# Kinetics of the *p*-Aminodiphenylamine Radical in Organic Solution: An Electrochemical and Electron Spin Resonance Study

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In studying the reaction mechanism of anodic aniline oxidation the dimer *p*-aminodiphenylamine (ADPA) was found to be the main intermediate product in acidic solution. It is oxidized in both the free amine and the protonated form. The cyclic voltammograms have been simulated by taking into account an electrochemical reaction of both the protonated and the nonprotonated forms. Thus, it was also found that the ADPA concentration is determined by the protonation equilibrium. The oxidation product *N*-phenylquinone diimine (PQDI) undergoes a symproportionation reaction with ADPA forming the ADPA\*<sup>+</sup> cation radical. The equilibrium constant for this reaction of PQDI in dimethyl sulfoxide was determined and found to be independent of the concentration of the protons in solution. The ADPA\*<sup>+</sup> cation radical decay can be described by a rate equation based on a second-order reaction for the radical dimerization and a pre-equilibrium for the radical formation by symproportionation. The reaction mechanisms of the anodic oxidation of *p*-aminodiphenylamine and its chemical follow-up reactions are given.

## 1. Introduction

The role of *p*-aminodiphenylamine as an intermediate in the anodic oxidation of aniline is widely recognized in former studies.<sup>1–4</sup> The reaction of this intermediate is important for the preparation of polyaniline as one of the most prominent members of the family of electrically conducting polymers. This polymer is studied in detail because of its great potential applications in, e.g., sensor materials, electrochromic devices, corrosion protection, photochemical devices, and other fields. It is studied to a large extent with respect to the influence of the preparation conditions on the polymer properties.<sup>1</sup> As the initial stages of the electropolymerization of aniline in aqueous solutions are very important for the polymer formation, it was pointed out by other authors<sup>2</sup> that *p*-aminodiphenylamine is the dominant intermediate in these early stages. In acidic aqueous solutions the anodic oxidation of aniline goes through further different intermediates to form finally polyaniline (PANI), which was formerly called aniline black.1 Large differences in the structure of PANI due to various influences in the electropolymerization were found. The dimeric intermediate p-aminodiphenylamine (ADPA) is formed by an alternate electron transfer<sup>2</sup> and dimerization step of aniline. Due to the various ways it takes part in redox and/or chemical reactions, it is the main intermediate in aniline oxidation.<sup>1-4</sup> Its occurrence was already qualitatively proved by numerous studies in the past.

Their have been several studies on the anodic oxidation of ADPA itself<sup>5–9</sup> to follow both the mechanism of the oxidation and the formation of a polymer which is obviously different from polyaniline.

The ADPA<sup>++</sup> radical, which can be detected by ESR spectroscopy,<sup>8</sup> is formed by symproportionation of ADPA and N-phenylquinone diimine (PQDI) according to

 $2 \qquad \stackrel{H}{\bigcirc} \qquad \stackrel{H}{\longrightarrow} \quad$ 

and not in a one-electron oxidation. This symproportionation reaction has been compared with that of the p-phenylenediamine.<sup>10</sup>

In their extensive and fundamental work on the electrochemistry and ESR spectroscopy of ADPA, Allendoerfer et al.<sup>8</sup> draw the conclusion from electrochemical measurements of the differences in the peak potentials that  $K_{eq}$  in aqueous solutions must be less than 1. Due to this fact, the ESR spectrum was weak.

A further point in the ESR spectroscopic and electrochemical study of ADPA oxidation is the formation of a polymer layer on the electrode giving rise to an ESR signal interfering with that of the less intense signal from the ADPA radical. Thus, conditions had to be found to avoid this interference.

Because of the slow, radical decay and the special ESR technique applied in this study as described below, it will be shown that the determination of that equilibrium constant is possible within an estimated error of 30%. The error is reasonable for that technique and nevertheless the best value available in the present state of the technique.

Furthermore, there is a contradiction in the literature concerning the follow-up reaction. In ref 10 an acid-catalyzed coupling rate of PQDI is discussed which should be of second order with respect to PQDI. On the other hand in refs 7 and 11 a dimerization of the ADPA radical cation is assumed. It is also important for the discussion of further polymer-growing steps that this radical reaction in the aniline polymerization is different

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from that of the polymerization of PQDI. Therefore, there is a need for a detailed study of the kinetics of the anodic reaction of ADPA especially with respect to the equilibrium of ADPA and PQDI. It is the aim of this work to find the valid rate equation for the ADPA radical decay, and to estimate the equilibrium constant of the symproportionation and the rate constant of the chemical reaction by measuring the absolute radical concentrations as a function of time. Thus, we can find the most probable reactions by excluding different rate equations. Therefore, a reasonable reaction scheme is provided.

#### 2. Experimental Section

**2.1.** Substances. *p*-Aminodiphenylamine (ADPA) was purchased from Fluka in analytical grade and was recrystallized twice from a methylene chloride—petroleum ether mixture under inert conditions in a glovebox. The product obtained by this procedure was faintly colored. The melting point was 66-67 °C (lit. mp 66-67 °C<sup>12</sup>). Dimethyl sulfoxide (DMSO) with a maximum water content of 0.02% was used as the organic solvent. Concentrated H<sub>2</sub>SO<sub>4</sub> p.a. (Merck) and Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O were the supporting electrolytes for nonaqueous and aqueous solutions, respectively. In general, 0.1 M H<sub>2</sub>SO<sub>4</sub>/DMSO solutions have been used. The aqueous solutions were prepared with deaerated bidistilled water.

**2.2. Equipment.** ESR spectroscopy was done with an X-band spectrometer ESP 300 E (Bruker) with an  $H_{102}$  cavity. All measurements were carried out at room temperature with 100 kHz modulation and a microwave power of 1 or 2 mW.

Electrochemical generation of the radicals as well as the different electrochemical measurements in the electrochemical ESR cell were carried out with a potentiostat PG 285 (HEKA Lambrecht). The potentiostat was PC controlled. The potential was varied under control of a locally written Turbo Pascal program. For DA conversion a plug-in board ACAO (Strawberry Tree) was used, which was also the trigger source for the ESR spectrometer and the pump of the electrolyte solution. A block diagram of the apparatus setup used in this study is given in ref 13. Cyclic voltammetry was done in either a conventional electrochemical cell or the ESR flat cell using the potentiostat PG 285 (HEKA Lambrecht).

For the simulations of the cyclic voltammograms, the program DIGISIM 2.0 (Bioanalytical Systems) was used. For those of the ESR spectra, the program SIMFONIA (Bruker) was used.

**2.3. Cell Design.** For the EC-ESR investigations, we used a special flat cell situated in a rectangular cavity as shown in Figure 1. The central part of this flat cell is 0.5 mm thick, 8 mm wide, and 40 mm long. This part is situated inside the cavity. The working electrode for the standard procedure consists of a coil made from platinum wire 12 cm in length and 0.5 mm in diameter. This coil is mounted at the end of the quartz tube on top of the flat part of the EC-ESR cell, which is therefore used in an *ex situ* mode.

As the reference electrode a AgCl-coated silver wire within a Luggin capillary was used. The end of this capillary and an additional glass tube for gas bubbling were inside the Pt coil. However, all potentials mentioned in this paper are referred to the potential of the ferrocene couple. The counter electrode was a Pd sheet situated below the flat part of the cell.

For our kinetic investigations we used the following procedure: In the beginning of the measurement we brought exactly 1 mL of the ADPA solution in the upper part of the cell and applied a definite charge to the solution. The simultaneous bubbling with nitrogen provided both a homogeneous solution of PQDI as well as ADPA and allows the application of higher current densities in the electrolysis.



Figure 1. View of the ESR electrochemical cell for low-volume measurements in the three-electrode system. The thin layer part of the flat cell inside the ESR cavity is 0.5 mm thick, having an effective probe volume of 45  $\mu$ L.

When an appropriate charge had been applied to the ADPA solution, the working electrode was disconnected immediately by an electronic switch. Then gas bubbling was stopped, and a volume of 0.5 mL of the electrolyzed solution was moved down as fast as possible from the upper part of the ESR cell into the flat cell region where the ESR measurement was done. It was done by pumping off the electrolyte solution in the flat cell via the counter electrode compartment (Figure 1). This solution was replaced by the electrolyzed one. By this way it could be ensured that the whole part of the flat cell was filled with the homogeneous reaction mixture. This procedure was carried out with the help of a syringe connected to the lower end of the cell. The volume of the solution in the upper part of the cell was determined to get the exact concentration of the reaction product. For this purpose the glassware was marked for a certain volume. For the in situ EC-ESR investigations of the kinetics of ADPA formation, the in situ EC-ESR cell described earlier<sup>13</sup> was used.

**2.4. Solutions.** The organic ADPA solutions were prepared under nitrogen atmosphere in a glovebox. They were fed through a Teflon tube directly from the glovebox into the EC-ESR cell. In the spectra accumulation technique, the electrolyte at the working electrode was renewed by transferring the electrolyte using a computer-driven injection pump. For measurements in DMSO, the sulfuric acid concentration was varied in the range between 0.1 and 0.5 M. Any contact of the acidic electrolyte solutions with other metal parts except platinum was avoided. For measurements in aqueous solutions, the solid ADPA was added to a thoroughly deaerated 0.1 N Na<sub>2</sub>SO<sub>4</sub>—water solution. After the dissolution of ADPA, the pH value of the solution was adjusted to 1.5 by the addition of 0.1 N H<sub>2</sub>SO<sub>4</sub>.



**Figure 2.** (a) Cyclic voltammogram of ADPA measured at a Pt working electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub>/DMSO with an Ag/AgCl wire as a reference electrode. Potentials are referred to the potential of the ferrocene couple; sweep rate was 150 mV/s; concentration of ADPA was  $10^{-3}$  M. (b) Simulated cyclic voltammogram of ADPA with  $E_1 = 0.15$  V,  $E_2 = 0.49$  V,  $E_3 = 0.66$  V, and  $E_4 = 0.06$  V. For explanation, see text; for mechanism see eqs 1–8.

### 3. Results

A cyclic voltammogram of ADPA in acidic DMSO solution is shown in Figure 2, curve a. The peak separation of the oxidation and the re-reduction peak is 320 mV. This result is quite different from that in neutral and HClO<sub>4</sub>-acidic acetonitrile (MeCN).<sup>5,14</sup> The H<sub>2</sub>SO<sub>4</sub>/DMSO solution gives a quite different protonation equilibrium of ADPA and PQDI from that in HClO<sub>4</sub>/ MeCN, resulting in different cyclic voltammograms. The current increase at potentials higher than 800 mV is due to the starting formation of an oxide layer on the platinum electrode in DMSO. This effect is not as significant as it is in sulfuric acid solution where it has been known for a long time from potentiodynamic measurements.<sup>15</sup> The current increase is also due to the beginning decomposition of the electrolyte. The weak voltammetric wave at the foot of the anodic peak increases and results in an additional peak at lower sweep rates.

It is known from *in situ* UV–vis electrochemical measurements<sup>16</sup> that within the time scale of our measurements PQDI is the only product formed during oxidation of ADPA. In the same study it is shown that the amount of the starting material is re-formed during re-reduction.

For the simulation of the cyclic voltammograms, we tried different reaction mechanisms like deprotonation before and after oxidation or the electron transfer reaction of only the protonated ADPA, but the simulations of the voltammograms failed.

Furthermore, we simulated the cyclic voltammograms on the basis of three two-electron transfer reactions at three different potentials according to three different protonated species of ADPA. With this mechanism a good fit was possible, but the fitted constants for the protonation equilibria showed that the PQDI should be unprotonated. This fact is contradictory to our *in situ* UV-vis measurements, where only the spectra of the protonated PQDI were found. All our attempts to find a data set with protonation constants which meet these facts failed.

We propose the following mechanism

$$AH_2 \rightleftharpoons AH_2^{\bullet +} + e^- \tag{1}$$

$$AH_2 + H^+ \rightleftharpoons AH_3^{\bullet+}$$
(2)

$$AH_3^+ \rightleftharpoons AH_2^{\bullet +} + e^- + H^+$$
(3)

$$AH_3^+ + H^+ \rightleftharpoons AH_4^{\bullet +} \tag{4}$$

$$AH_4^{2+} \rightleftharpoons AH_2^{\bullet+} + e^{-1} + 2H^+$$
(5)

$$AH_2^{\bullet+} \rightleftharpoons QH^+ + e^- + H^+$$
 (6)

$$Q + H^+ \rightleftharpoons QH^+ \tag{7}$$

$$AH_3^+ + QH^+ \rightleftharpoons 2AH_2^{\bullet +}$$
(8)

with AH<sub>2</sub> = unprotonated ADPA, AH<sub>3</sub><sup>+</sup> = single-protonated ADPA, AH<sub>4</sub><sup>2+</sup> = double-protonated ADPA, AH<sub>2</sub><sup>•+</sup> = radical cation of ADPA, and Q = PQDI. It meets all results mentioned in the present paper and is based on three one-electron transfer reactions of three different protonated ADPA species forming the corresponding cation radicals. These cation radicals undergo quick protonation/deprotonation reactions and are oxidized to PQDI, which also undergoes protonation/deprotonation. With this mechanism we were also able to fit the experimental cyclic voltammograms. The following parameter set was found to be representative but probably overvalues the amount of the double-protonated ADPA: formal potentials according to eq 1, E = -0.15 eV; eq 2, E = 0.49 V; eq 5, E = 0.66 V; eq 6, E = 0.06 V, and equilibrium constants for eq 2,  $K = 2 \times 10^5 \text{ L/mol}$ ; eq 4, K = 10 L/mol; eq 7,  $K = 10^5 \text{ L/mol}$ .

The equilibrium constant for the symproportionation reaction (eq 8) is not determined by simulation but by our independent measurement to be K = 0.027 as described later. On the basis of these simulations we can interpret the measured cyclic voltammograms as follows:

The weak voltammetric wave at the foot of the anodic peak is due to the oxidation of the nonprotonated ADPA. Its concentration is low because the equilibrium according to eq 2 is shifted to the right side. This wave becomes the most intense peak at very slow sweep rates due to the back reaction (eq 2).

The main oxidation peak at 0.49 V is due to the oxidation of the single-protonated ADPA, while the small amount of twiceprotonated ADPA is oxidized at 0.66 V where the electrolyte starts to decompose. As it can be concluded from the protonation constants resulting from the simulation, nearly the whole amount of the cation radicals is present in the nonprotonated form which has a low formal potential for their oxidation. This causes the immediate oxidation to PCDI and the large voltammetric peak separation.

At the very beginning of this study of ESR spectroscopy of ADPA, it turned out that neither the lifetime of the radical nor the low radical concentration was the main problem in the ESR measurements, but it was the formation of an adhering polymer layer at the electrode surface. This polymer itself gives a strong single ESR line (Figure 3a) well-known for polyaniline and other conducting polymers which interferes with the highly resolved ESR spectra of the low molecular structures. Especially, the quantitative determination of the ADPA<sup>•+</sup> radical concentration is impossible. Therefore, DMSO was used as the solvent. Thus, the polymer layer formation is suppressed, and no single ESR line of the polymer observed by making sensitive ESR measurements of the monomeric radical structures is possible. It was found furthermore that the addition of DMSO in a small amount of an aqueous electrolyte of 0.5 mM ADPA is the reason for the suppression of the polymer layer formation. Figure 3b



**Figure 3.** ESR spectrum of the electrochemically formed ADPA radical cation from  $5 \times 10^{-4}$  M ADPA (a) in aqueous 0.1 M H<sub>2</sub>SO<sub>4</sub> and (b) in aqueous 0.1 M H<sub>2</sub>SO<sub>4</sub> with 3% DMSO added.



**Figure 4.** Formation and decay of the ADPA radical cation in acidic DMSO solution. The Pt electrode is situated in the center of the cavity. At point A the potential is switched from 0.1 to 0.5 V. At point B the electrode was off-circuited.

shows the ESR spectrum of the ADPA<sup>•+</sup> cation radical measured in an aqueous solution containing 3% DMSO. This ESR spectrum is well resolved and equals that described in the literature.<sup>8</sup> A high signal to noise ratio made the comparison of simulated spectra with the experimental ones more stringent. An ESR spectrum simulated on the basis of the hyperfine coupling constants given in ref 8 was in good agreement with our experimental spectrum. Therefore, the spin density at the radical is not influenced by the change from water to DMSO containing water as the solvent.

The radical cation of ADPA<sup>•+</sup> is formed due to the symproportionation of ADPA and PQDI according to eq 9. Furthermore, a series of *in situ* EC-ESR investigations was done to demonstrate that the radicals are formed immediately after oxidation of ADPA (Figure 4). At point A (Figure 4), the potential was changed from -0.1 to 0.5 V. Without any time delay, the increase of the radical concentration is observed. The

 TABLE 1: Equilibrium and Rate Constants of the ADPA

 Symproportionation Determined for Different ADPA, PQDI,

 and Acid Concentrations<sup>a</sup>

concentration of H <sub>2</sub> SO <sub>4</sub> (mol/L)	concentration of ADPA (10 <sup>-3</sup> mol/L)	concentration of PCDI (10 <sup>-3</sup> mol/L)	equilibrium constant	rate constant $(L \text{ mol}^{-1} \text{ s}^{-1})$
0.10	0.15	0.80	0.024	
0.10	0.36	0.57	0.026	34
0.10	0.40	0.52	0.030	
0.10	0.41	0.50	0.032	
0.10	0.43	0.53	0.029	
0.10	0.52	0.40	0.028	34
0.10	0.55	0.37	0.031	
0.10	0.60	0.34	0.019	
0.10	0.67	0.28	0.019	
0.10	0.79	0.19	0.031	
0.10	2.60	0.30	0.028	30
0.10	3.67	1.03	0.025	40
0.10	4.00	0.74	0.027	31
0.10	4.49	0.32	0.026	35
0.20	2.03	0.74	0.031	31
0.20	2.04	0.74	0.031	31
0.20	2.40	0.41	0.028	35
0.50	1.80	0.10	0.021	40
0.50	2.10	0.67	0.022	33

<sup>*a*</sup> The mean value of the equilibrium constants is  $K_{eq} = 0.027$  (standard deviation 0.004) and of the rate constants  $k_d = 34 \text{ L mol}^{-1} \text{ s}^{-1}$  (standard deviation 3.4 L mol<sup>-1</sup> s<sup>-1</sup>).

radical concentration increases after switching off the working electrode (point B). This increase is caused by the high concentration of PQDI near the electrode surface and its low concentration in the bulk electrolyte. In pure solutions of ADPA and PQDI, the radical concentration is zero but turns to the maximum if the concentrations of both species are equal. Homogenization of the solution by either diffusion or convection is therefore responsible for the increase in the radical concentration after off-circuiting the electrode. This is important for the interpretation of the radical decay because in that case the preequilibrium condition is fulfilled. Two things facilitate the estimation of the kinetic data. First, the bubbling with nitrogen during the generation of PQDI provides a homogeneous solution. Therefore, the rate equations for homogeneous reactions can be applied. Without homogenization a gradient in the ADPA and PQDI concentrations has to be taken into account. Therefore, the analysis of the kinetic data would be more difficult. Secondly, the fulfilled pre-equilibrium condition simplifies the rate equation. Otherwise we had to consider two further rate constants according eq 9. To check our assumption concerning the equilibrium

$$ADPA + PQDI \leftrightarrow 2ADPA^{\bullet+}$$
(9)

$$K_{\rm eq} = \frac{[\rm ADPA^{*}]^2}{[\rm ADPA][\rm PQDI]}$$
(9a)

we determined the equilibrium constants for different ADPA, PQDI, and acid concentrations. The radical concentrations were measured by ESR spectroscopy, the concentrations of PQDI were known from the transferred charge corrected by one-half of the radical concentration, and the ADPA concentrations were given by the starting concentration minus the PQDI and the radical concentration. The equilibrium constant was determined for different PQDI and ADPA concentrations and also for different H<sub>2</sub>SO<sub>4</sub> concentrations.

The results are summarized in Table 1. As expected from eq 9, the equilibrium constant did not depend on the acid concentration. In the case of the PQDI reaction with the nonprotonated or double-protonated form of ADPA in contrast to that reaction with the single-protonated one, the equilibrium



Figure 5. Time dependence of the ADPA radical cation concentration at different concentrations of ADPA and PQDI in acidic DMSO solution. Starting concentrations of ADPA were 3 mM for the curves at the top and 1 mM for the curves at the bottom.

constant should be influenced by the acid concentration, which was not observed. Furthermore, the decay of the radical concentrations was followed. Some of the measured decay curves are shown in Figure 5. The data of the single experiments were fitted by first- as well as second-order rate equations, but in varying the concentrations of the reactants the obtained rate constants changed to a great extent.

In the most favorable mechanism, the radical cation is produced (eq 9) by a symproportionation (ADPA + PQDI  $\leftrightarrow$  2ADPA<sup>++</sup>) and is diminishing (eq 10) according to

$$2ADPA^{\bullet+} \rightarrow ADPA - ADPA \qquad (10)$$

In contrary to the reaction of thiophene oligomer cation radicals<sup>17,18</sup> where a  $\pi$  dimer is reversibly formed, the ADPA<sup>•+</sup> radical of this study undergoes an irreverisble chemical reaction. Using both reactions 9 and 10, it is possible to find a rate equation for the radical cation reaction.

The starting point of the calculations are the equations

$$\frac{-\mathrm{d}[\mathrm{ADPA}^{\bullet^+}]}{2\,\mathrm{d}t} = k_\mathrm{d}[\mathrm{ADPA}^{\bullet^+}]^2 + k_{-1}[\mathrm{ADPA}^{\bullet^+}]^2 - k_1[\mathrm{ADPA}][\mathrm{PQDI}] \quad (11)$$

$$\frac{-\mathrm{d}[\mathrm{ADPA}^{\bullet+}]}{2\,\mathrm{d}t} = k_{\mathrm{d}}[\mathrm{ADPA}^{\bullet+}]^2 + \frac{\mathrm{d}[\mathrm{ADPA}]}{\mathrm{d}t} \qquad (12)$$

where  $k_{-1}$ ,  $k_1$  and  $k_d$  are the rate constants of the backward reaction, the forward reaction, and the dimerization reaction, respectively.

To get the expression d[ADPA]/dt the equation

$$[ADPA] = \frac{[ADPA^{\bullet+}]^2}{K_{eq}[PQDI]}$$
(13)

was differentiated, which is a good approximation in this case.

By subsequent substitution we obtained a rate equation in the different form

$$\frac{d[ADPA^{\bullet^+}]}{dt} = \frac{-K_{eq}k_d[ADPA^{\bullet^+}]^2 ([ADPA] + [PQDI])}{(4[ADPA^{\bullet^+}] + (K_{eq}([ADPA] + [PQDI])))}$$
(14)

Considering the slope of the measured decay curves at t = 0in Figure 5, the behavior of the radical can be interpreted in the following manner. Taking a fixed starting concentration of ADPA, the slope of the decay curves at t = 0 increases with increasing radical concentration. The term (2[ADPA<sup>•+</sup>] +  $K_{eq}$ -([ADPA] + [PQDI])) considerably influences the theoretical decay curves. When the rate constant is derived by the initial stage method, the experimental error becomes however too large. An analytical solution of the differential rate equation was not possible. For a more precise evaluation of the rate constant, we did not try to find a numerical solution of the rate equation but solved the following system of equations

$$K_{\rm eq} = \frac{[\rm ADPA^{\bullet^+}]^2}{[\rm ADPA][\rm PQDI]} \text{ and } \frac{\rm du}{\rm dt} = k_{\rm d}[\rm ADPA^{\bullet^+}]^2 (15)$$

with  $du = d([ADPA] + [ADPA^{+}] + [PQDI])$  by the polygon method which is equivalent to eq 14 and gives the same result in a more evident way.

The numerical procedure was as follows: The rate for the product formation is calculated for a small time interval. The new concentrations of ADPA and PQDI were calculated on the basis of the converted starting material. Then the new ADPA<sup>•+</sup> radical concentration according to the equilibrium was calculated, and the procedure was started again. As a step width, 1 s was used. A further reduction of the step width by a factor of 2 had only a slight influence. It is worth mentioning that the rate of the product formation (ADPA–ADPA) is not the reaction rate of the radical cation. The concentration of the symproportionation equilibrium.

By this given calculation method we obtained in any case the same rate constants for different experimental conditions as shown in Table 1. The full lines drawn in Figure 5 are the calculated decay curves. Thus, this supposed reaction mechanism of the electrode reaction of ADPA is strongly supported.

The occurrence of a cationic intermediate in the reaction of ADPA and PQDI is also supported by our attempts to prepare PQDI by electrochemical synthesis in polar solvents which failed throughout, and only higher dimerization products were obtained. It was demonstrated already in the classical work of Willstätter and Moore<sup>19</sup> that PQDI can only be produced in nonpolar solvents where the cationic intermediate is not formed and not stabilized by solvation. This result is important for the interpretation of the influence of the solvent on the rate of the aniline electropolymerization and on the mechanism and the structure of the polymer formed.

#### 4. Conclusions

(1) The rate of the slow ADPA<sup>•+</sup> radical decay made the evaluation of the equilibrium constant for the symproportionation of ADPA and PQDI possible.

(2) The equilibrium constant for the symproportionation of ADPA with PQDI in organic solutions like DMSO is  $K_{eq} = 2.7 \times 10^{-2}$ .

(3) The equilibrium constant is independent of the acid concentration.

(4) Using the dimerization reaction of the ADPA cation radical, all of the experimental data could be described by the rate equation with a single rate constant.

(5) The rate constant for ADPA radical dimerization at room temperature is  $k = 34 \text{ L mol}^{-1} \text{ s}^{-1}$ .

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