Rate-determining electron-transfer reactions in highly aqueous alcohol–water mixtures. A quantitative analysis of solvent effects on the oxidation of 4-methoxyphenylacetate by potassium 12-tungstocobaltate(III)

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Kinetic solvent effects on the rate-determining outer-sphere electron-transfer reaction between 4-methoxyphenylacetate and potassium 12-tungstocobaltate(III) in highly aqueous alcohol–water mixtures are quantitatively analysed in terms of pairwise Gibbs energy parameters for interaction of the initial and transition state with the cosolvent.

Organic electron-transfer processes represent a field that has attracted intense attention in recent years, both from the theoretical and practical points of view.[1] Despite this growing interest, little is known about solvent effects on these reactions, apart from some studies of highly exergonic photoinduced electron-transfer processes.[2] Moreover, the Marcus dielectric continuum model[3] appears generally not satisfactory, and other more recent models are too detailed for general application.[4] Thus, it was considered of interest to apply the quantitative analysis of medium effects on reaction rates in highly aqueous binary mixtures, recently developed by one of us,[5,6] to electron-transfer processes. This approach, using Savage and Wood's theory for the analysis of the thermodynamics of solute–solute interactions in water,[7] combines thermodynamics with transition-state theory and leads to a quantitative description of solvent effects on reaction rates, as shown in eqn. (1).

$$\ln[k(m_c)/k(m_c = 0)] = (2/RT)G(C)m_c \qquad (1)$$

In this equation, $k(m_c = 0)$ is the rate constant for the reaction in the reference solvent (water) and $k(m_c)$ for the reaction in the mixed solvent containing m_c mol kg^{-1} of alcohol. $G(C)$ represents the difference in pairwise Gibbs energy for interaction of the initial and transition state of the reaction with the cosolvent. Thus, in dilute mixed aqueous solvents a plot of $\ln[k(m_c)/k(m_c = 0)]$ *vs.* the molality of the added cosolvent m_c is linear, with slope $2G(C)/RT$. Deviation from linearity occurs if higher-order interactions are involved. Recent applications of this theory include the analysis of solvent effects on hydrolysis reactions of activated amides in the presence of monomeric *n*-alkyl sulfates[8] and α-amino acids.[9]

The electron-transfer reaction of choice is the oxidation of 4-methoxyphenylacetic acid by potassium 12-tungstocobaltate(III) {$K_5[Co^{III}W_{12}O_{40}]$, indicated as $Co^{III}W$}, a well known outer-sphere electron-transfer reagent.[10,11] This reaction can be carried out in water and it has been shown that the electron transfer is the rate determining step, followed by a fast fragmentation of the radical cation to yield a benzyl radical. Both the 4-methoxyphenylacetic acid and its anion contribute to the reaction rate, with the anion reacting about thirty times faster than the neutral acid.[12] We have performed the oxidation reactions† in aqueous solution at pH 7.4 (KH_2PO_4–NaOH buffer) containing 0–3 mol% of alcohol (ROH; R = Me, Et, Pr^n, Bu^n, Bu^t, CF_3CH_2). Under these conditions the acid is completely dissociated and the removal of an electron from the aromatic ring leads to a radical zwitterion (Scheme 1).

Using an excess of substrate, good first-order kinetics are observed. Accordingly, $k_{-1}[Co^{II}W]$ can be neglected with respect to k_2 and the general rate expression for the mechanism in Scheme 1[10,11] reduces to a pseudo-first-order equation: $-d[Co^{III}W]/dt = k_{obs}[Co^{III}W]$ where $k_{obs} = 2k_1$ [substrate].

Plots of $\ln[k_1(m_c)/k_1(m_c = 0)]$ *vs.* m_c show an excellent linear behaviour in agreement with the theory, as shown in Fig. 1. All the alcohols induce a decrease of the rate and markedly large effects have been observed in the relatively small range of solvent compositions. This is particularly interesting if we

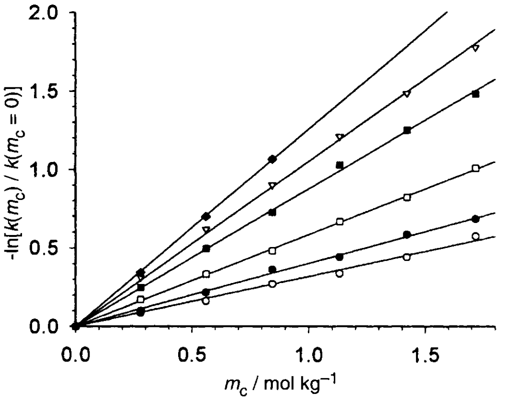
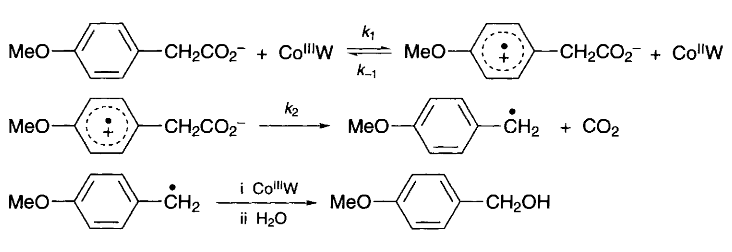


Fig. 1 Plots of $\ln[k_1(m_c)/k_1(m_c = 0)]$ *vs.* the molality of added alcohol for the reactions of 4-methoxyphenylacetate with $Co^{III}W$ in water (pH 7.4) at 30 °C: (○), methanol, (●), 2,2,2-trifluoroethanol, (□), ethanol, (■), propan-1-ol, (▽), 2-methylpropan-2-ol, (◆), butan-1-ol



Scheme 1

Table 1 G(C) values for the reaction of 4-methoxyphenylacetate with $\mathrm{Co^{III}W}$ in water (pH 7.4) containing 0–3 mol% of alcohol at 30 °C

Cosolvent	G(C)/J kg mol^{-2}
Methanol	−405
Ethanol	−732
Propan-1-ol	−1095
Butan-1-ol[a]	−1588
2,2,2-Trifluorethanol	−513
2-Methylpropan-2-ol	−1299

[a] 0–1.5 mol%.

consider that in outer-sphere electron-transfer reactions no chemical bonds are formed or broken and that the reactants on going to the transition state undergo only a change in charge distribution.[1] Apparently, this elementary reaction step in water responds markedly to the presence of low concentrations of additives that offer the possibility to form 1 : 1 encounter complexes. The G(C) values evaluated from the plots are listed in Table 1. It appears that in the series of alkan-1-ols, the G(C) values decrease linearly with increasing number of methylene groups in the alkyl chain. Thus, the apolar methylene group retards the reaction and the observed additivity presumably reflects a loss of hydrophobicity of the reactants (particularly the organic anion) during the activation process. Since it is well known that redox potentials are influenced by the nature of the solvent,[13] we are currently carrying out a cyclic voltammetric study to determine the effect of the alcohols and other cosolvents on the oxidation potential of $\mathrm{Co^{III}W}$;[14] these data can be helpful for a deeper understanding of the origin of the observed kinetic medium effects.

In summary, the theoretical model employed provides a basis for understanding solvent effects on electron-transfer reactions. It is shown that the electron-transfer process in water-rich media is accompanied by large changes in solvation as quantitatively expressed in the G(C) parameters. We contend that the present results are also of immediate relevance for understanding electron-transfer processes in biological systems.

Footnote

† Kinetics were carried out spectrophotometrically (Perkin-Elmer λ5 UV–VIS spectrophotometer) by monitoring the decrease of the absorption due to $\mathrm{Co^{III}W}$ at 390 nm. The concentration of $\mathrm{Co^{III}W}$ (1 mmol dm^{-3}) was 15 times smaller than the concentration of the substrate (15 mmol dm^{-3}); since two moles of $\mathrm{Co^{III}W}$ are needed to oxidize one mole of substrate, it is in fact a 30-fold excess of substrate. Pseudo-first-order rate constants were reproducible to within 2%.

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