkylation of the amino groups in the case of DEPPD can be elucidated analogously. The influence of the electrode material can be attributed to a different adsorption of the products on the electrode surface. The dimerization product, a substituted hydrazobenzene, can undergo a further electrode reaction at more positive potentials.

The hitherto not quite clear influence of the depolarizer concentration and the reversal time t_1 on the rate constant k_1 (other conditions being equal) may be caused by additional relatively slow reactions with a complicated mechanism. The dyes formed as by-products replace the electrode products and the solvent molecules from the electrode surface so that the changes of the formally calculated rate constants are quite conceivable.

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