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Introduction

In 1995 I joined the working group of Prof. Günter Grampp at Graz University of Technology. I started working on thermal and photo-induced electron transfer (ET) reactions in solution. A few years later we recognized that the physical properties of the solvent influence the rate constant of ET reactions in many ways.

Since 2015 I lead an independent research area at the Institute of Physical and Theoretical Chemistry. Besides collaborations with several international partners on special topics in the analysis of kinetics of chemical reactions there are three main topics of research.

Weak effects on electron transfer reactions

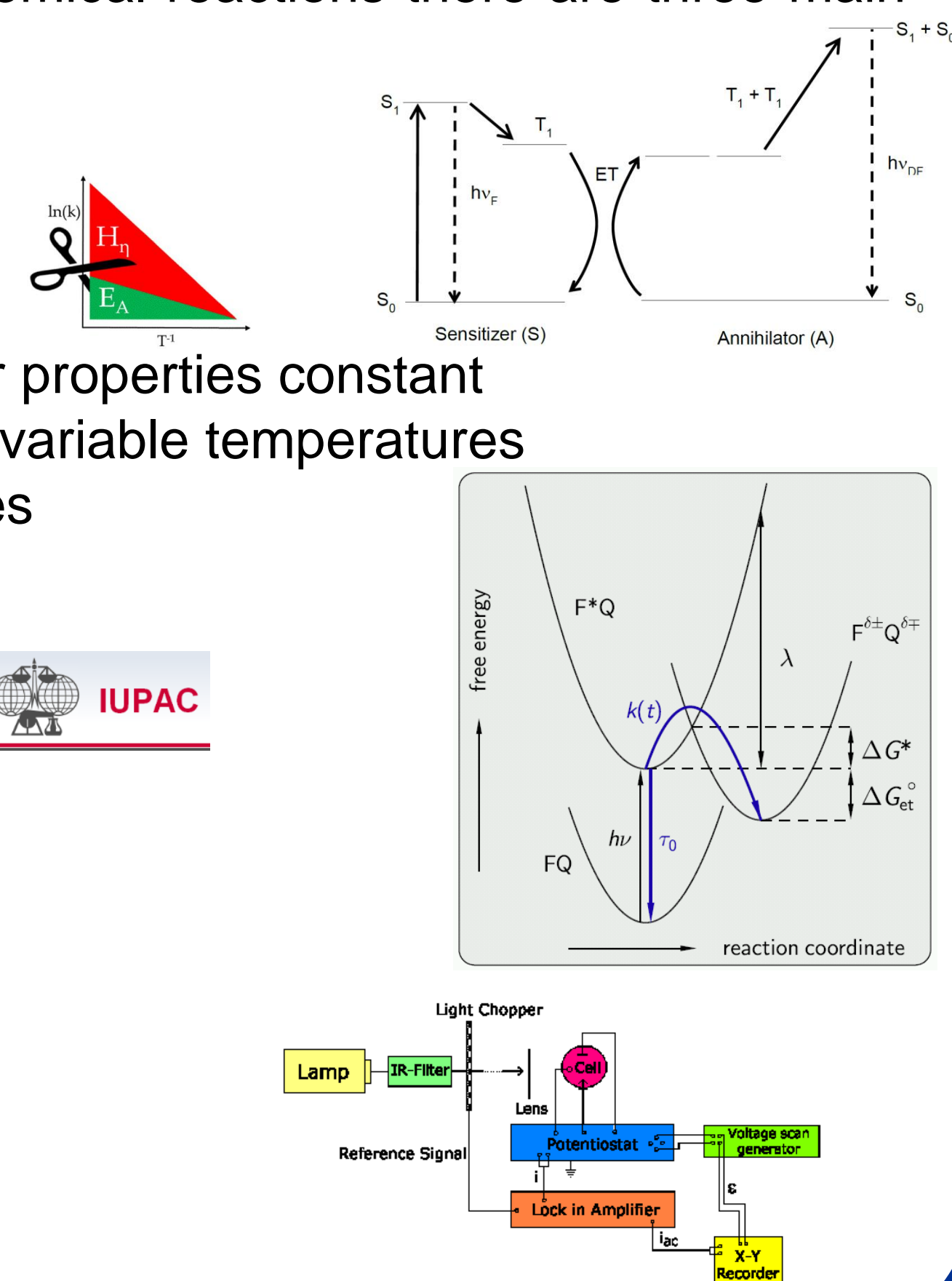
Magnetic field dependent reaction yield

e.g. Triplet-triplet-annihilation (TTA)

Working with variable η or ϵ_r , keeping all other properties constant

Working with constant solvent parameters at variable temperatures

Properties and applications of tertiary mixtures



Photochemical Methods

Application of semiconductor light sources

Fluorescence standards (IUPAC project)

Theory of electron transfer reactions



Pure and applied electrochemistry

Electrochemical methods,

e.g. photo-modulated voltammetry

Kinetics in electrochemistry

Electrochemistry in ionic liquids

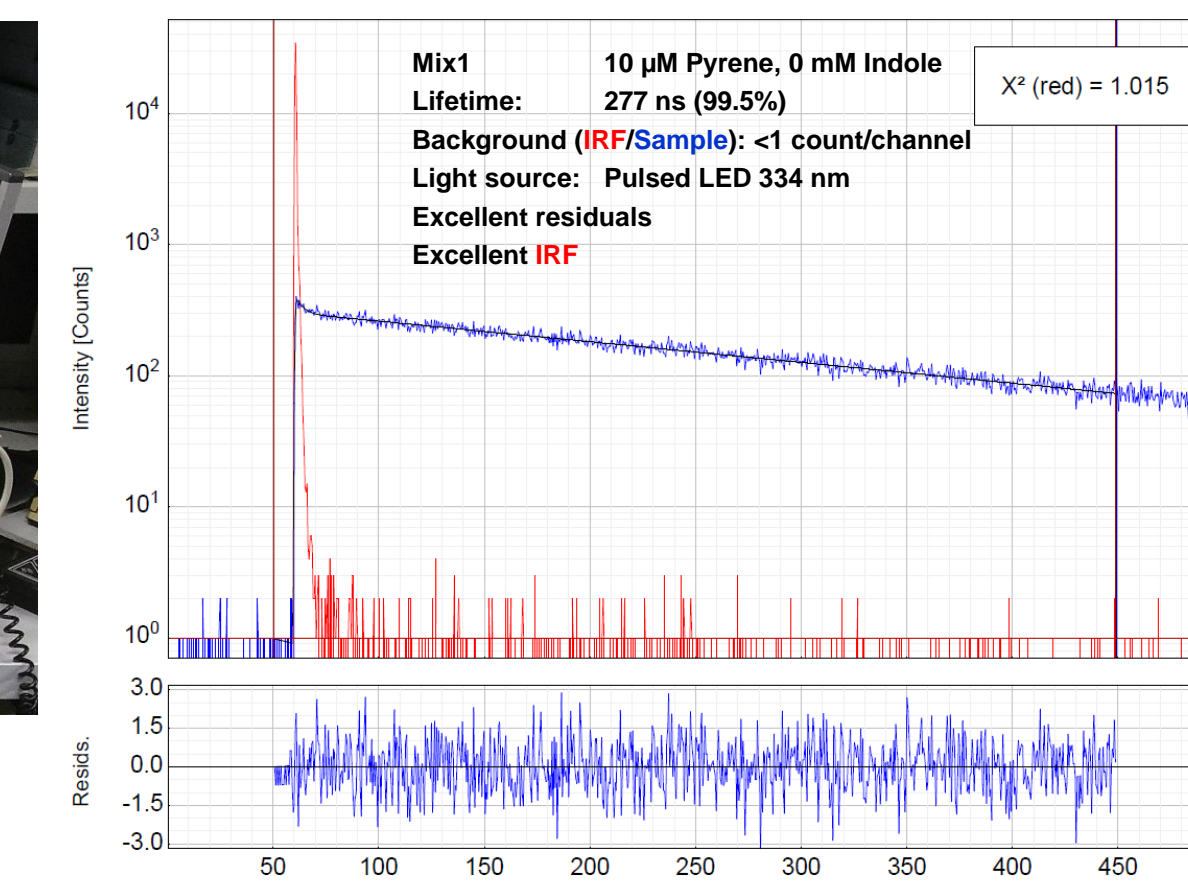
Photochemical Methods

Application of semiconductor light sources and fluorescence standards

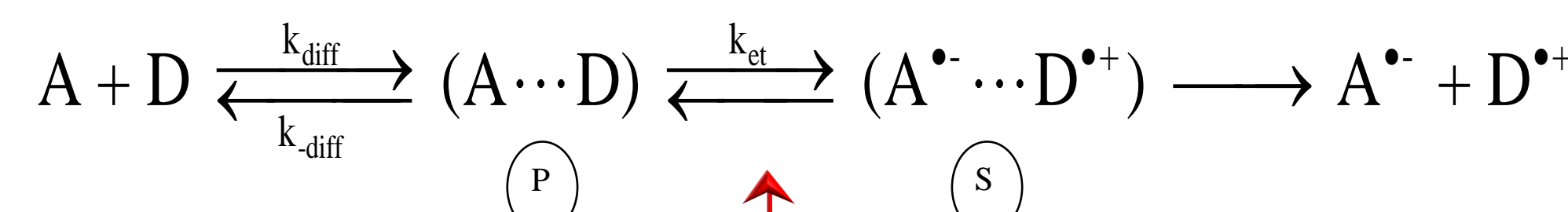
Since 1996 I developed a new LD/LED-based modulation fluorometry. With a time-resolution of 100 ps using digital storage oscilloscopes it was the cheapest way to reach this time scale. Later the TCSPC method was improved by removing the background signal and electronic artefacts measuring short pulses and decays.



Current TCSPC-setup in the laboratory.

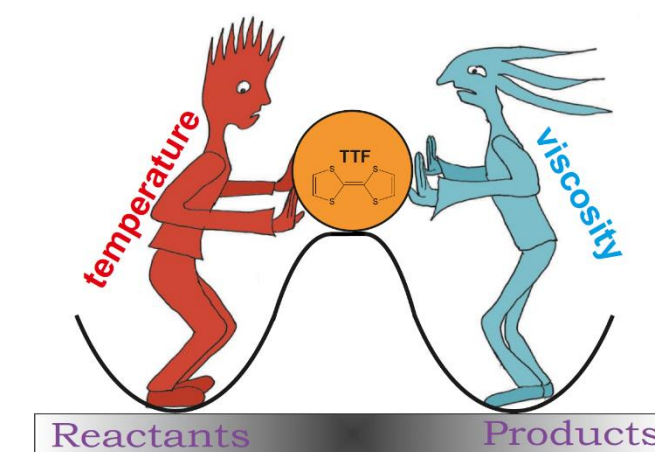


Theory of electron transfer reactions



ET step

ET reactions can be described as step-wise processes with two diffusion affected steps and the charge transfer in between. The two limiting cases are diabatic and adiabatic processes depending on the size of the resonance splitting energy.



Weak effects on electron transfer reactions

Classical electrochemical description of the solvent reorganization energies in ET theories use the Pekar factor $\gamma=(1/n^2-1/\epsilon)$ as a solvent parameter. Dielectric constant ϵ and refractive index n influence the solvent dipole reorientations and contribute to the activation energy of the ET reactions. That is why solvent-dependent measurements of ET reactions start quite early. But, electron-transfer kinetics is also influenced by diffusion and therefore by the solvent viscosity η . Unfortunately, most measurements published use different solvents in a not consequent way. Results of polar and nonpolar solvents are compared with high- and low viscous ones.

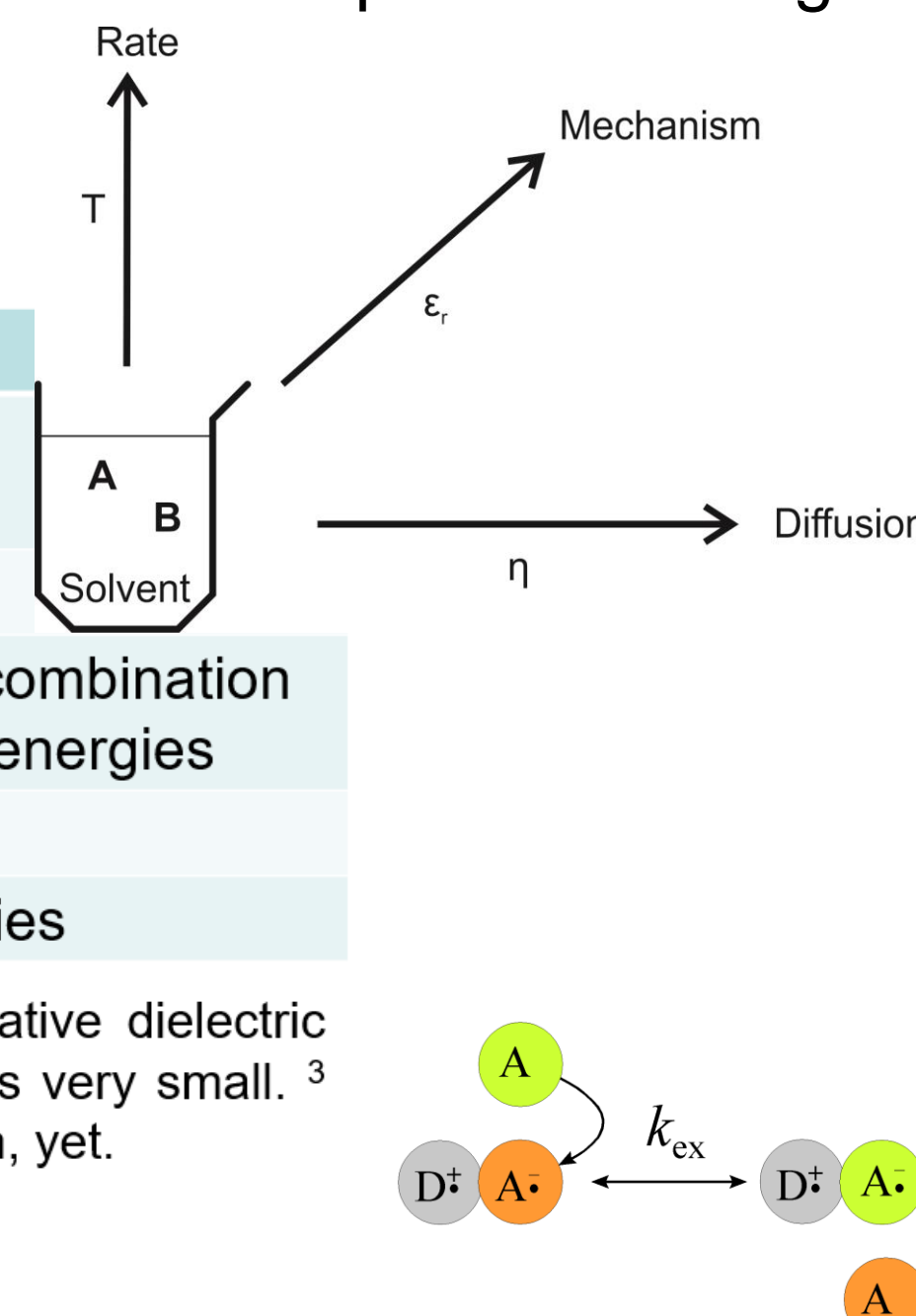
Individual tuning of single solvent parameters:

Parameter	Organic solvents	RTILs	Application
η	2-62 polar 0.6-92 non polar	1	Diffusion Recombination
n_D	2	2	-
ϵ_s	6-24	3	Free ions vs. recombination Tuning reaction energies
ρ	2	4	-
T	15-55°C	25-65°C	Activation energies

η is the viscosity in cP [6], n_D is the refractive index at 589 nm, ϵ_s is the relative dielectric constant, and ρ is the density. ¹ applicable but not used, yet. ² available range is very small. ³ complex behaviour makes tuning difficult. ⁴ nothing done due to missing application, yet.

Magnetic field-effected Reaction Yield (MARY):

Although the energy differences induced by a weak magnetic field are much smaller than the thermal energy in the laboratory, the yield of some photo-induced ET reactions can be influenced significantly, recombination of radicals or the TTA.



Pure and applied electrochemistry

Electrochemistry can be used to study the mass transport and electrode kinetics parameters in room temperature ionic liquids (RTILs) and in its binary mixture with organic solvent. For tiny amounts of solutions a new apparatus has been developed.

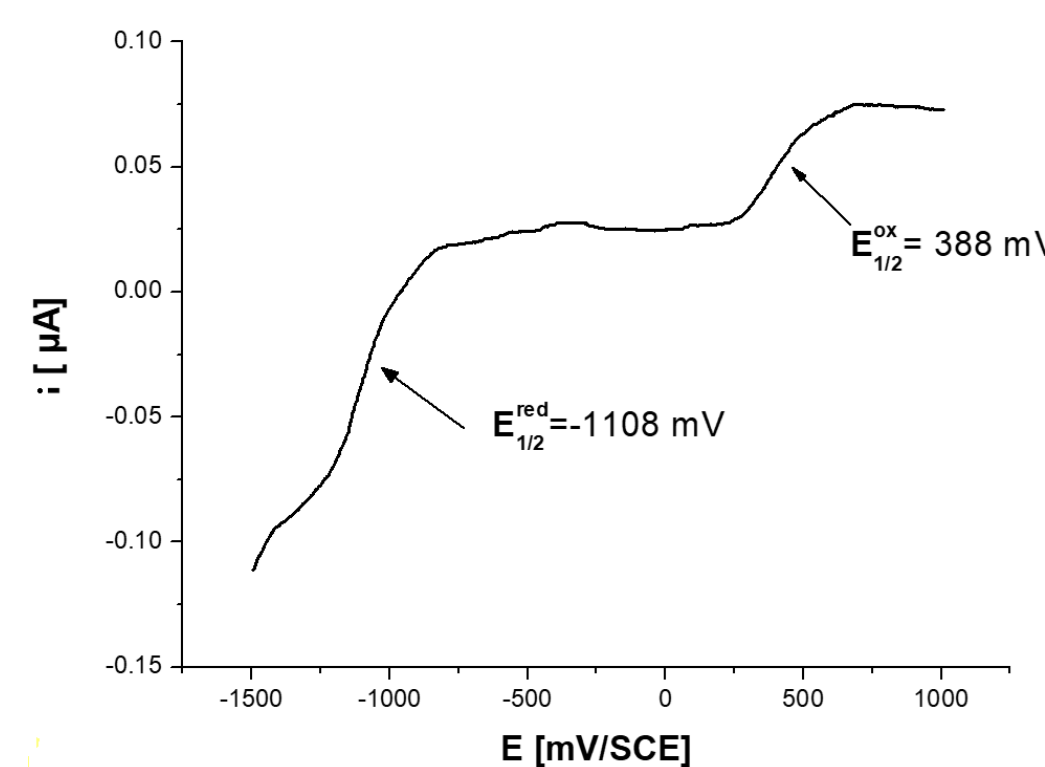
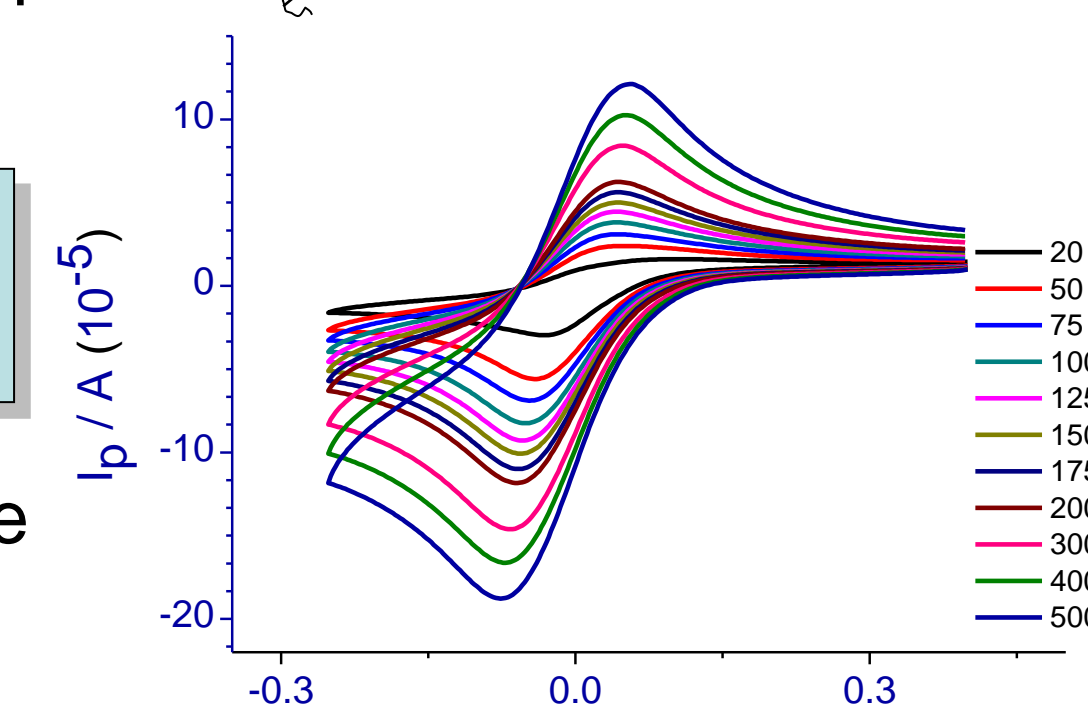
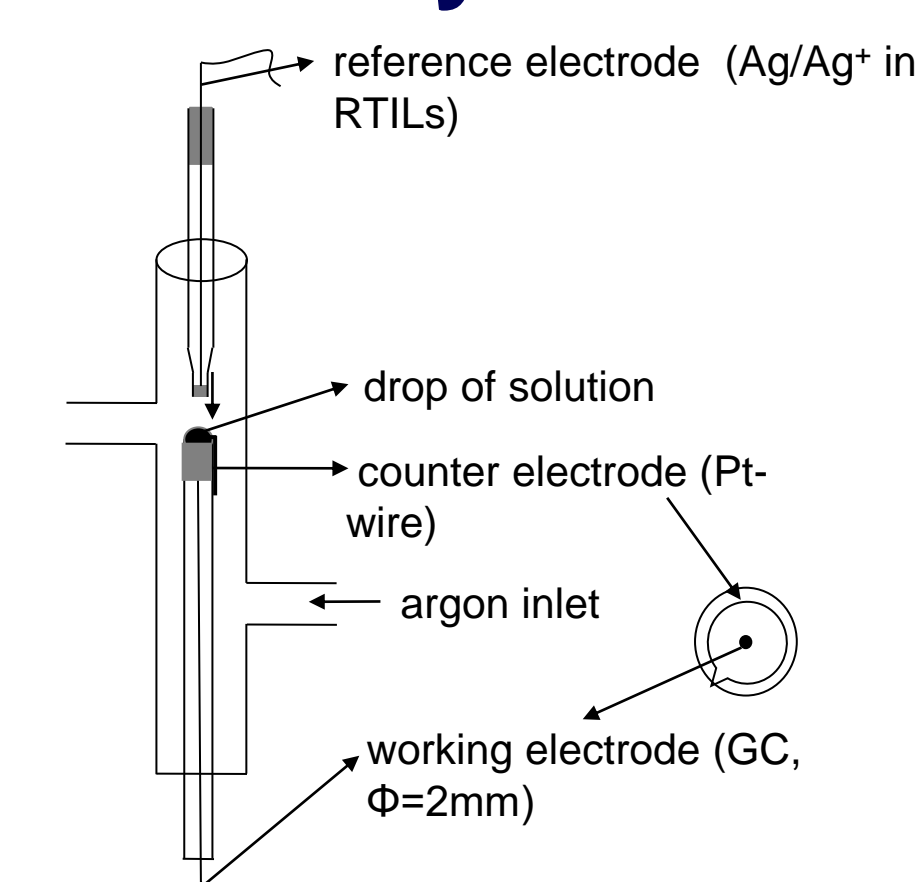
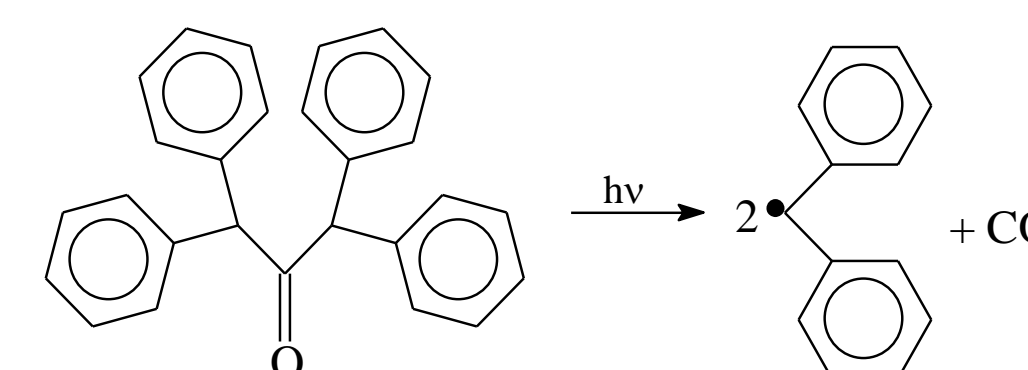
Cyclic voltammetry is the method of choice for analyzing electrode processes using the Randles-Sevick's equation and the Nicholson method.

$$I_p = 0.4463nF \left(\frac{nF}{RT} \right)^{1/2} AD^{1/2} C v^{1/2}$$

$$k_{\text{het}} = \frac{\psi}{\gamma^e} \sqrt{\frac{\pi n F v D}{RT}}$$

For further studies rotating disc electrodes are also available.

Photo-modulated voltammetry is a method to measure redox potential of short-lived intermediates or excited states on the μ s to ms scale, e.g. radicals formed from peroxide splitting.



Current Research Partners

Dr. Jens Sobek, Functional Genomics Center Zurich

Prof. Albert Brouwer, University Amsterdam
- IUPAC Subcommittee Photochemistry

Dr. Steffen Jokus, Bowling Green State University

Dr. Patcharanan Choto, Mae Fah Luang University

Dr. Nikola Basarić, Ruđer Bošković Institute, Zagreb

Prof. Uwe Pischel, University Huelva



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