EFFECT OF THE SOLVENT BASICITY AND ADDITIVES ON THE ELECTROREDUCTION OF PICRIC ACID AND TETRAMETHYLAMMONIUM PICRATE IN APROTIC MEDIA

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Received April 19, 1996
Accepted December 5, 1996

The electroreduction of picric acid and tetramethylammonium picrate in acetonitrile, acetone, *N*,*N*-dimethylformamide, dimethyl sulfoxide and hexamethylphosphoramide has been studied by normal pulse polarography, cyclic voltammetry and by coulometric analysis. The reduction of undissociated acid starts in all aprotic media with consumption of one electron. The reduction potential is shifted to more negative potentials with rising basicity of the solvent, *i.e.* with rising dissociation constant of picric acid. The formation of anion radicals is followed by the sequence of acido-basic selfprotonation reactions as well as by the disproportionation leading to a nitroso intermediate. The reduction mechanism does not change by addition of proton acceptor (basic alumina) or by amfiprotic species (anthranilic acid). In the presence of a strong acid, picric acid can mediate the electroreduction of added protons. Proposed mechanisms were supported by comparison with electrochemical behaviour of related nitrophenols in the same aprotic media.

Key words: Picric acid; Polynitrophenols; Aprotic media; Pulse polarography; Acido-basic reactions; Coulometry; Voltammetry; Electroreduction.

Picric acid, 2,4,6-trinitrophenol, has found diverse applications in analytical chemistry, biochemistry and many fields of chemical technology. In spite of that, informations about the electrochemical behaviour of this species are scarcely published, if papers appearing before 1970 are disregarded. Revival of investigations on the mechanism of the electroreduction of aromatic nitro compounds in aqueous buffered solutions has been the main aspect of series of papers by Zuman *et al.* starting in ref.[1]. A detailed analysis of the pH dependence and the stepwise sequence of intermediates involved in the reduction process of several important nitro compounds are subjects of recent papers published by Laviron *et al.*[2,3].

In dry, aprotic media, there is a deficiency of proton donors for the reduction in the aqueous buffered solutions, which proceeds in the pathway nitroaromate, nitroso intermediate, phenylhydroxylamine derivative, aromatic amine. Therefore, 20 years ago, the selfprotonation mechanism[4,5] was proposed for the electroreduction of series of *ortho*-, *meta*- and *para*-nitrophenols in dimethyl sulfoxide. The phenolic group should supply protons required in the reaction; thus, for the production of one mole of aminophenol six moles of nitrophenol must be converted to adequate phenolate anions.

Further impulses for our work have been found in the studies devoted to nitroaromatic compounds (without phenolic groups) in aprotic solvents. In the case of reversible electroreduction the composition of investigated solution can influence the standard potential of the electrode process. Effects of ionic strength and tetraalkylammonium cations of the base electrolyte were successfully studied at microelectrodes[6]. The results imply that the interaction between the primary reduction product – the anion radical – and the tetraalkylammonium cations are weak. Nevertheless, the intermediates produced in further steps interact more strongly. The meaningful values of association constants of picrate anions as well as negatively charged intermediates with the cations of the base electrolyte can be expected in solvents with low permittivities (in our study especially in acetone). In solvents of higher permittivities the effect of ion-pair formation at the half-wave potential will be decreased. If dianions as intermediates are produced then the formation of ion pairs promotes the shift of their half-wave potentials to more positive values[7].

The effect of water additions on the successive reduction of nitrobenzenes in acetonitrile and dimethylformamide was investigated by Savéant and coworkers in the presence of stable radical anions and dianions generated by reversible electrode reactions[8,9]. The reduction of large number of polynitro compounds, however, becomes irreversible after small additions of water and the interpretation of their reduction mechanism is difficult. Electrochemical reduction of aromatic nitro compounds in the presence of proton donors (nonreducible acids) in nonaqueous solvents was the subject of the paper elaborated by Cadle, Tice and Chambers[10]. It was suggested that the rate-determining step is the reduction of a hydrogen-bonded complex formed at the electrode surface. The pre-protonation wave observed in such cases can be used for the determination of low acid concentrations in nonaqueous solvents. The effect of benzoic acid on the cathodic processes of a great number of substituted aromatic nitrobenzenes in DMF was studied in 1990 (ref.[11]). The reduction pathways of halonitro compounds in aprotic media proposed by Nelson and coworkers[12] were interesting for our study in particular. The authors assumed the participation of hydrogen atom abstracted from the solvent in the reduction process.

In our work, we have concentrated our attention to first reduction steps of both examined substances only because of the complexity of reduction mechanism at more negative potentials. For solving the arising problems the normal pulse polarography (NPP) at static mercury drop electrode, linear sweep voltammetry (LSV) and cyclic voltammetry (CV) at hanging mercury drop and at platinum minidisc were applied. Coulometry at constant voltage at a mercury pool working electrode was also combined with the voltammetric methods.

EXPERIMENTAL

All chemicals were from Lachema, Czech Republic (analytical grade), except of *N*,*N*-dimethylformamide (BASF), acetonitrile (Laboratorchemie, Germany) and perchloric acid (VEB Jenapharm, Germany). The picric acid (HPi) was two times recrystallized using hot ethanol and dried in vacuum in the presence of phosphorus pentoxide. Tetramethylammonium picrate was prepared by neutralizing tetramethylammonium hydroxide with picric acid in ethanol. The crude product was recrystallized several times from hot ethanol by adding water, cooling and drying in the same way as picrid acid. Acetone (AC), *N*,*N*-dimethylformamide (DMF), acetonitrile (AN), dimethyl sulfoxide (DMSO) and hexamethylphosphoramide (HMPA) were purified and dried by standard methods[13]. Sodium perchlorate (crystallized from water) and alumina (for chromatography) were dried at 80 °C for five days at least. All chemicals were stored in desiccator with P_2O_5. Perchloric acid was used without further purification. Nitrogen (Linde-Technoplyn, Czech Republic) purified by passing through BTS catalyst and dried by the molecular sieve Nalsit A4 was used for removing oxygen from the solutions studied.

For NPP studies a polarographic analyzer PA4 (Laboratorni pristroje, Czech Republic) and a static drop mercury electrode with 1 s lifetime were used. Parameters of electrochemical experiment were as follows: Potential sweep rate 2 mV s^{-1}, pulse width 100 ms with the sampling time 20 ms before the end of the drop lifetime. The hanging mercury drop with the surface of 1.320 ± 0.005 mm^2 and a platinum disc with the surface of 0.57 ± 0.02 mm^2 were polarized by the sweep rates of 20–500 mV s^{-1} in CV or linear sweep regime.

Coulometric measurements were carried out using a potentiostat OH 405 with an integrator OH 404 (both Radelkis, Hungary) connected with an auxiliary electrode. The mercury pool of 2.05 cm^2 geometric surface served as a working electrode. An auxiliary electrode made from platinum net was separated by a glass frit from the studied solution stirred by nitrogen bubbling, the depletion of picric acid was followed by the NPP. A reference electrode (saturated aqueous Ag/AgCl/NaCl electrode) used in a three-electrode system was connected to the studied solution by a salt bridge filled with the supporting electrolyte and the solvent identical to that in the cell. Bis(biphenyl)chromium(I) was added to the solution at the end of each measurement series and all potentials indicated in this work have been related to its half-wave potential measured in the same solvent. All measurements were performed at 22 °C.

RESULTS AND DISCUSSION

The solvents used in our study are of various basicity ranging from the acidic solvents (AN and AC) characterized by low values of Lewis basicity expressed in donor numbers N_D, see Table I, to solvents of medium basicity (DMF and DMSO) and, finally, to HMPA, the most basic known aprotic solvent applied in electrochemistry. The donor numbers are related to the dissociation constants of HPi which are included in Table I as well. In acidic solvents, HPi is present in form of molecules even at low concentrations used in our experiments. In more basic solvents anions the Pi^- prevail. In Table I further useful parameters are listed: Acceptor numbers (N_A, measure of Lewis acidity of solvents), relative permittivities, ε_r, being decisive for the ion-pair formation in the solution, and potentials of zero charge E_{zc}, important for the discussion of the adsorption effects.

Normal Pulse Polarography (NPP) and Cyclic Voltammetry (CV)

Characteristic NP polarograms and cyclic voltammograms are demonstrated in Figs 1–3. The overall picture of NP polarograms of HPi in solvents containing 0.1 mol l^{-1} sodium perchlorate can be described in the following way:

A rather positive wave wI appears in all studied media of $N_D < 30$ (*i.e.* with exception of HMPA) with the pronounced shift to less positive potentials in solvents of increasing basicity. The wave wI appears always at more positive potentials when electrolysis at a static MDE is compared to experiments with platinum minidisc and linear dependence of its height on the concentration of HPi can be proved.

Reduction wave wII is twice or three times higher than wave wI and it is situated in the potential region between zero and –0.3 V. The wave wII is splitted in DMF and

TABLE I
Donor numbers, N_D, acceptor numbers, N_A, and relative permittivities, ε_r, of the studied solvents[14], dissociation constants of picric acid (pK_a in molar scale) and potentials of zero charge, E_{zc}, of the mercury surface[15] in the same media

Solvent	N_D	N_A	ε_r	pK_a	Ref.	E_{zc} [d], V
AN	14.1	18.9	27.2	11.0	[a]	0.461
AC	17.0	12.5	20.7	9.26	[b]	0.499
DMF	26.6	16.0	36.7	1.4	[a]	0.436
DMSO	29.8	19.3	46.7	–0.5	[b]	0.406
HMPA	38.8	10.6	30.0	<–0.5	[c]	–

[a] Ref.[17]; [b] ref.[18]; [c] values estimated by authors; [d] data given in ref.[15] recalculated into the Cr(I/0) scale according to ref.[16].

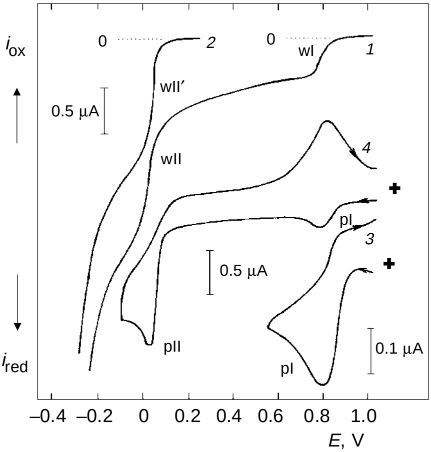

FIG. 1
Electrochemical reduction of HPi and Me_4NPi in AN on a static mercury drop. Supporting electrolyte 0.1 M $NaClO_4$. NP polarograms of *1* HPi, *2* Me_4NPi, concentration of both species $8.5 \cdot 10^{-5}$ mol l^{-1}; *3* and *4* CV curves of HPi at the sweep rate 0.1 V s^{-1}. Concentration of HPi *3* $8.6 \cdot 10^{-5}$ and *4* $1.0 \cdot 10^{-4}$ mol l^{-1}, the sweep reversal at *3* 0.5 V, *4* –0.1 V

DMSO into two parts (wIIa, wIIb). Wave wIIa (more positive) rises with increasing of HPi concentration only to a certain limit, while the height of the wave wIIb shows linear dependence in the whole range of concentration of HPi.

The reduction wave of HPi in HMPA is situated more negatively compared to DMF and DMSO. It coincides with the reduction wave of picrate in the same medium.

Both, the wave wII in AN, AC, DMF and DMSO and the wave wI in HMPA, are followed immediately by a region characterized by very large currents of irregular course. These currents belong, evidently, to further reduction stages of HPi disregarded in this study.

The NP polarograms of picrate are characterized by the absence of the wave wI and the reduction of Pi^- starts at potentials of the wave wII.

Evidently, the reduction peak potentials at CV correspond to the half-wave potentials. The reduction steps of HPi are presented in Table II where the peak potentials obtained at the static mercury drop and at the Pt minidisc are listed. The peak potentials (as well as corresponding half-wave potentials) are affected by the acido-basic properties of the solvents. In view of the fact that the logarithms of the dissociation constants of HPi are linearly dependent on the donor numbers of solvents the peak potentials are linearly shifted to more negative values with decreasing pK_a (see Fig. 4).

The difference between the peak potentials of the first reduction step of HPi recorded at the static MDE and at the Pt minidisc can be interpreted assuming rapid adsorption of the first reduction product, $\mathrm{HORNO}_2^{\bullet-}$, according to the reduction (*A*), on the mercury surface which facilitates the whole reduction process. Due to rather large pulse width (0.1 s) no adsorption peak can be expected on the NPP waves. In contrast to the potential of the first reduction step, the second peaks are independent on the electrode material. These experimental results support the adsorption hypothesis and allow us to identify the species which react in the wave wI as anion radicals $\mathrm{HORNO}_2^{\bullet-}$. The poten-

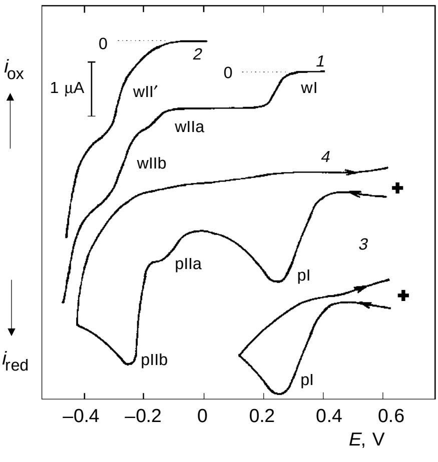

FIG. 2
Curves analogous to Fig. 1 but recorded in DMSO. NP polarograms of *1* HPi and *2* Me_4NPi. Concentration of both species $1.5 \cdot 10^{-4}$ mol l^{-1}, CV curves in the solution of $8.5 \cdot 10^{-4}$ mol l^{-1}; the sweep reversal at *3* 0.1 V and *4* –0.4 V

tials of the peak pI in AN and AC are more positive than the zero charge potential, E_{zc}, in identical solvent (Table I). In DMF and DMSO the first step proceeds at potentials negative from E_{zc} where the adsorption of anion radicals is less probable. Therefore, the potential differences between the electroreduction at Hg and Pt electrodes diminish from AN to DMSO. The anionic intermediates reacting in the second step at even more negative potentials are, obviously, non-adsorptive.

As can be seen in Figs 1–3, the cyclic voltammograms show no anodic response to the reduction products. The primary reduction product (anion radical) is not stable enough to be detected at the sweep rate of 0.5 V s^{-1} (the maximum sweep rate attain-

TABLE II

Potentials of the LSV peaks E_{pI}, E_{pIIa}, E_{pIIb} of picric acid in studied solvents at the static mercury drop (Hg) and at a small platinum disc (Pt) at the sweep rate of 0.1 V s^{-1}. Concentrations of HPi in AN, AC, DMF and DMSO: 2 . 10^{-4} mol l^{-1}, in HMPA 3.8 . 10^{-4} mol l^{-1}

Solvent	E_{pI}, V		E_{pIIa}, V		E_{pIIb}, V	
	Hg	Pt	Hg	Pt	Hg	Pt
AN	0.760	0.510	–	–	0.05	0.04
AC	0.650	0.425	–	–	–0.23	–0.23
DMF	0.270	0.245	–0.17	–0.18	–0.27	–0.28
DMSO	0.230	0.060	–0.17	–0.18	–0.27	–0.29
HMPA	–	–	–0.63	–	–0.78	–

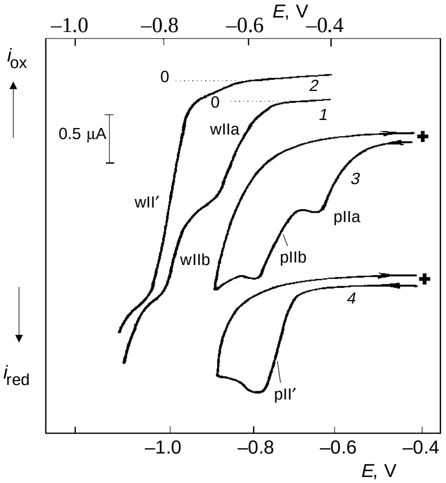

FIG. 3

Curves analogous to Fig. 1 but recorded in HMPT. NP polarograms of *1* HPi and *2* Me_4NPi, CV curves of *3* HPi and *4* Me_4NPi, both with the sweep reversal at –0.9 V. Concentration of both species identical, 3.85 . 10^{-4} mol l^{-1}

able under our experimental conditions). An anodic peak can be observed in acidic solvents, AN, AC and in DMF only when the potential of the sweep reversal is more negative than the peak potential of the second reduction step. Although this anodic peak is located at the potential of the first reduction step, it does not belong, evidently, to the oxidation of primary reduction product. In DMSO and HMPA no anodic peaks were observed.

In all solvents the limiting currents are linear functions of concentration of HPi and picrate, respectively. In Table III the comparison of the limiting current i_L in the studied solvents is presented by means of the slope of currents normalized *vs* concentration c of HPi and picrates and corrected for the change of viscosity η in each solution:

$$i_{L,norm} = i_L \, \eta^{1/2} c^{-1} \quad . \tag{1}$$

Validity of the Cottrell equation for the NPP current and the inverse proportionality of the diffusion coefficient to the viscosity have been assumed. As can be seen in Table III, the slope S_c, corresponding to concentration dependences of the first reduction step, decreases with increasing basicity of the solvent and, consequently, with increasing dissociation constant of HPi. The equilibrium is shifted towards free picrate ions with increasing basicity of the solution. The height of the wave WI decreases (of about 10%) with the decreasing concentration of undissociated molecules HPi when acetonitrile is replaced by acetone.

The set of successive reaction steps can be suggested for the interpretation of the main effects observed in the first stage of HPi reduction in aprotic media without any superfluous proton donors:

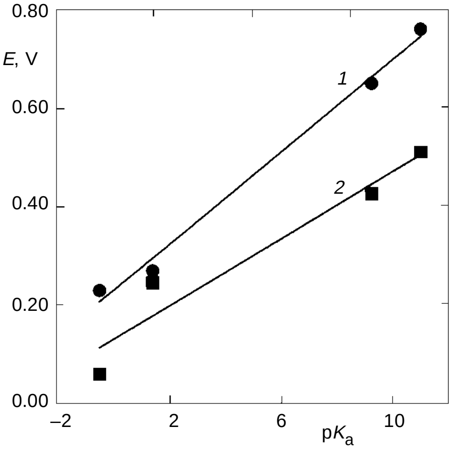

FIG. 4

CV peak potentials of the first reduction step of HPi *vs* pK_a values for the dissociation of picric acid in DMSO, DMF, AC and AN. Electrodes: *1* static mercury drop, *2* Pt mini disc. Supporting electrolyte 0.1 M $NaClO_4$, concentration of HPi $2.0 \cdot 10^{-4}$ mol l^{-1}, sweep rate 0.1 V s^{-1}

$$2\ \mathrm{HORNO_2} + 2\ \mathrm{e} \longrightarrow 2\ \mathrm{HORNO_2^{\bullet -}} \qquad \text{(fast)} \tag{A}$$

$$\mathrm{HORNO_2^{\bullet -}} + \mathrm{HORNO_2} \xrightarrow{k_1} {}^{-}\mathrm{ORNO_2} + \mathrm{HORNO_2H^{\bullet}}$$

$$\text{(acido-basic selfprotonation)} \tag{B}$$

$$\mathrm{HORNO_2H^{\bullet}} + \mathrm{HORNO_2^{\bullet -}} \xrightarrow{k_2} [\mathrm{HORNO_2H}]^{-} + \mathrm{HORNO_2}$$

$$\text{(disproportionation)} \tag{C}$$

$$[\mathrm{HORNO_2H}]^{-} \xrightarrow{k_3} {}^{-}\mathrm{ORNO} + \mathrm{H_2O}\ . \tag{D}$$

In compiling this set of reactions, it was assumed that phenolic hydrogen atom in HPi bound by a hydrogen bond to the oxygen of the neighbouring nitro group facilitates the first stage of HPi reduction (*A*). The overall reaction scheme

$$2\ \mathrm{HORNO_2} + 2\ \mathrm{e} \longrightarrow {}^{-}\mathrm{ORNO_2} + {}^{-}\mathrm{ORNO} + \mathrm{H_2O} \tag{E}$$

TABLE III

Slopes of $S_c = \Delta(i_L\,\eta^{1/2})/\Delta c$ (in μA mol^{-1} l Pa$^{1/2}$ s) and $S_{\log} = \Delta E/\Delta \log i$ (ΔE in mV, i in μA) for picric acid. Data for Me_4NPi are summarized in the text. In case of S_c limiting NPP currents i_L on the static mercury drop are corrected for the solvent viscosity η (assuming the validity of the Cottrell equation); $S_{\log}$ represents slope of the logarithmic analysis of the NPP waves (Heyrovsky–Ilkovic equation)

Solvent	Wave	S_c	$S_{\log}$
AN	wI	2.00	62
	wII	3.73	29
AC	wI	1.93	63
	wII	5.57	26
DMF	wI	1.81	63
	wII	2.21	25
DMSO	wI	1.80	63

can be explained as follows:

– One electron is consumed in the first reduction step of HPi molecule. The consecutive reactions (*B*) and (*C*) can change the apparent number of electrons.

– The primary product of the reduction is an anion-radical inactivated in less than 0.5 s (*cf*. results in CV).

– HPi molecules themselves provide two protons necessary for the production of the nitroso derivative.

– Both follow-up homogeneous second-order reactions, (*B*) and (*C*), can explain the positive shift of the first reduction peak pI with increasing concentration of HPi.

– The selfprotonation involved in the mechanism (*B*) may be hampered in media of higher basicity (DMF and DMSO). A separate wave wIIa can result due to this effect.

The mechanism (*A*)–(*D*) based on fast disproportionation (*C*) was proposed in ref.[19] for the reduction of aromatic hydrocarbons in aprotic media. In our experiments the symbol R represents either 4,6-dinitro- or 2,4-dinitroaromatic derivative. Both equivalent nitro groups neighbouring the OH phenyl group may be involved in the above summarized mechanism.

The height of waves wII in AN and AC is linearly dependent on the concentration of HPi like the height of the wave wI. The slopes of currents normalized *vs* concentration, S_c, can be found in Table III. The slope ratios S_{cII}/S_{cI} are 1.87 and 2.89 for AN and AC, respectively. At low concentration of HPi in DMF (up to $8 \cdot 10^{-5}$ mol l^{-1}) only wave wIIa appears. The wave wIIb starts to grow linearly with increasing concentration of HPi both in DMF and in DMSO. Analogous relations for the wave wIIa are curved. The existence of separate wave wIIa (together with its nonlinear concentration dependence) in both solvents was discussed in connection with the mechanism (*A*)–(*D*). The height of reduction wave wII in AC indicates four-electron reduction proceeding in the studied potential interval under polarographic conditions. In other solvents, the analogous four-electron reduction is displaced in a wider potential interval, when further one or two electrons are received (in voltammetric experiments) at more negative potentials.

The logarithmic analysis of the wave wI yields slopes corresponding to a diffusion limited process in all studied solvents where the separate positive wave wI appears (see Table III). Slope of 25–26 mV *vs* log *i* at potentials more positive than $E_{1/2}$ and a steeper slope of about 60 mV *vs* log *i*, at potentials more negative than $E_{1/2}$ can be noticed as a common feature of wave wII in AC, DMF and DMSO. A combination of two steps consuming more than two electrons seems to be an adequate explanation.

The reduction of picrates gives an analogous picture though the slope of the section at less negative potentials never drops below 29 mV. A significant distinction between the shape of reduction waves in media of $N_D < 30$ (AN, AC, DMF and DMSO) and in HMPA has to be stressed. The electroreduction in HMPA proceeds, evidently, in an irreversible way with slopes rising from 47 to 125 mV. A slight shift of half-wave potential toward the positive values with rising concentration of HPi and picrate, respectively, should be mentioned. The reactions (*B*) and (*C*) transforming the primary produced anion-radical to the radical $[\mathrm{HORNO_2H}]^\bullet$ and the formation of ion pairs with the dianionic intermediates during the processes taking place in waves wII and wII′ (reduction of Pi^-) lie, probably, at the root of this phenomenon.

As far as the influence of the scan rate *v*, in CV was investigated the relationship

$$I_\mathrm{p} = kv^x \qquad (2)$$

reflected the diffusion control for both reduction peaks in DMF and DMSO (Fig. 2) where $x = 0.5$. Due to the complex reduction mechanism exponents $x < 0.4$ (in AN and AC) and $x > 0.6$ (found especially for the reduction of picrates) can be hardly attributed to distinct processes influencing the peak currents. Exponent $x = 0.384$ should be expected if the disproportionation (*C*) is the rate determining step[20]. The negative shift of the reduction peak potential with increasing sweep rate in ECE and DISP mechanism predicted in ref.[21] can be more instructive. The value of the slope $S_\mathrm{E} = \mathrm{d}E_\mathrm{p}/\mathrm{d}\log v$ in the range of 0.029–0.030 V was verified later[22] in connection with the reduction of aromatic hydrocarbons in dry DMF. Our determination of $0.030 < S_\mathrm{E} < 0.040$ V both in DMF and DMSO can support the proposed disproportionation mechanism. These shifts are attributed to both peak pI and peak pIIa indicating the close kinetic similarity of both steps.

Coulometric Analysis

The coulometric analysis of $4 \cdot 10^{-4}$ mol l^{-1} HPi in DMF solution monitored by decreasing height of the NP polarographic waves wI and wII is presented in Fig. 5. Interpolated

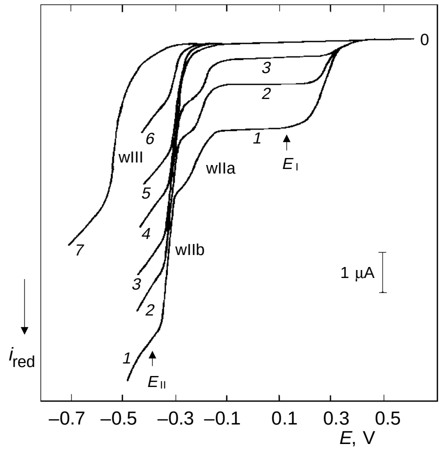

FIG. 5

Course of the coulometric analysis followed by the NPP method. 25 ml of $4.0 \cdot 10^{-4}$ M HPi solution in DMF with 0.1 M $\mathrm{NaClO_4}$. The working electrode: mercury pool. Consumed charge (coulombs): *1* 0, *2* 0.340, *3* 0.576, *4* 1.147, *5* 1.746, *6* 2.807, *7* 3.97; the interpolated charge consumption for vanishing of the first and second wave is 0.660 and 3.78, respectively values of consumed charges give 0.68 electrons for vanishing wave wI at the reduction potential E_I = 0.1 V. After changing the potential to E_{II} = –0.45 V both waves wIIa and wIIb vanish giving total 4 electrons per one molecule of picric acid. It must be noticed that the linear dependence of the height of the wave wI with consumed charge is valid only in the first stage of reduction potential. Simultaneously with the decreasing wave wI, wave wIIa diminishes as well, but not in the same manner. The height of wave wIIb (*i.e.* $i_{IIb} - i_{IIa}$) remains unchanged in this period. Wave wIIb decreases linearly with the charge consumed at the reduction potential E_{II} while both the wave wI and the wave wIIa are already absent. An appearance of the wave wIII (curve *7*) at potential of about –0.55 V at the end of the electrolysis indicates the electroactive product of the electrolysis at E_{II}. The height of wave wIII can be estimated as one half of the sum of waves wI and wII at the start of the electrolysis.

The most important results of coulometric analysis are summarized in Table IV. Two features of the long-lasting reduction processes must be stressed:

– The number of consumed electrons in the first reduction stage in polar aprotic media decreases in the direction mono- > di- > trinitrophenols. The explanation of this effect by the term "selfprotonation" seems to be plausible. Differences may be connected with dissociation constants of the studied substances in the applied media.

TABLE IV
Apparent number of electrons, n_{app}, consumed *per* one molecule of indicated compound during the electroreduction. Values were determined in coulometric analysis at potentials of the first step, and at potentials of the limiting current of wave wIIb

Compound	Solvent	E, V	n_{app}
Picric acid	AN	E_1	0.78 ± 0.05
Picric acid	DMF	E_1	0.68 ± 0.02
Picric acid	DMSO	E_1	0.63 ± 0.03
2,4-Dinitrophenol	DMF	E_1	0.76 ± 0.02
2-Nitrophenol	DMF	E_1	0.94 ± 0.02
4-Nitrophenol	DMF	E_1	0.96 ± 0.02
Picric acid	DMF	E_2	4.0 ± 0.3[a]
Picric acid	DMSO	E_2	4.3 ± 0.5[a]
Picric acid	HMPA	E_2	4.1 ± 0.5
Tetramethylammonium picrate	DMF	E_2	4.0 ± 0.3

[a] Data evaluated after exhausting electrolysis at potentials of the limiting current wave wI.

– Only four-electron process can take place during the reduction of picric acid in absence of any proton donor and under the condition that the potential does not exceed the limit of the reduction wave wII.

Experiments with Additives

Three types of additives influencing the protonation were applied. Interesting, but not unexpected results were obtained after addition of basic Al_2O_3 (0.2 g/20 ml solution). Alumina absorbs all present hydrogen ions (together with traces of water) and thus transforms HPi into picrate, similarly as does HMPA. Therefore, wave wI and wave wIIa disappear, though up to 10^{-3} mol l^{-1} of HPi was dissolved in the solution. Only one four-electron wave can be observed at potentials characteristic for the reduction of picrates in the same solution.

When anthranilic acid was stepwise added as proton donor to the solution of HPi in DMF, the wave wI was shifted gradually to more positive potentials (as it is characteristic for follow-up protonation). The wave wII, originally splitted into two waves, forms only one wave due to the shift of the wave wIIb to positive potentials. Analogous behaviour can be observed for the picrate waves wIIa and wIIb. Their splitting disappears and only the positive wave, wIIa, remains. The height of this wave increases and its half-wave potential is shifted toward positive values (see Fig. 6). All these effects can be explained by similar approach to the reaction mechanism as in the case of aqueous protonating medium.

More pronounced effects have been observed by gradual addition of strong acid, $HClO_4$, up to the concentration of 10^{-2} mol l^{-1} to the solution of picric acid, picrate and 2,4-dinitrophenol in DMF and AN. Test solutions were prepared by adding an adequate volume of 0.1 M $HClO_4$ in dry solvent to 0.1 M $NaClO_4$ in the same solvent.

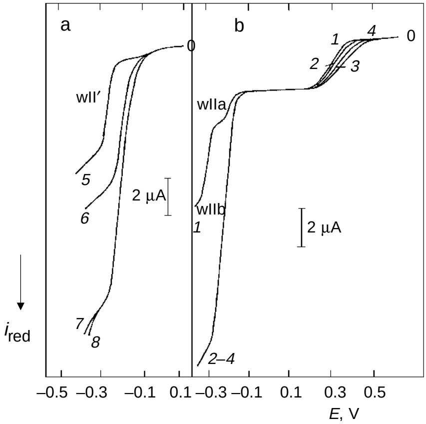

FIG. 6
Addition of proton donors (anthranilic acid, HA) to the solution of HPi (curves *1–4*) and Me_4NPi (curves *5–8*) in DMF. Concentration of both electroactive species 4.0 . 10^{-4} mol l^{-1}. Concentration of HA (mmol l^{-1}): *1* 0, *2* 2.13, *3* 4.78, *4* 6.91, *5* 0, *6* 1.75, *7* 3.09, 8 5.75 (NPP curves)

The wave wI of HPi increases linearly with rising concentration of $HClO_4$ (up to approximately 4 . 10^{-3} mol l^{-1}). The wave can be more than five times higher than in HPi solution without any acid added (see Fig. 7). However, at concentration of $HClO_4$ greater than 4 . 10^{-3} mol l^{-1} a maximum exceeding about twenty times the height of primary wave was formed. At this moment, the increase of wave height with rising concentration of perchloric acid is not linear any more. The half-wave potential of this wave shifts gradually to more positive values by $\Delta E_{1/2} \approx 0.045$ V. Important is the simultaneous decrease of the wave wII. Its half-wave potential $E_{1/2} \approx 0.05$ V remains unchanged, but its height decreases with rising concentration of perchloric acid. While an enormous increase of wave wI can be ascribed to the H^+ reduction mediated by the picrid acid, the adsorbed hydrogen atoms can evoke the observed diminution of wave wII. Analogous effects were observed when perchloric acid was added to solutions of 2,4-dinitrophenol in DMF.

The following set of reactions may be assumed in this mechanism:

$$\mathrm{HORNO_2} + \mathrm{e} \longrightarrow \mathrm{HORNO_2^{\bullet -}} \qquad (A)$$

$$\mathrm{HORNO_2^{\bullet -}} + \mathrm{H^+}\ (\mathrm{solv}) \longrightarrow \mathrm{HORNO_2H^{\bullet}} \qquad (F)$$

$$2\ \mathrm{HORNO_2H^{\bullet}} \longrightarrow \mathrm{H_2} + 2\ \mathrm{HORNO_2}\ . \qquad (G)$$

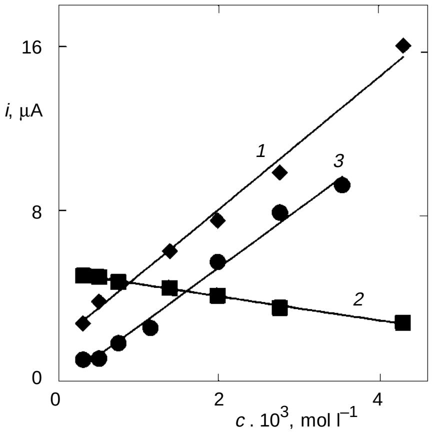

FIG. 7
Influence of $HClO_4$ addition on the height of NP waves in AN: *1* the wave wI of HPi (5.27 . 10^{-4} mol l^{-1}), *2* the wave wII of HPi, *3* the NPV wave of Me_4NPi (2.30 . 10^{-4} mol l^{-1})

Analogous effects can be expected in solutions of picrates with added perchloric acid. The amount of acid equivalent to the picrate consumed by its conversion to picric acid (Fig. 7) must be subtracted, of course.

Water, an unwanted additive present in traces (less than 10 ppm) in solvents or added with perchloric acid does not influence our experiments which can be supported by the fact, that water belongs (with respect to other components) to compounds of medium basicity. Investigation of interaction between nitrobenzene radical anions and univalent cations in DMF proved undetectable changes in the half-wave position in solutions containing less than 10^{-2} mol l^{-1} of water[20]. In our experiments, no difference was observed between the normal pulse polarograms of picrates in dry DMF and curves recorded with HPi converted into picrate by addition of the base alumina in the same medium.

Traces of water not exceeding the concentration of 5 . 10^{-4} mol *per* kg of solvent may be considered as an unwanted agent competing against HPi in protonation reactions. But, in the reduction of picrates, the water content may be considered as a sufficient additive for the production of (dinitro)phenylhydroxyl derivative. On the other side, the assistance of solvent molecules (containing at least one CH_3 group) has to be taken into account if "dry" solvents (with water content below 10^{-4} mol l^{-1}) are applied. Analogous solvent participation was considered in the reduction mechanism of aromatic nitriles[23]. Slow irreversible abstraction of hydrogen atoms from anhydrous DMF was assumed as the rate-determining step preceding the follow-up disproportionation analogous to the proposed reaction (*C*). A minor effect of Me_4N^+ cations can be expected in the presence of 0.1 mol l^{-1} Na^+ ions which more incline to the formation of ion pairs with anionic and dianionic species produced during the reduction process.

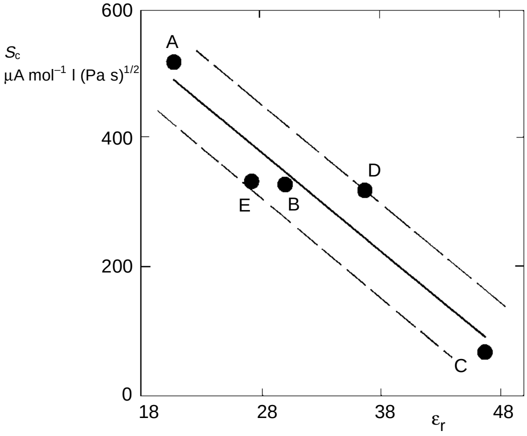

FIG. 8

Dependence of normalized slopes, S_c, on the solvent permittivity, ε_r. Borders of the region where the influence of solvent permittivity on the ion-pair formation, Na^+Pi^{2-}, may be expected (dsahed lines). Solvents: A AC, B HMPA, C DMSO, D DMF, E AN

CONCLUSIONS

There are few remarks to complete the results acquired in this work. The key role for the propagation of the electroreduction of picric acid and picrates in polar aprotic solvents belongs to protons originated either from the phenolic group of picric acid or from other components (additives) in the solution. The selfprotonation mentioned in the preface and in our experimental results can influence the concentration dependence of polarographic waves only a little. This effect can be unequivocally proved by coulometric experiments only.

In media without any proton donors (solutions of picrates without any additive) the cations of base electrolyte may be engaged in the reduction mechanism, especially in formation of ion pairs with dianionic intermediates. This effect was proved[20] for a series of aromatic dinitro compounds in DMF. Low permittivity of the solvent enhances the proportion of the produced pairs. The decrease of the effective charge of intermediates facilitates further the access of electrons. This may be reflected in higher slopes of the current–concentration dependences (Fig. 8).

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