Spectroelectrochemical analysis of a N-aryl-Δ²-pyrazoline derivative

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Introduction

Spectroelectrochemistry (SEC) couples reaction-oriented electrochemistry and different species-focused spectroscopic methods (UV/VIS, IR, Raman, ESR, and NMR) for obtaining information on structural and molecular properties during electrochemical reactions. In particular, UV/VIS spectroelectrochemistry (UV/VIS-SEC) investigates chemical reactions involving or related to electron transfer and determines the structure of the reactants in situ.

UV/VIS-SEC is a powerful tool to monitor the anodic oxidation of N-aryl-Δ²-pyrazoline compounds. As a result of the one-electron removal, short-lived radical cations emerge that dimerize in a second reaction step (1). In this poster, we focus on the oxidation of methyl 5-methyl-3-phenyl-1-p-tolyl-4,5-dihydro-1H-pyrazole-5-carboxylate. The oxidation is accompanied by a significant shift of the absorption maxima (from yellow to green). Due to the methyl substituent in para position of the N-aryl group, dimerization of the N-aryl-Δ²-pyrazoline is inhibited (2). Instead, a stable radical cation is formed.

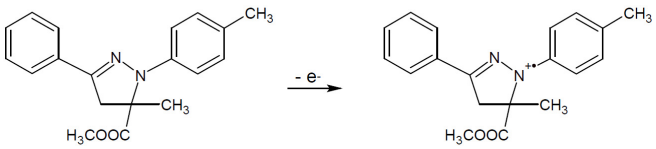


Figure 1: Oxidation of methyl 5-methyl-3-phenyl-1-p-tolyl-4,5-dihydro-1H-pyrazole-5-carboxylate

Experimental

Principle

A solution of 1 mmol/L methyl 5-methyl-3-phenyl-1-p-tolyl-4,5-dihydro-1H-pyrazole-5-carboxylate is electrochemically analyzed by cyclic voltammetry on a platinum gauze electrode. With every voltage step, the potentiostat sends a trigger signal to the spectrometer (Figure 2). The spectra are recorded from 215 nm to 800 nm.

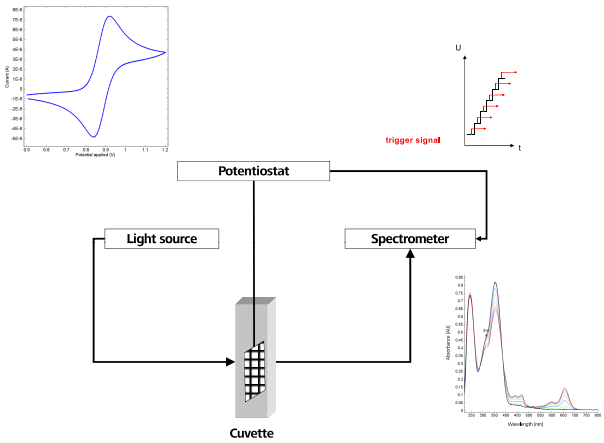
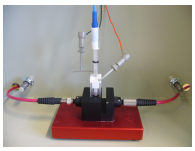


Figure 2: UV/VIS spectroelectrochemical setup

Electrolyte	c (tetrabutylammonium hexafluorophosphate) = 0.1 mol/L in acetonitrile
Working electrode	Platinum gauze (80 mesh)
Counter electrode	Platinum wire
Reference elecrode	Ag/c($AgNO_3$) = 0.01 mol/L in electrolyte

System setup: Potentiostat with spectroelectrochemical cell



Results

Cyclic voltammetry experiments indicate that the radical cations of the N-aryl-Δ²-pyrazoline derivative investigated are stable and can be reversibly reduced (Figure 3a). Despite the different diffusion characteristics on the platinum gauze and platinum disc electrode (Figure 3b), the spectroelectrochemical cell facilitates cyclic voltammetric analysis. Hence, the spectroelectrochemical setup allows for a direct correlation between spectra and data points of the cyclic voltammogramm.

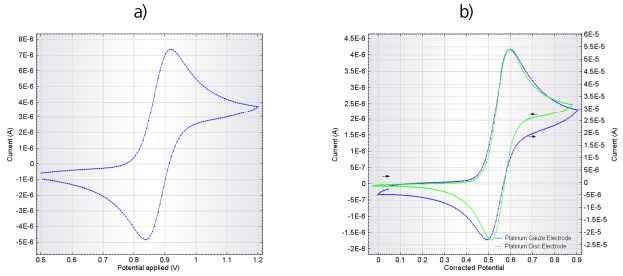


Figure 3: Cyclic voltammogramms of methyl 5-methyl-3-phenyl-1-p-tolyl-4,5-dihydro-1H-pyrazole-5-carboxylate on a) platinum disc electrode (Ø 2 mm) versus Ag/Ag^+ (0.01 mol/L), scan rate 100 mV/s and b) platinum gauze (80 mesh) and platinum disc electrode (Ø 2 mm) versus $Ag/AgNO_3$ (0.01 mol/L), scan rate 25 mV/s

The oxidation of methyl 5-methyl-3-phenyl-1-p-tolyl-4,5-dihydro-1H-pyrazole-5-carboxylate shifts the absorption maxima from 314 and 353 nm to 467, 597, and 652 nm (Figure 4). The two isosbestic points (287 and 385 nm) confirm the stability of the electrogenerated radical cation and the absence of subsequent reactions.

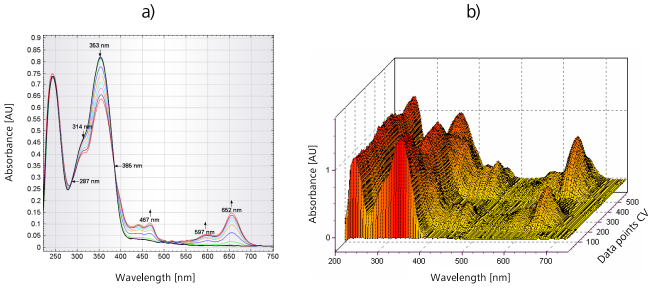


Figure 4: a) Two-dimensional and b) three-dimensional absorption spectra (two scans) for the anodic oxidation of methyl 5-methyl-3-phenyl-1-p-tolyl-4,5-dihydro-1H-pyrazole-5-carboxylate.

Conclusions

By combining the information from electrochemical and spectroscopic techniques, UV/VIS spectroelectrochemistry (UV/VIS-SEC) allows a comprehensive analysis of electron-transfer processes and complex redox reactions. The anodic oxidation of a 5,5-disubstituted N-aryl-pyrazoline was investigated by combining cyclic voltammetry and UV/VIS spectroscopy. In situ measured UV/VIS absorbance depicted the absorption changes that accompanied the anodic oxidation of the N-aryl-pyrazoline derivative and could therewith prove the stability of the electrogenerated radical cation.

Due to the direct control of the spectrometer by the potentiostat, the electrochemical and optical information can be easily cross-correlated. The combination of an Autolab Potentiostat with a triggerable spectrometer provides a convenient and powerful tool for the in situ study of shorter-lived species, reaction mechanisms, and kinetics in a wide variety of electrochemical active organic, inorganic, and biological molecules (3).

References

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