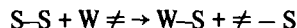of adsorption of S. Moreover, c is the coordination number in the adsorbed monolayer and ΔG_{lat} measures the energy involved in the process

$$S–S + W \neq \rightarrow W–S + \neq - S$$

where the hyphen denotes lateral interactions between contiguous particles in the adsorbed monolayer. The derivation of eqn. (1) relies on the following assumptions: (*i*) the activated complex for the electrode reaction is specifically adsorbed and is the same independent of whether it is formed by displacement of adsorbed solvent molecules or of adsorbed surfactant molecules; (*ii*) the theory of absolute reaction rates applies; (*iii*) the surfactant is adsorbed under equilibrium conditions. The expression for ΔG_{lat} depends both on the particular model of the adsorbed monolayer and on the particular mechanical statistical treatment of this model.

For all systems investigated the quantity (cn$_{\neq}$ $\Delta G_{lat}/RT$) turns out to be notably positive. This behaviour can be explained by the ability of adsorbed water molecules to establish strong ion–dipole interactions — and, possibly, further interactions of a more specific nature — with the charged activated complex, no such strong interactions with this complex being established by adsorbed aliphatic molecules.

The experimental dependence of $k_{\theta=1}$ for Pb-(OH)$_3^-$ and Bi^{3+} reduction and for Pb$^\circ$(Hg) oxidation upon the bulk concentration of n-butanol, under certain experimental conditions, suggests a gradual passage from the mechanism previously outlined to an alternative mechanism in which the rate determining step involves the tunnelling of the transferring electron for the Me(II) + e $\rightleftharpoons$ Me(I) charge-transfer step, across the adsorbed monolayer of the alcohol. This gradual passage takes place as the n-butanol bulk concentration is progressively decreased.

The dependence of the rate constant $k_{\theta=1}$, suitably corrected for diffuse-layer effects, upon the applied potential in the presence of the various normal aliphatic alcohols, is in qualitative agreement with an expression which accounts for the progressive increase in the compact-layer thickness with an increase in the length of the hydrocarbon chain.

Reference

1 R. Guidelli, M. L. Foresti and M. R. Moncelli, 'On the Inhibitory Effect of Neutral Organic Surfactants upon Simple Electrode Reactions at High Surface Coverages', *J. Electroanal. Chem.*, submitted.

Solvent Effect on the Electrode Reduction Mechanism of Phenyl Substituted Ethylenes

G. FARNIA, G. SANDONÁ, M. G. SEVERIN and E. VIANELLO

*Institute of Physical Chemistry, University of Padua, Padua, Italy*

This communication presents some preliminary results on the electrochemical reduction of tri- and tetraphenylethylenes in dimethylformamide (DMF) and hexamethylphosphoramide (HMPA), as part of a more extensive study on the correlation between kinetic and thermodynamic properties of radical anions and electrode reaction mechanism of the parent molecules.

Triphenylethylene (ϕ_3E)

Cyclic voltammetry of ϕ_3E in DMF with 0.1 M TBAP as supporting electrolyte shows two reversible reduction peaks, corresponding to the formation of the anion radical (R + e $\rightleftharpoons$R$^-$) and of the dianion (R$^-$ + e $\rightleftharpoons$ R$^=$), provided the solvent is carefully anhydrified, the last traces of water being eliminated by addition of alumina or molecular sieves directly into the cell. Traces of H_2O, in fact, cause the irreversibility of the second reduction peak (disappearance of the corresponding anodic peak) even at a scan rate of 400 V sec^{-1}. Further addition of H_2O affects also the reversibility of the first reduction peak, which increases in height giving eventually a single irreversible two-electron peak.

Macroscale electrolysis in the presence of H_2O yields quantitatively triphenylethane.

The anion radical R$^-$, stable in absence of proton donors, undergoes a relatively slow decay in the presence of H_2O at low temperatures ($-30\,°C$) according to the following mechanism:

$$2\ R^- \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}}\ R + R^= \tag{1}$$

$$R^- \xrightarrow[HS]{k_p} RH_2 \tag{2}$$
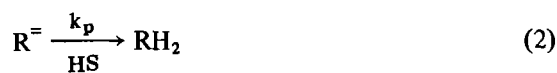
HS being the proton donor. Holding for R$^=$ the stationary state hypothesis the decay rate of R$^-$ results $-dC_{R^-}/dt = 2k'_p k_d C_{R^-}^2/(k'_p + k_{-d}C_R)$ with $k'_p = k_p C_{HS}$. This results in a second order reaction when $C_R \gg C_{R^-}$, so that C_R is practically constant. Values of k_d, k_{-d} and k'_p can thus be obtained, the equilibrium dismutation constant having been derived from the peak potential separation. On the other hand, for $k_{-d}C_R \ll k'_p$ one has $-dC_{R^-}/dt = 2k_d C_{R^-}^2$. These conditions, which can be realised at higher temperatures in voltammetric conditions,

correspond to an irreversible dismutation and allow an easy determination of k_d; the latter results 9×10^3 M^{-1} sec^{-1} at 40 °C with an activation energy of 10 kcal mol^{-1}, which compares very well with the value of 9×10^1 M^{-1} sec^{-1} obtained at −30 °C.

The voltammetric behaviour of ϕ_3E in HMPA is analogous to that in DMF, except for a higher peak separation, which is consistent with a lower tendency to ion pair formation in HMPA.

Tetraphenylethylene (ϕ_4E)

In HMPA, ϕ_4E presents two one-electron reversible reduction peaks, the second one being about 220 mV less negative than the corresponding one of ϕ_3E, in the same conditions. This is to be attributed to a higher delocalisation of the negative charge in the dianion of ϕ_4E.

In DMF only a single reversible two-electron wave can be observed, resulting from the overlapping of two one-electron processes, separated by about 60 mV. This lower peak separation is in agreement with the effect already observed for ϕ_3E, passing from HMPA to DMF, the latter solvent enhancing the formation of ion pairs.

Kinetic runs carried out in DMF at 0 °C have shown that the decay mechanism of the radical anion of ϕ_4E is the same already observed for ϕ_3E.

Further investigations are in progress with the aim of evaluating the role of the solvent and of the cations of the supporting electrolyte on the kinetic and electrochemical behaviour of the radical anions of substituted ethylenes.