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ELECTROSYNTHETIC ASPECTS OF ANODIC REACTIONS OF ANILINES AND INDOLES

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Abstract: The electrochemical oxidation of aniline, indole and their various alkyl-subsituted derivatives leads to the formation of various products including intrinsically conducting polymers.

The application of electrochemical techniques, preferably in situ methods, to the characterisation of radical intermediates and of solid state properties of the polymers is described.

Introduction

During the initial electron transfer step of an electrochemical oxidation process usually very reactive radical cations are formed:

$$HM \longrightarrow HM^{+} + e^{-} \qquad (1)$$

Various subsequent reaction pathways are possible:

- Abstraction of a proton:

$$HM^{+} \longrightarrow M + H^{+} \qquad (2)$$

- Nucleophilic substitution:

$$HM^{+} + Nu \longrightarrow MNu + H^{+} \qquad (3)$$

- Dimerization (radical recombination)

$$2\ HM^{+} \longrightarrow M_2 + 2\ H^{+} \qquad (4)$$

The preferred pathway depends on the respective rate constants. The rate constants are influenced by the nature and inherent stability of the radical cation and interactions with the solvent in case of (2); whereas the rates of (3) and (4) of course also depend on the concentrations of the radicals and of nucleophiles in the solution.

In case of the initial formation of a 1,5-Dimethyl-2-pyrrolcarbonitrile-radical-cation abstraction of a proton of the 1-methyl group predominates /1/. In case of a slow proton abstraction and a low concentration of nucleophiles radical recombination is the preferred reaction, in particular in case of high current densities and correspondingly high stationary concentrations of the radical cation.

Subsequent oxidation of the dimer and further radical recombination as well as nucleophilic substitution at HM (instead of a different nucleophile Nu) may lead to the formation of a polymer film on the electrode or oligomers in the solution phase. In case of the compounds investigated here the polymer film itself is electrochemically active in most cases, its reversible oxidation causes formation of radical cations in the polymer chain (polarons), which may recombine forming bipolarons. These electronic states and a heavily conjugated bond system in the polymer provide the necessary conditions (free and mobile charge carriers) for intrinsic electronic conductivity.

Synthetic aspects of electroorganic reactions involving the anodic oxidation of nitrogen containing compounds have been reviewed extensively by various authors /2 - 7/, a bibliography has been compiled /8/.

Most of these reactions feature the oxidation of N-containing compounds via formation of radical cations with the nitrogen atom playing a central role. The products are usually monomers, in some cases intramolecular coupling of two different educt molecules occurs. In recent years, rapidly increasing interest has been focused onto reactions, where dimerisation of radical cations with substrate molecules of its kind occur (via dimerisation, oligomerisation, polymerisation). In many cases these reactions lead to the formation of intrinsically conducting polymers ("synthetic metals") with high electronic conductivities and various additional properties (electrochromism, pH-sensitivity, etc.) caused by their particular molecular structure.

These properties can be controlled by external experimental parameters, making conducting polymers an intriguing new class of materials. Recent reviews covering many aspects of these materials have been published /9 - 11/; special attention to the electrochemistry of these compounds has been given in /12, 13/.

In this paper we present results obtained with aromatic amines (aniline and its methyl-substituted derivatives) and nitrogen containing heteroaromates (indole and its methyl-substituted derivatives).

This report deals mainly with preparative aspects and the investigations of radical intermediates present during the formation of polymers, some properties of the polymer films are discussed, too. Besides classical electrochemical techniques **in situ** electron spin resonance spectroscopy (ECESR) has been used to study radical intermediates as well as spin states in the polymer film. This method has been used recently in studies of the electrooxidation of aliphatic alcohols /14, 15/ or the electroreduction of nitrobenzyl chloride /16/.

Experimental

Indole, aniline and their derivatives used in this study were distilled under vacuum or recrystallised from isopropanole, resp.. In case of indoles acetonitrile distilled over phosphor pentoxide and deaerated with dried nitrogen was used as a solvent for the supporting electrolyte solution. The supporting electrolyte was 0.25 M $LiClO_4$ p.a. grade (as will be shown later this combination favours reaction (4)). In case of anilines 1 N aqueous sulphuric acid was used as electrolyte system.

Electrochemical experiments were carried out at smooth platinum electrodes at room temperature in a three compartment H-cell with a BANK POS 73 scan generator/potentiostat and a Philips PM 8132 xy-recorder. An Ag/AgCl-Electrode (E=197 mV NHE) served as reference electrode; all electrode potentials are quoted with respect to this reference. **In situ** ESR experiments were made with a coaxial three-electrode cell with a helical platinum wire serving as the working electrode and as the inner part of a coaxial microwave resonator of the spectrometer BRUKER 200D, for details see /14, 15, 17/. The computer based interpretation (simulation) of ESR-spectra has been described elsewhere /14, 15/; for a description of **in situ** conductivity measurements see /24/.

Results and Discussion

Fig. 1 (following page) shows the typical behaviour of 1,2-dimethylindole (see Tab. 1) at a concentration of 100 **mmol** during a voltage scan experiment.

The electrooxidation starts at E= 800 mV, oxidation peak potentials are E= 1050 and E= 1350 mV resp.. With an increasing number of cycles the current density rapidly decreases. Simultaneously a polymer film of dark green colour covering the electrode becomes visible. (Alternatively the polymer can be formed at stationary electrode potentials (E> 900 mV)).

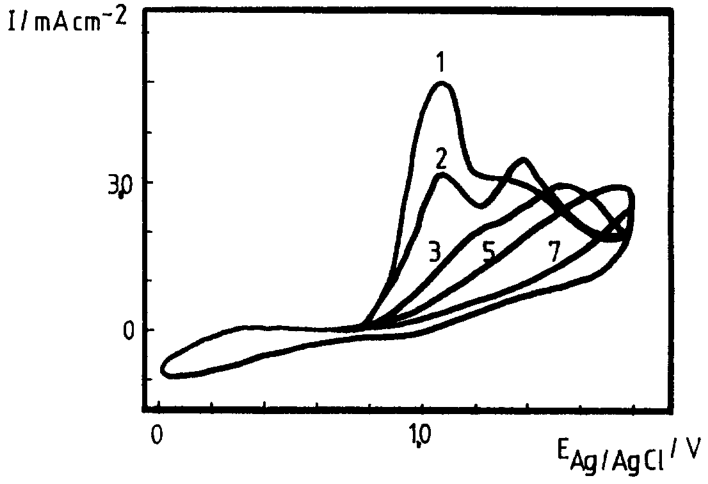

Fig. 1: Cyclic voltammogram of 1,2-dimethylindole (100 mmol), smooth platinum electrode, 0.25 N $LiClO_4$ in acetonitrile, dE/dt = 100 mV s^{-1}, cycles 1 to 7 are plotted

The identification of radical intermediates must take place before the polymer film is formed, since spin states in the conducting polymer film show a broad absorption line dominating the ECESR-spectrum. In order to enable their identification, the radicals must desorb and show sufficient life times ($t_{1/2} > 10^{-4}$ s, for a detailed discussion see /18/). In case of 1,2-dimethylindole at E= 900 mV the 1,2-dimethylindole-radical cation was identified (Fig. 2, following page). The suggested structure of the radical derived from a comparison of measured and simulated ECESR-spectra preserves the aromatic character of the benzene ring, in addition the positive charge is located at the most electronegative atom.

Based on literature data on the reactivity and preferred substitution patterns of the indole radical cation /19 - 21/ position 6 in the benzene ring and position 3 in the pyrrole unit are most likely positions for substitution, i.e. intermolecular bonding. A reaction mechanism based on these observations including a dimer showing this 3-6-connection is shown in Fig. 3 (following page). Further oligomerisation involving 3-6-, 3-3- and 6-6-connections leads to the formation of the polymer film. Mechanism and structure are further supported by the fact, that in case of 3-substituted indoles no polymerisation takes place. In case of unsubstituted indole in addition a N-N-bond has been suggested by Tourillion and Garnier /22/ based on the absence of the N-H-stretch mode of ex situ infrared spectra of polyindole.

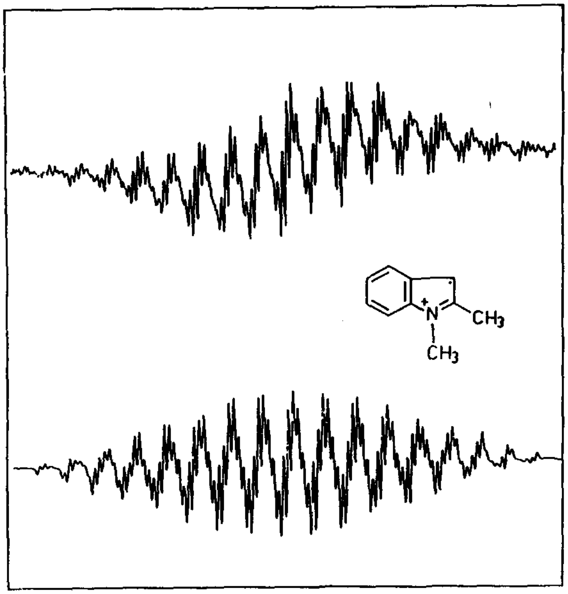

Fig. 2: ECESR-spectrum of the radical formed during oxidation of 40 mmol 1,2-dimethylindole in acetonitrile/0.25 M $LiClO_4$,
top: measured spectrum,
bottom: calculated spectrum
insert: suggested structure of the radical cation

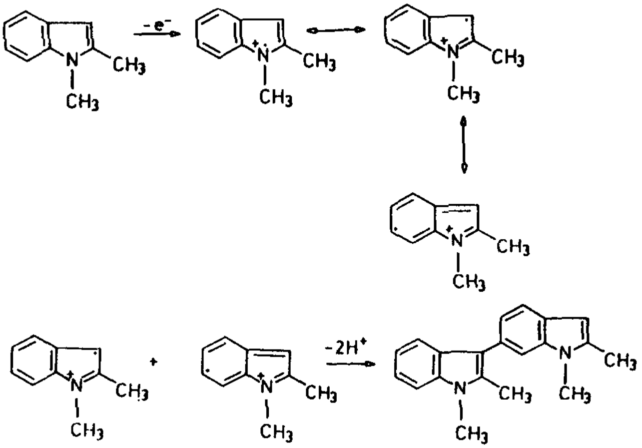

Fig. 3: Suggested reaction mechanism of polymer formation showing the possible charge distributions in the radical (upper part) and the dimer formation (lower part) as initial step

Subsequent voltage scan experiments carried out in the supporting electrolyte solution without the monomer show a reversible oxidation/reduction behaviour of an electroactive species attached to the electrode (as inferred from the shape of the voltammogram, its scan rate dependence etc).

In ECESR experiments the concentration of spin states in the polymer film (spin density) corresponding to the height of the Lorentzian-shape single absorption line as a function of the electrode potential (oxidation state of the film, see /23/) was measured. The result is shown in **Fig. 4**.

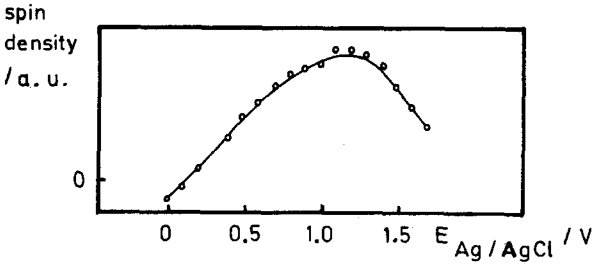

Fig. 4: Spin density signal (film of poly-1,2-dimethylindole). The signal was taken at stationary potentials.

The decrease in spin density observed at electrode potentials beyond E= 1,2 V can be explained by formation of spinless bipolarons.

With the exception of indoles substituted in position 3 (see above) all investigated derivatives of indole showed a similar behaviour in acetonitrile electrolyte solution. In case a polymer film was formed a single line ECESR-spectrum was recorded; the film showed a reversible electrochemical redox activity.

Analogous results were obtained with aniline and its N-methyl-substituted derivative, whereas N,N-dimethylaniline could be oxidised in aqueous solution only yielding a polymer without electrochemical activity. A radical cation of the latter compound could be identified after chemical oxidation (with conc. HNO_3). In this radical the positive charge is localised at the nitrogen atom, the free electron is most likely in the para-position of the benzene ring. This implies a head-to-tail coupling in the polymer chain; the quaternary nitrogen atom cannot be oxidised resulting in the missing electrochemical activity of the film.

Table 1 gives a summary of our experiments with indole, aniline and their substituted derivatives.

Table 1

Electrolyte system for the indoles 0.25 N $LiClO_4$ in acetonitrile, for the anilines 1 N aqueous H_2SO_4.

The peak potentials (in mV Ag/AgCl) refer to values observed in the first anodic scan at dE/dt= 100 mV s^{-1}.

compound	peak potentials	polymerization	identification of an intermediate radical cation	oxidisable polymer	spin density signal of the polymer
indole	1200,1700	yes	no	yes	yes
1,2-dimethyl-indole	1050,1350	yes	yes*)	yes	yes
2,3-dimethyl-indole	850,1000	no	-	-	-
2,5-dimethyl-indole	not observed	not observed	yes**)	not observed	not observed
2-methyl-indole	920,1300	yes	no	yes	yes
3-methyl-indole	1050,1250	no	-	-	-
N-methyl-indole	1150,1500	yes	no	yes	yes
aniline	1000	yes***)	no	yes	yes
N-methyl-aniline	900	yes***)	no	yes	yes
N,N-methyl-aniline	900,1000	yes	yes**)	no	no

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*) also observed during chemical oxidation (conc. HNO_3)

**) only observed during chemical oxidation

***) also observed in acetonitrile solution

In situ conductivity measurements with these polymers deposited in a small gap (< 0.05 mm) between two platinum rod electrodes (diam. 2 mm, see /24/) showed a change of polymer resistance as a function of the applied potential. A comparison of ESR-signal intensity and polymer conductivity as obtained with a polyindole film (Fig. 5, see next page) shows a minimum in resistance (ie a maximum conductivity) in the potential range where a maximum ESR signal (ie polaron concentration) is observed. Upon further oxidation the resistance increases again, whereas the ESR signal decreases. In this case polarons seem to be closely related to the electrical conductivity.

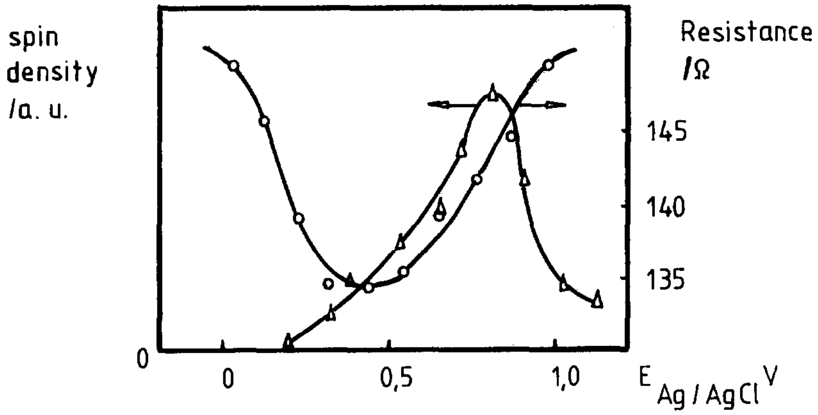

Fig. 5: Spin density signal and resistance of a polyindole film, platinum electrodes, 0.25 N $LiClO_4$ in acetonitrile

With other polymers studied here the ESR signal also increases corresponding to the electrochemical oxidation current and drops subsequently. Its maximum coincides in many cases much closer with the transition from the insulating to the conducting form of the polymer in the resistance vs. potential diagram.

Since the experimental arrangement used here shows results significantly influenced by the ionic conductivity of the electrolyte solution in contact with parts of the platinum electrode surface a new experimental setup operating with electrodes not exposed to the solution and a small DC test voltage was developed. Preliminary results have confirmed the findings reported here; the change in conductivity extends over several orders of magnitude /25/.

Acknowledgements

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