

## The effect of pressure on the kinetics of the TEMPO/TEMPO<sup>+</sup> self-exchange reaction.

Kenneth Rasmussen and Günter Grampp

*Institute of Physical and Theoretical Chemistry, Graz University of Technology,  
Technikerstrasse 4/1, A-8010 Graz, email: [rass@ptc.tugraz.at](mailto:rass@ptc.tugraz.at)*

It is well-known that the kinetics of electron self-exchange reactions may be studied by ESR.



Kinetic data are extracted from linebroadening experiments, where the concentration of the diamagnetic species (TEMPO<sup>+</sup>) is varied at constant concentration of TEMPO. The measured rate constants, after correcting for diffusion, can be described using an Eyring-like equation, applying the Marcus approach for the energy of activation. The latter mainly depends on the outer reorganisation energy,  $\lambda_o$ , which is characterised by substrate parameters (geometry of the precursor complex) as well as solvent specific ones (refractive index, dielectric constant). In many cases, however, the time scale of the reaction becomes comparable to that of the solvent dynamics and the expression must be modified to take this into account.

$$k_{\text{ET}} = \frac{1}{\tau_L} \left( \frac{\lambda_o}{16\pi RT} \right)^{1/2} \exp\left( \frac{-\lambda_o}{4RT} \right), \quad \lambda_o = \frac{e_0^2 N_A}{4 \pi \epsilon_0} \left( \frac{1}{r} - \frac{1}{d} \right) \left( \frac{1}{n_D^2} - \frac{1}{\epsilon_s} \right)$$

Classically both static and dynamic solvent effects have, not unexpectedly, been studied by choosing solvents with appropriate variations of the properties mentioned. This method, however, is limited by other properties of the solvents, chemical as well as physical, rendering many desired combinations of redox pairs and solvents useless.

In an attempt to circumvent these problems we have built a high-pressure system enabling us to apply pressures of up to 80 MPa to solutions and since several key solvent properties (viscosity, dielectric constant, relaxation times, refractive index) are pressure dependent, i.e.  $\eta = f_1(p)$ ,  $\epsilon_s = f_2(p)$ ,  $\tau_L = f_3(p)$ ,  $n = f_4(p)$ , we are now able to emulate 'solvent effects' through pressure variations.

A number of experiments have been carried out on the TEMPO/TEMPO<sup>+</sup> system in acetonitrile at various pressures, determining the *volume of activation* of the reaction.

$$\Delta V^\ddagger = -RT \left( \frac{\partial \ln k_{\text{et}}}{\partial p} \right)_T$$

This has enabled us to reinvestigate the solvent dynamic effect of the reaction and compare with the results obtained using the traditional method.

Sample reference: G. Grampp and K. Rasmussen, *Phys. Chem. Chem. Phys.*, **4** (2002), 5546