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Comparison of Spectroscopic and Electrochemical Studies of Disproportionation Equilibria of 1,3,5-Triphenylverdazyl Radical in *DMF* Containing Carboxylic Acids

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Summary. Stoichiometry and equilibrium constants for the disproportionation of the title radicals in N,N-dimethylformamide containing salicilic, chloroacetic, and phenylacetic acids were determined on the basis of absorption spectra. On the other hand, only apparent equilibrium constants depending on concentrations of an acid and a radical could be obtained from electrochemical measurements at a mercury electrode. Significant differences in reaction stoichiometry and in order of magnitudes of disproportionation constants found under spectroscopic and electrochemical conditions were discussed in terms of an influence of the electric field in the double layer on the distribution of different associates formed by verdazyl species with acids.

Keywords. Disproportionation equilibrium; Effect of the electrode field.

Vergleich spektroskopischer und elektrochemischer Untersuchungen von Disproportionierungsgleichgewichten von 1,3,5-Triphenylverdazylradikalen in *DMF*/Carbonsäure-Mischungen

Zusammenfassung. Die Stöchiometrie und die Gleichgewichtskonstanten für die Disproportionierung der Titelradikale wurden in N,N-Dimethylformamid mit einem Gehalt an Salizyl-, Chloressig- bzw. Phenylessigsäure auf Basis der Absorptionsspektren bestimmt. Andererseits wurden lediglich effektive Gleichgewichtskonstanten – in Abhängigkeit der Konzentration von einer Säure und einem Radikal – aus elektrochemischen Messungen an der Quecksilberelektrode erhalten. Signifikante Unterschiede der Reaktionsstöchiometrie und die Größenordnungen in den Disproportionierungskonstanten, die bei den spektroskopischen bzw. elektrochemischen Bedingungen gefunden wurden, werden im Hinblick auf den Einfluß des elektrischen Feldes in der Doppelschicht auf die Verteilung verschiedener Assoziate von Verdazylspezies mit Säuren diskutiert.

Introduction

Effects of the electric field in the double layer on the chemical reactivity of molecules at electrodes have long been the subject of experimental study as was recently reviewed by Mairanovskii [1]. In particular, changes in dielectric properties of a medium as well as a redistribution of an electron density in organic molecules caused by a high potential gradient at an electrode can influence acid-base properties of a reactant affecting dissociation and protonation equilibria, the direction of reactions and yields of products [1]. Very recently, Kwiatek and Kalinowski [2–4] studied the formation in the double layer of hydrogen-bonded adducts with 1 : 1 stoichiometry during the cathodic reduction of series of aromatic compounds in N,N-dimethylformamide (*DMF*) containing proton donating agents. A dramatic change in the basicity of carbonyl [2] and nitro [3, 4] groups at the electrode was concluded. On the other hand, if associates of a different stoichiometry coexist in a solution the change in the distribution of different species caused by the electrode field can be expected. Such a case is reported in this paper in which electrochemical and spectroscopic investigations of disproportionation equilibria of 1,3,5-triphenylverdazyl free radicals (*TPV*$^\bullet$) in *DMF* containing carboxylic acids are compared.

Kuhn and Trischmann were the first to find [5] that verdazyl radicals react with mineral as well as organic acids forming a cation and a leuco base in the rapid equilibrium:

$$2\,TPV^\bullet + HA \overset{K_d^{(1)}}{\rightleftharpoons} TPV^+A^- + TPV^-H^+ . \qquad (1)$$

Further investigations of Polumbrik and coworkers [6, 7 a] showed that the stoichiometry of the reaction depends on the medium used, e. g., in *DMF* containing chloroacetic acid:

$$2\,TPV^\bullet + 2\,HA \overset{K_d^{(2)}}{\rightleftharpoons} TPV^+A^-HA + \mathrm{TPV}^-\mathrm{H}^+ \qquad (2)$$

Disproportionation equilibria of verdazyl radicals have not been studied electrochemically yet, although their polarographic reduction and oxidation was described [7 b, 8, 9].

Materials and Methods

1,3,5-triphenylverdazyl radical was prepared and crystallized as described in [5]; *DMF* and tetraethylammonium perchlorate (*TEAP*) were purified and dried as in our previous paper [10]. Phenylacetic acid (Xenon, Łódź) was purified by sublimation under reduced pressure, chloroacetic (POCh) and salicilic (POCh) acids were recrystallized from benzene and water, respectively.

Electronic visible spectra were recorded in a 1 cm cell using a Zeiss (Jena) Specord UV/VIS spectrophotometer. Spectroscopic determination of equilibrium constants were performed with concentrations of verdazyl radical equal to $4.4 \cdot 10^{-4}\,M$ for the reaction with phenylacetic acid and $5 \cdot 10^{-4}\,M$ for two other acids. Concentrations of acids were changed in ranges: 0.5–5.0, 0.2–1.6, and 0.02–0.5 *M* for phenylacetic, chloroacetic, and salicilic acid, respectively.

The dropping mercury electrode (with $t_1 = 3.6\,\mathrm{s}$ and $m = 0.9\,\mathrm{mg\,s^{-1}}$ in 0.1 *M TEAP*, *DMF*) and the hanging mercury drop electrode of Kemula [11] were used in polarographic and cyclic voltammetric measurements, respectively. All electrochemical curves were registered using a Radelkis OH-105 apparatus. An aqueous SCE was employed for preliminary measurements but further a two electrode system with a Hg pool as a reference was used. The potential of the Hg pool was equal to $-0.515\,\mathrm{V}$ vs. SCE under experimental conditions (*DMF*, 0.1 *M TEAP*). All solutions were deaereted by pure argon gas which was presaturated by bubbling through the solvent.

All measurements were performed at a room temperature.

Results and Discussion

Spectroscopic Measurements

The addition of each acid to a dimethylformamide solution of verdazyl radical causes instantly a change of the color from green to violet in full accordance with

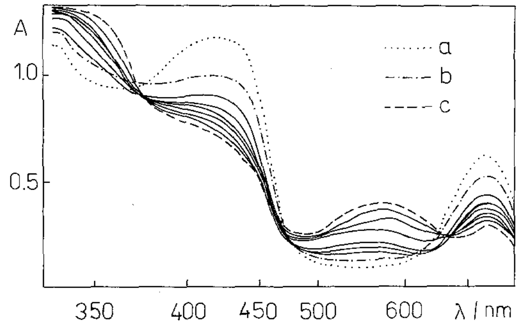


Fig. 1. Absorption spectra of $2.5 \cdot 10^{-4} M$ 1,3,5-triphenylverdazyl radical in *DMF* (*a*) and with the addition of chloroacetic acid in the concentration range from $0.2 M$ (*b*) to $1.6 M$ (*c*)

the literature data [7 b]: $TPV^{\bullet}$ radicals absorb at ≈400 and 740 nm whereas cations TPV^+ at ≈550 nm. The absorption bands of triphenylverdazyl radical decrease with the increase in the acid concentration whereas at the same time the absorption band at 550 nm increases. The above behaviour is shown for the case of the reaction with chloroacetic acid in Fig. 1. The equilibrium constants $K_d^{(1)}$ or $K_d^{(2)}$ corresponding to disproportionation equilibria (1) and (2) were determined on the basis of the absorption band at 740 nm in a similar manner as in Ref. [6]. It was found that the disproportionation with salicilic acid occurs according to Equ. (1) in contrast to the reaction with chloroacetic and phenylacetic acids when Equ. (2) is valid. The final results are presented in Table 1 (errors of K_d values were determined on the basis of Student's distribution with the confidence level 0.95).

The stoichiometry and the value of $K_d^{(2)}$ obtained for the reaction with chloroacetic acid are in a good agreement with literature data: $K_d^{(2)} = 0.13 \pm 0.01$ in Ref. [6]. On the other hand, $K_d^{(1)} = 0.37 \pm 0.08$ for the reaction of salicilic acid with 1,5-diphenyl-3-(*p*-methoxyphenyl)verdazyl was reported [6].

An inspection of the data collected in Table 1 indicates that values of K_d decrease with an increase of pK_a values of acids (values of dissociation constants of acids, determined also in *DMF*, were extracted from references given in Table 1). A similar linear correlation between pK_d and pK_a values was earlier discussed [6] in terms of a fundamental role of the proton transfer in both disproportionation equilibria (1) and (2). However, it should be pointed out that $K_d^{(1)}$ and $K_d^{(2)}$ values have different units and thus, a more quantitative discussion seems to be worthless.

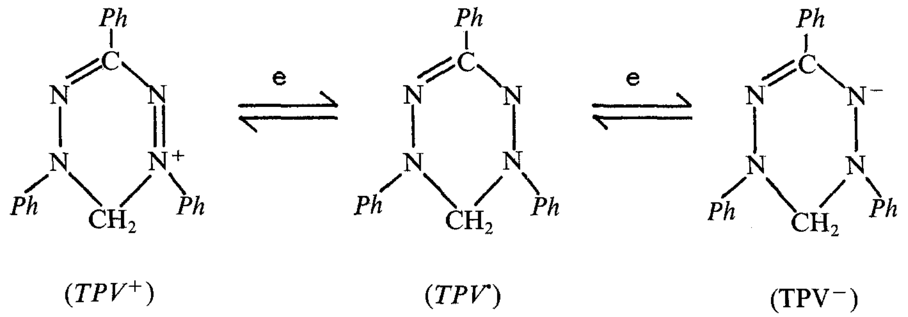
Electrochemical Behaviour of the Verdazyl Radical

Polumbrik and coworkers [7 c, 8, 9] found that 1,3,5-triphenylverdazyl radical and its derivatives with a substituted phenyl ring at position 3 are – in aprotic as well

Table 1. Equilibrium constants for the disproportionation of 1,3,5-triphenylverdazyl radical in *DMF* from spectroscopic data

Acid	pK_a	Ref.	$K_d^{(1)}/M^{-1}$	$K_d^{(2)}/M^{-2}$
Salicilic	8.3	[13]	0.27 ± 0.03	–
Chloroacetic	11.5	[14]	–	0.14 ± 0.01
Phenylacetic	13.5	[14]	–	0.018 ± 0.006

as alcoholic solutions – polarographically reduced and oxidized in one-electron, reversible processes giving an anion and a cation, respectively:



(3)

Substituent and solvent effects on $E_{1/2}$ values were also discussed [7c, 8, 9].

Our polarographic as well as cyclic voltammetric experiments indicated that the oxidation process is indeed reversible but the reduction is quasi-reversible. In a three electrode system (a hanging mercury electrode, SCE and Hg pool) in a $5 \cdot 10^{-4}\,M$ solution of $TPV^{\cdot}$ the potential differences between anodic and cathodic peaks were $\Delta E_p^{ox} = 60$ mV and $\Delta E_p^{red} = 110$ mV for oxidation and reduction processes, respectively. However, ratios of cathodic to anodic currents were close to 1.0 for both processes. Semilogarithmic analyses of cathodic waves (in the absence and presence of salicilic acid) are shown in Fig. 2. Non-linear dependences indicate evidently the quasi-reversible character of the reduction process. Fortunately, reversible $E_{1/2}$ values can be obtained from dependences presented in Fig. 2 taking into account only a foot of the wave.

Moreover, it was found that the oxidation as well as the reduction process is diffusion-controlled and respective $E_{1/2}$ potentials are independent of the concentration of $TPV^{\cdot}$ radicals only for $[TPV^{\cdot}] > 4 \cdot 10^{-4}\,M$. In solutions with a lower reactant concentration the $E_{1/2}$ potentials shift to more positive values [12] with the increase in $[TPV^{\cdot}]$. Moreover, in the same concentration range the polarographic limiting current is not proportional to the reactant concentration (cf., Fig. 1 in Ref. [12]). This behaviour was explained in terms of a weak adsorption of verdazyl species at a mercury electrode up to a full coverage of its surface. Nevertheless,

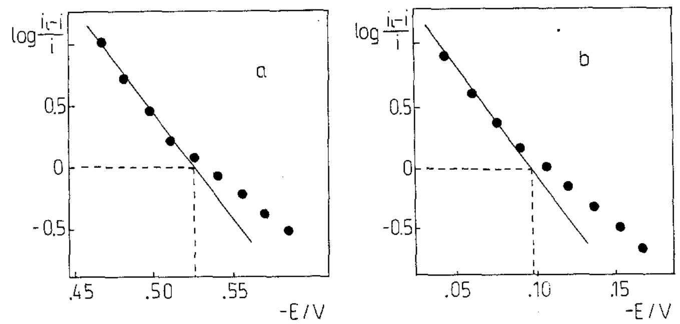


Fig. 2. Semilogarithmic analysis of polarographic waves for the reduction of $5 \cdot 10^{-4}\,M$ $TPV^{\cdot}$ radical in *DMF* in the absence (**a**) and in the presence (**b**) of $1.3 \cdot 10^{-3}\,M$ salicilic acid; solid lines correspond to the theoretical slope for the reversible process (59 mV/decade)

half-wave potentials obtained in solutions with radical concentrations $[TPV^{\bullet}] \geqslant 5 \cdot 10^{-4} M$ can be considered as thermodynamic values and may be used for the estimation of equilibrium constants.

The addition of carboxylic acid to a solution of verdazyl radical causes shifts of the oxidation wave to less positive potentials and the reduction wave to less negative potentials; finally, both waves merge into one anodic-cathodic wave. Thus, in order to obtain well-shaped, separate waves for both processes it was necessary to use much smaller concentrations of acids than in spectroscopic measurements. The employed concentrations were: 0.012 – 0.085, $6.25 \cdot 10^{-3} - 0.075$, and $1.0 \cdot 10^{-3} - 2.0 \cdot 10^{-3} M$ for phenylacetic, chloroacetic, and salicilic acid, respectively.

It was found that the experimental half-wave potentials depend linearly on the logarithm of acid concentration and the obtained slopes of these correlations are collected in Table 2. Moreover, $E_{1/2}$ potentials of the reduction process depend also on the reactant concentration; the related slopes (calculated for the $[TPV^{\bullet}]$ range $5 \cdot 10^{-4} - 1 \cdot 10^{-3} M$) are given in Table 2 as well.

For reversible, diffusion-controlled waves changes in $E_{1/2}$ values with the addition of an acid indicates most probably a formation of associates. Let us consider at first the oxidation process. Negative values of slopes collected in Table 2 correspond to a stronger interaction of an acid with a verdazyl cation than with a parent, neutral radical; such behaviour is reasonable. The values of obtained derivatives, $\delta E_{1/2}{}^{ox}/\delta \log[A^-] = \delta E_{1/2}{}^{ox}/\delta \log[HA]^{1/2}$, where $[HA]$ is an analytical concentration of the weak acid, indicate the stoichiometry of salts formed by a verdazyl cation with an anion of a given acid. The obtained stoichiometry is 1 : 1 (i.e., TPV^+A^-) for salicilic and phenylacetic acids but 1 : 2 for chloroacetic acid, i.e., $TPV^+(A^-)_2$. Note, that only for salicilic acid the stoichiometry found is in accordance with the results of spectroscopic measurements (Table 1).

For the formation of verdazyl anions in the reduction process positive values of slopes $\delta E_{1/2}{}^{red}/\delta \log[HA]$ indicate a stronger interaction of an acid with verdazyl anions than neutral radicals. On the other hand, shifts in the opposite direction of $E_{1/2}$ values with the increase in radical concentration indicate that verdazyl radicals also interact with an acid. Assuming that only one species of each redox form dominates under experimental conditions it is possible to obtain from the Nernst equation an expression for the half-wave potential of the reduction. However, the

Table 2. Slopes (in mV/decade) of dependences of half-wave potentials for the oxidation and the reduction of $TPV^{\bullet}$ radicals in *DMF* against concentrations of a reactant and an acid

Acid	Oxidation			Reduction			$\Delta E_{1/2}$	
	A	*B*	*C*	*A*	*B*	*D*	*E*	*F*
Salicilic	0	−29	−58	−33	60	120	−29	90
Chloroacetic	0	−60	−120	−60	31	62	−60	90
Phenylacetic	0	−31	−62	−62	67	134	−32	90

A $\delta E_{1/2}/\delta \log [TPV^{\bullet}]$; *B* $\delta E_{1/2}/\delta \log [HA]$; *C* $\delta E_{1/2}/\delta \log [A^-]$; *D* $\delta E_{1/2}/\delta \log [H^+]$; *E* $\delta \Delta E_{1/2}/\delta \log [TPV^{\bullet}]$; *F* $\delta \Delta E_{1/2}/\delta \log [HA]$

coexistence of reduced and oxidized verdazyl forms should be taken into account. Fortunately, the ratio of anodic to cathodic limiting currents is related to an apparent disproportionation constant, if differences in diffusion coefficients of various verdazyl species are neglected:

$$(K_d^{app})^{1/2} = -i^a_{lim}/i^c_{lim}\,. \tag{4}$$

For example, in the presence of chloroacetic acid Eq. (5) is obtained assuming the domination of triple associates $(TPV^{\bullet})_2\mathrm{H}^+$ and $TPV^-(\mathrm{H}^+)_2$ in a solution:

$$E^{red}_{1/2} = E^0 - (RT/F)\ln\{K^{(1)}_{as}(2\,K_d^{app})^{1/2}\,[TPV^{\bullet}]\}/\{K^{(2)}_{as}[\mathrm{H}^+]\} \tag{5}$$

where association constants are:

$$K^{(1)}_{as} = [(TPV^{\bullet})_2\mathrm{H}^+]/[TPV^{\bullet}]^2[\mathrm{H}^+]\,, \tag{6}$$

$$K^{(2)}_{as} = [TPV^-\,(\mathrm{H}^+)_2]/[TPV^-][\mathrm{H}^+]^2\,. \tag{7}$$

Eq. (5) explains experimental dependences of $E^{red}_{1/2}$ values on concentrations of $[TPV^{\bullet}]$ and $[\mathrm{H}^+]$ in the presence of chloroacetic acid (Table 2). It should be added here that experimental slopes were obtained assuming that $\delta E^{red}_{1/2}/\delta\ \log[\mathrm{H}^+] = \delta^{red}_{1/2}/\delta\log[\mathrm{H}A]^{1/2}$, as for a weak acid. However, for other acids an existence of more complex associates, e.g., $(TPV^{\bullet})_3\mathrm{H}A$, should be assumed for the explanation of the experimental behaviour characterized in Table 2, if a domination of only one species is considered. It looks more probably that verdazyl radicals as well as anions coexist in forms of different associates and their populations depend on the concentrations of both, radical and acid. However, an identification of individual species is impossible.

Electrochemical Equilibrium Constants

The equilibrium constant of the disproportionation under electrochemical conditions may be calculated on the basis of a difference between reversible potentials proper for reduction and oxidation processes:

$$(RT/F)\ln K_d = \Delta E_{1/2} = E^{red}_{1/2} - E^{ox}_{1/2}\,. \tag{8}$$

However, it was found that $\Delta E_{1/2}$ values depend on concentrations of acids as well as radicals and slopes of respective linear correlations are collected in Table 2. This means that only apparent disproportionation constants, K_d^{app}, can be obtained:

$$K_d^{app} = [TPV^+]_{total}[TPV^-]_{total}/[TPV^{\bullet}]^2_{total} \tag{9}$$

where total concentrations express the sums of concentrations of different associates. When it is possible to assume a domination of one form of each species for the reaction of chloroacetic acid Eq. (9) can be expressed as:

$$\begin{aligned} K_d^{app} &= \{[TPV^-\,(\mathrm{H}^+)_2][TPV^+\,(A^-)_2]\}/\{[TPV^{\bullet}][(TPV^{\bullet})_2\mathrm{H}^+]\} \\ &= \{[TPV^-][TPV^+]/[TPV^{\bullet}]^2\}\,\{K^{(2)}_{as}\,K^{(3)}_{as}[\mathrm{H}^+]^2[A^-]^2\}/\{K^{(1)}_{as})[\mathrm{H}^+][TPV^{\bullet}]\} \\ &= K^0_d K^{(2)}_{as}\,\mathrm{K}^{(3)}_{as}[\mathrm{H}A]^{3/2}/K^{(1)}_{as}(K_a)^{3/2}[TPV^{\bullet}] \end{aligned} \tag{10}$$

where $K^{(3)}_{as}$ is the association constant of triple ions $TPV^+\ (A^-)_2$, K_a is the dissociation constant of a weak acid, and $K_d{}^0$ denotes the disproportionation constant in the absence of any acid. On the basis of Eqs. (8) and (10) following derivatives can be predicted at 298 K: $\delta\Delta E_{1/2}/\delta\log[TPV^{\bullet}] = 59$ and $\delta\Delta E_{1/2}/\delta\log[HA] = 88.5$ mV/decade, which is in agreement with experimental data presented in Table 2.

Values of apparent disproportionation constants proper for electrochemical conditions calculated for $[TPV^{\bullet}] = 5\cdot 10^{-4}\,M$ and $[HA] = 0.01\,M$ are equal to $pK_d^{app} = -\log K_d^{app} = 3.13$, 5.15, and 6.67 for salicilic, chloroacetic, and phenylacetic acid, respectively. It is evident that pK_d^{app} are $4-5$ times greater than spectroscopic pK_d values and that they also increase with pK_a of acids used. The last observation can indicate the role of the proton-transfer step, similarly as for homogeneous experiments.

What is the reason of differences in the reaction stoichiometry and values of disproportionation constants in electrochemical and spectroscopic experiments? Two answers should be considered: the difference in acids concentrations and the effect of the electrode field. As was already discussed it was impossible to perform electrochemical experiments in more concentrated solutions of acids. However, the disproportionation constant for the reaction with salicilic acid was obtained by the spectroscopic method also for a similar concentration range as in electrochemical measurements ($5\cdot 10^{-4} - 2\cdot 10^{-3}\,M$). In this case changes in absorption with the acid concentration were small giving a big error in the K_d value. Nevertheless, the same order of magnitude for the obtained value, $K_d^{(1)} = 0.6 \pm 0.2$, and those given in Table 1 indicates that differences in electrochemical and spectroscopic behaviour cannot be explained by different acid concentrations.

Thus, it is reasonable to assume that an electric field in the double layer is responsible for changes of acid-base properties of verdazyl reactants and carboxylic acids. Further, these changes influence the formation of different associates between verdazyl species and an acid. The proposed behaviour is also supported by results obtained in the reaction with chloroacetic acid. Namely, it is clear from concentration dependences of $E_{1/2}$ values that verdazyl radicals exist mainly as free (unassociated) radicals at more positive potentials, corresponding to the oxidation process, but as triple associates, $(TPV^{\bullet})_2H^+$, at negative potentials, which correspond to the reduction process (cf., Table 2 and Eq. 10). On the other hand, changes of acid and radical concentrations influence the distribution of different associates, yielding experimental apparent equilibrium constants and their concentration dependences.

Acknowledgements

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