π-Dimer of an Aniline Dimer: An ESR−UV−Vis Spectroelectrochemical Study

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It is shown for the first time that the most important intermediate formed during aniline polymerization, the *p*-aminodiphenylamine, forms a π-dimer under oxidation at room temperature in acidified organic solvents that are used in electropolymerization. *N*-Phenylquinonediimine, which is generally assumed to be formed under oxidation, is only formed in basic solutions and in ionic liquids. Most of the mechanistic studies reported so far take the formation of *N*-phenylquinonediimine under consideration, although it is not consistent with the UV−vis spectra measured during oxidation of *p*-aminodiphenylamine. The formation of a π-dimer is very well consistent with the electronic spectra of the oxidation product. In this way the π-dimer is very important for the interpretation of the UV−vis spectra of higher oligomers and polyaniline as well. Furthermore, it offers a new interpretation of the redox behavior of *p*-aminodiphenylamine as found by cyclic voltammetry and has to be considered in the mechanism of the electrochemical polyaniline formation.

1. Introduction

To get more insight in the electrochemical and optical behavior of conducting polymers, the oligomer approach is often used.[1] This was also applied for the elucidation of the electronic spectra obtained during the oxidation of aniline oligomers. These oligomers were selectively synthesized[2−5] or fractions of the reaction mixture were separated.[6] Due to the high reactivity of the aniline oligomers in the oxidized state, end-capped oligomers have mainly been synthesized and investigated.[7−12]

In early studies of conducting polymers, the oxidation products of oligomers were usually considered to be cation radicals or dications of the starting materials. With respect to the polymeric structure, the existence of polarons and bipolarons at the polymer chain was discussed. On the basis of the experimentally determined low number of spins formed by electron transfer, the formation of σ-dimers or π-dimers was assumed. Another reason for the assumption of the formation of dimers is the discrepancy in the electronic excitation spectra between the number of expected lines and lines measured for the dication in the visible region. Due to symmetry reasons, only one line can be expected for the dication, although two lines have been observed.[13]

Surprisingly, there are only few reports on the UV−vis spectra of the oxidation products of the unsubstituted *p*-aminodiphenylamine (ADPA), which can be considered as the dimer of aniline.[2,4,14,15] It is generally assumed that the formation of the ADPA cation radical takes place during anodic oxidation. This radical reacts by a head-to-tail coupling,[2,16,17,22] and the formation of *N*-phenylquinonediimine (NPQD)[18−24] is assumed. There is an early paper that suggests the formation of a π-dimer or a charge-transfer complex for very similar compounds.[25] As ADPA is formed as an intermediate product during chemical or electrochemical polymerization of aniline, the same structures as mentioned above have been discussed in such studies.[2,26,27] Although the formation of a π-dimer has been investigated in the oxidation of several substituted *p*-phenylenediamines and quinonediimines,[28,29] the formation of a π-dimer of ADPA was never taken into account in the oxidation of ADPA and aniline and its electropolymerization as well until now.

2. Experimental Section

2.1. Equipment. For ESR-spectroscopy, an ELEXSYS (Bruker) X-band spectrometer was used. All measurements were carried out at room temperature with 100 kHz modulation. The standard optical transmission cavity ER 4104 OR (Bruker) resonant in the TE_{103} mode allowed the connection of two optical light guides to measure in situ the electronic absorption spectra at the same time when the ESR-spectra were obtained. In measuring the UV−vis−NIR absorption in situ, a photodiode array spectrometer (TIDAS, J&M, Analytische Mess- und Regeltechnik, Aalen, Germany) was used. The electrochemical measurements were carried out using a PC-controlled PG 285 potentiostat (HEKA Electronic, Lambrecht, Germany) equipped with Pot-pulse software v. 8.53. In the electrochemical ESR−UV−vis investigations, a spectroelectrochemical flat cell was used. The central part of this flat cell was 0.5 mm thick, 8 mm wide, and 45 mm long. The working electrode consists of a platinum mesh with a size of 5 mm × 4 mm purchased from Goodfellow. The platinum mesh was made from a wire with 0.06 mm diameter and had 1024 meshes per cm^2. An AgCl-coated silver wire served as the pseudoreference electrode. For more details, see refs 22, 30, and 31.

In situ measurements were done by dividing the sweep of a cyclic voltammogram into 10 equidistant parts. At the beginning and at the end of such an acquisition, the measurements of the UV−vis−NIR spectrum and the ESR spectrum were started.

The UV−vis measurements in the quantitative electrolysis of ADPA were done with a MPC-3100 (Shimadzu) spectrometer.

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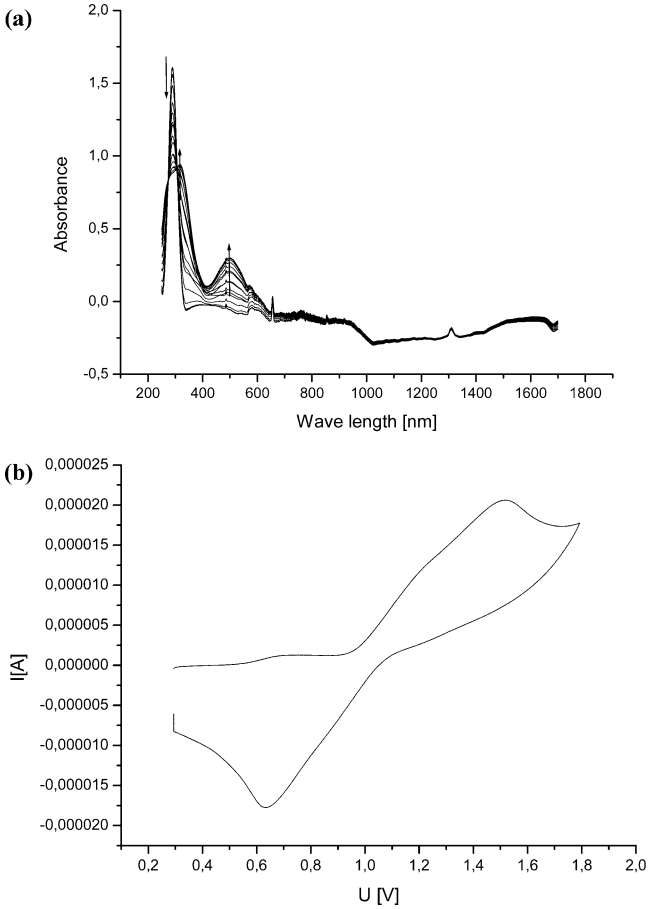

Figure 1. Cyclic voltammogram (b) and simultaneously measured UV−vis−NIR absorption spectra (a) of 2 mM ADPA in 0.1 M H_2SO_4/DMSO solution. Sweep rate 5 mV/s. Potentials are referred to Ag/AgCl. Every 34 s one UV−vis−NIR spectrum was simultaneously measured. The absorption at 290 nm is decreasing upon oxidation and increasing during reduction. The absorbance maxima at 320 and 500 nm appear and increase during oxidation and were strongly diminished during rereduction. The arrows indicate the sense of change during oxidation.

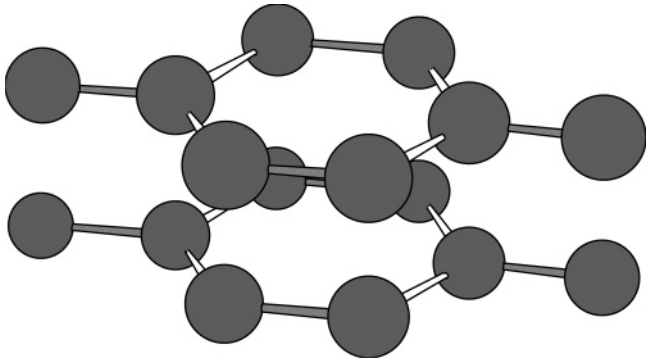

Figure 2. Schematic view of the π-dimer.

The in situ FTIR spectroelectrochemical study was performed with an IFS66/S spectrometer (Bruker) using an MCT detector. The spectra were measured with a resolution of 4 cm^{-1}. Each IR signal obtained during the electrochemical reaction was divided by the electrolyte background.

2.2. Substances and Solutions. *p*-Aminodiphenylamine was purchased from Aldrich and was purified by vacuum sublimation. Acetonitrile with a water content of 0.002%, dimethyl sulfoxide with a water content of less than 0.01%, tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6, electrochemical grade), and the concentrated sulfuric acid were purchased from Fluka and were used without further purification. For the ESR and UV−vis spectroelectrochemical experiments, the concentration of ADPA was 1−2 mM. The concentration of Bu_4NPF_6 respective to H_2SO_4 in the organic solution was 0.1 M. After each measurement set the electrolyte was renewed by moving the electrolyte across the working electrode in the spectroelectrochemical cell with the help of a syringe.

The in situ external FTIR measurements were performed in DMSO containing 10 mM ADPA and 0.1 M H_2SO_4.

The ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIPF_6$) was purchased from Merck. To remove organic impurities it was purified by solid-phase extraction with neutral alumina (Brockman I, standard grade, Aldrich). The alumina was filtered (PTFE filter, 0.2 μm) and the final colorless product was held at 35 °C and 10 mbar for 2 weeks to remove water.

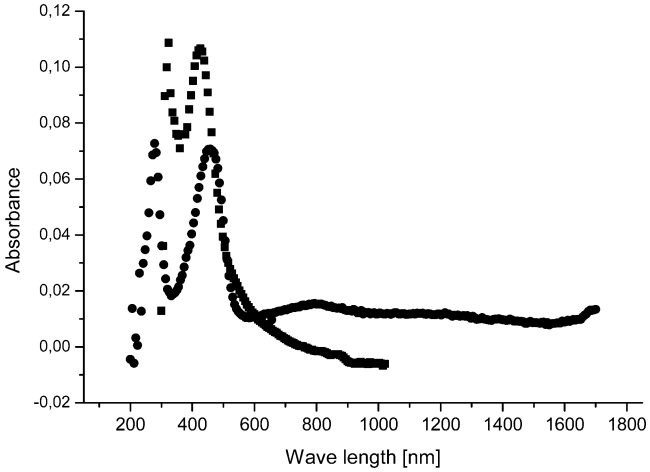

Figure 3. UV−vis−NIR spectra of NPQD in 0.1 M Bu_4NPF_6/acetonitrile solution with pyridine (circles) and in an ionic liquid $BMIPF_6$ (squares).

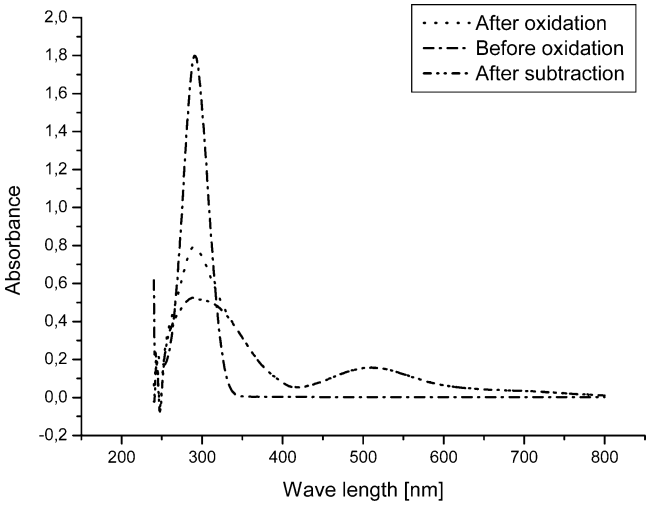

Figure 4. UV−vis spectra of a ca. 0.5 mM solution of ADPA in 0.1 M H_2SO_4/DMSO before and after electrochemical oxidation. The spectrum obtained after oxidation is corrected by subtracting the spectrum of the starting material from the product spectrum weighted by a factor of 0.15. The correction is made because only 85% of the overall charge for oxidation was used.

3. Results and Discussion

The UV−vis−NIR spectra and the cyclic voltammogram obtained during electrochemical oxidation/reduction of ADPA in 0.1 M H_2SO_4/DMSO and measured in the ESR spectroelec-

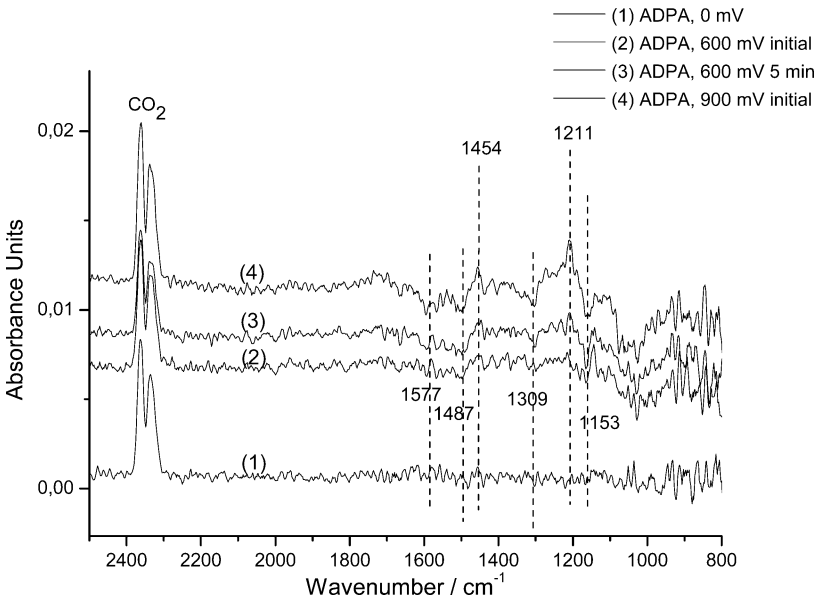

Figure 5. In situ FTIR spectra taken in 0.1 M H_2SO_4/DMSO solution containing 10 mM ADPA. The spectrum of ADPA at 0 mV (1) is taken as a reference. The spectra were recorded when applying a potential of +600 mV immediately (2) and after 5 min of electrolysis (3), as well as at an electrode potential of 900 mV (4).

trochemical flat cell are shown in Figure 1. The absorption of the ADPA at 290 nm decreases during oxidation in the forward scan and increases during the rereduction of the formed oxidation product. In the applied potential range only one oxidation product is formed, which has absorption maxima at 320 nm and 500 nm.

By in situ ESR−UV−vis spectroelectrochemical investigations we have shown earlier that the main absorption in the UV−vis spectrum does not arise from a cation radical.[32] The concentration of the radical is very low and its potential-time-behavior is different from that of the UV−vis absorption. Therefore, it can be ruled out that the strong UV−vis absorptions arise from the radical cation. At potentials at which radicals of ADPA were detected,[32] we find a weak broadening of both absorption lines. We expect that the radical has two absorptions at a similar wavelength as the product formed. Because of the low concentration of the radical, these absorptions are covered by the strong absorptions of the spinless oxidation product. For that reason these two absorption peaks have been assigned to the NPQD[22] in an earlier work.

Spectroelectrochemical experiments in acetonitrile performed in this work gave very similar results. Two oxidation peaks in the cyclic voltammogram are formed, but only one oxidation product with peaks at 350 and 590 nm is detected. These absorption peaks shift with the increasing oxidation to 320 and 474 nm due to the released protons. Already after a few minutes at higher potentials reaction products were observed in acetonitrile. In aqueous solutions the product absorbs at 320 and 490 nm, and a follow-up product absorbing at 775 nm is formed very fast.

For comparison, we synthesized NPQD according to ref 33 and measured the UV−vis absorption in *n*-hexane. In this solution the NPQD absorbs at 280 and 430 nm. If one takes into consideration that the absorption at 280 nm is covered by the absorption of ADPA, we should clearly see an absorption at 430 nm. No absorption, however, is observed at that wavelength.

The absorption of chemically prepared NPQD in 0.1 M H_2SO_4/DMSO is difficult to measure because of a fast follow up reaction that prevents the reliable determination of the UV−vis absorption of the diimine. This is in accordance with the observations of Willstätter and Moore.[33] Even in acetonitrile, the polymerization of the NPQD was too fast to get the absorption data of the initial compounds. In ethanol, a peak at 422 nm has been measured.[2] Although the protonation of the NPQD will dramatically increase the reactivity of the molecule, the UV−vis absorption spectra should not be changed very much because the protonation will take place at an orbital that is not included in the quinoid π-system and therefore does not change the number of mesomeric structures. In other words, it will not change the π-bonding network of the compound. Therefore, the related compound *p*-benzoquinonediimine was not found to change its absorption significantly when the pH of the solution is changed from 5.3 to 8.2.[34]

The longevity of the product formed in 0.1 M H_2SO_4/DMSO shows that another structure is formed beyond NPQD. For that reason we propose a π-dimer formed by two radical cations of ADPA. A schematic view of such a π-dimer is shown in Figure 2.

Evidence for the influence of the proton content of the electrolyte on the reaction pathway is demonstrated in Figure 3. Here we oxidize the ADPA in the presence of a 3-fold excess of pyridine and observed the formation of NPQD that absorbs at 424 nm in 0.1 M Bu_4NPF_6/acetonitrile, which is in good agreement with earlier measurements[2] and those measurements mentioned above. The oxidation of ADPA in the ionic liquid $BMIPF_6$ gives absorption bands at 250 and 450 nm. These maxima are somewhat shifted but give a clear indication that NPQD is formed even in an ionic liquid.

We assume that the strong interaction of the oxidation product with the solvent in the ionic liquid leads to the formation of NPQD and prevents the formation of the π-dimer.

Symmetry considerations show that NPQD should have only one absorption maximum in the visible range. This absorption band should be in between those of the radical, which is in accordance with our experimental findings.

In acidic solutions, the position of the absorption bands and also the number of the absorptions are in contradiction with the formation of NPQD but can be explained by the formation

of a π-dimer. Therefore, the π-dimer is formed solely in acidified or self-acidified solutions, where it is much more stable than NPQD.

To prove the formation of the π-dimer, we determined furthermore the charge needed for a complete conversion of ADPA into the oxidation product. Due to the short lifetime of the product, a long lasting exhaustive electrolysis cannot be used for this determination. In a reasonable electrolysis time span, only 85% of the charge needed for a one-electron oxidation could be applied. Therefore, the absorption spectrum of the starting material was weighted by 0.15 and subtracted from the absorption spectrum of the oxidation product. The result is shown in Figure 4. This is a further proof of the formation of a π-dimer.

In order to get an additional proof of the π-dimer formation, in situ FTIR spectroelectrochemsitry at different oxidation potentials was performed immediately after applying an electrode potential and also after 5 min of elctrolysis. The spectrum of ADPA at 0 mV was taken as a reference. The obtained spectra are shown in Figure 5. The negative peaks at 1577, 1487, 1309, and 1153 cm^{-1} are caused by ADPA due to its consumption. These peaks are comparable with the peaks reported for diphenylamine structures.[35] Two positive peaks at 1454 and 1211 cm^{-1} appeared when applying the oxidation potentials. The absorption at 1454 cm^{-1} is assigned to the mixed response of C−H bending and C−N and C−C stretching in benzenoid structures, and that at 1211 cm^{-1} is assigned to the C−N stretching vibration.[36] No bands from the pure quinoid structures contribute to the spectrum during the initial oxidation. This supports the assumption of π-dimers with increasing benzenoid signals with increasing electrode potentials instead of quinoid signals from NPQD.

Conclusion

It is shown for the first time that in aqueous solutions as well as organic solvents like acetonitrile and DMSO the main oxidation product of ADPA (chemical and electrochemical) is a spinless one-electron oxidation product that can be considered as a π-dimer of two radical cations of ADPA.

This structure is confirmed by several experimental findings and is in accordance with symmetry considerations. The expected diimine NPQD is only formed in the presence of a strong base, which is binding the released protons, as well as in ionic liquids like $BMIPF_6$, where the high ionicity prevents the dimer formation. In acidic solutions NPQD reacts fast to form higher oligomers up to polyaniline.

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