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Oxidation of a cysteinato ligand by peroxodisulfate in a water-methanol solvent

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The rate of peroxodisulfate oxidation of a cysteinato ligand in a water-rich binary solvent decreases with methanol content due to the preferential solvation of $\{Co(en)_2[SCH_2CH(COO)NH_2]\}^+$.

The metal complexes of cysteine and its derivatives are often used to probe the ligand redox activity. The amino acid in a Co^{III} complex is coordinated *via* sulfur and nitrogen atoms while the carboxyl group remains free.[1] Oxidation by strong agents results in the formation of stable sulfenato and sulfinato complexes.[2–4] The presence of sulfenic acid forms of cysteine in active sites of peroxidases, oxidases and reductases is well-known.[5] The reaction with peroxodisulfate proceeds by the transfer of peroxidic oxygen to the thiolato sulfur atom. The degree of oxidation can be conveniently controlled because the further reaction of a sulfenato complex with the oxidant is significantly retarded.[4]

Solvent effects on reaction kinetics have been investigated in typically aqueous and nonaqueous solvents.[6,7] In protic solvents, the reaction rate passes through a maximum in a water-rich area. The molar fraction of the maximum agrees well with the reported breaking effect of a co-solvent on the hydrogen-bonded network of liquid water.[8] However, in aqueous acetone and acetonitrile, the reaction rate decreases despite of different solvent–solvent interactions involved.[8–10]

$\{Co(en)_2[SCH_2CH(COO)NH_2]\}ClO_4$ (en = ethylenediamine) was prepared according to a published procedure.[2] Elemental analysis [found (calc.) (%)]: C, 21.0 (21.2); H, 5.35 (5.30); N, 17.6 (17.6). UV-VIS spectroscopy: absorption bands at 283, 483 and 600 nm. Binary solvent mixtures were prepared from twice-distilled methanol and water immediately before the experiment. The pH of solution was adjusted with $HClO_4$ ($[H^+] = 10^{-3}$ mol dm^{-3}). Ionic strength was controlled by a tenfold excess of $Na_2S_2O_8$ (Merck). The concentration of the Co^{III} complex was 2.2×10^{-4} mol dm^{-3}. Kinetic measurements were carried out using a Hitachi 2001 spectrophotometer (371 nm; 1 cm cell; 298.2±0.1 K).

The reaction rate was $v = k[Co(en)_2SCH_2CH(COO)NH_2{}^+][S_2O_8^{2-}]$ regardless of the methanol content.

The second-order rate constant gradually decreases with the molar fraction of methanol reaching a constant value at $x_{MeOH} = 0.4$. This behaviour sharply contrasts to previous observations in aqueous ethylene glycol, propan-2-ol and *tert*-butanol (Figure 1). The obvious similarity with water–acetone and water–acetonitrile systems is surprising. Theoretical investigations on the structural aspects of MeOH–H_2O mixtures by the Kirkwood–Buff theory indicate a hydrophobic interaction effect.[11,12] Methanol from the solvation shell can interact electrostatically through the OH group along with the Me hydrophobic tail. Hydrophobic solute–solvent interactions might be essential in the co-solvent-rich region where the oxidation rate decreased by a factor of 0.3. The surface charge of the Co^{III} complex, the polarity of the thiolato ligand and the presence of any uncoordinated functional group are also important in the final solvent effect. The relative retardation of peroxodisulfate oxidation in aqueous methanol in the group of $[Co(en)_2SCH_2CH_2NH_2]^{2+}$,[13] $[Co(en)_2SCH_2COO]^+$,[14] $[Co(en)_2SCH_2CH(COO)NH_2]^+$ is highest in the present case.

The solubility of $[Co(en)_2SCH_2CH(COO)NH_2]ClO_4$ in aqueous methanol was determined by the ordinary method.[†] The Gibbs free energies of transfer (ΔG_t) for the Co^{III} complex cation from water to aqueous methanol, calculated from the solubilities,[‡] are given in Figure 2. Ionic contributions in $\Delta G_t([Co(en)_2SCH_2CH(COO)NH_2]ClO_4)$ were evaluated by the TPTB convention.[§] Work related to cavity formation in the solvent network, proportional to the molar volume of the cation in a vacuum, is nearly the same for all of the three thiolato complexes and the difference in ΔG_t values is mainly due to solvation. The preferential solvation of $[Co(en)_2SCH_2CH(COO)NH_2]^+$ in a water-rich binary mixture is clear. This result is consistent with the expected balance between the hydrophobic and hydrophilic properties of complex surfaces. A recent DFT-based molecular dynamics study reveals that the local structural and short-time dynamic properties of water molecules remain almost unchained in the presence of methanol in dilute solutions.[17] The free ionised carboxyl group participates in a hydrogen-bonded solvent network while ethylenediamine ligands are probably solvated by the hydrophobic Me tail of the methanol molecule.

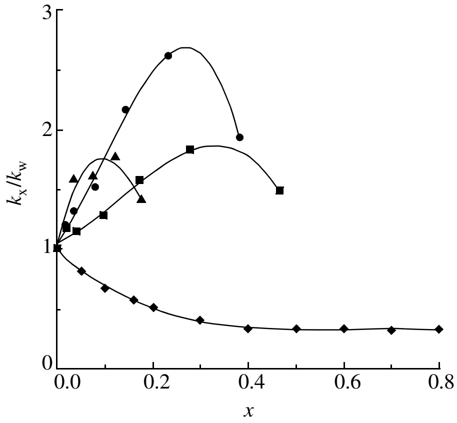


Figure 1 Rate constants for peroxodisulfate oxidation of cysteinatobis(ethylenediamine)cobalt(III) at 298.2 K in aqueous methanol (◆), water–ethylene glycol (▲), water–isopropanol (■) and water–*tert*-butanol (●), k_w = = (48.2±1.1) dm^3 mol^{-1} s^{-1}.

In agreement with the transition state theory, the solvent influences both transition and initial states of the reaction.[18] Gibbs free energies of transfer from water to the binary solvent[¶] are compared in Figure 2. The work of cavity formation inside the solvent network is only slightly larger for the initial state. The transition state is destabilised by transfer from water to the binary solvent. Peroxodisulfate, preferentially solvated by water,[19] makes the main contribution to the positive trend of ΔG_t(IS). The expected transition state for the reaction is given in Scheme 1.

[†] Saturated solutions were obtained by shaking appropriate solvent mixtures with a large excess of the solute for 6–8 h. The concentrations of the salt were determined spectrophotometrically (Hitachi 2001).

[‡] Gibbs free energies of transfer were calculated as $\Delta G_t = 2RT\ln(S_w/S_x)$, where S_x and S_w are the solubilities of $[Co(en)_2SCH_2CH(COO)NH_2]ClO_4$ in the mixed solvent and water, respectively. The Gibbs transfer functions of the salt were determined to within 0.3 kJ mol^{-1}.

[§] TPTB = tetraphenylphosphonium tetraphenylborate, Ph_4PBPh_4. The assumption equalises ionic contributions in $\Delta G_t(Ph_4PBPh_4)$, *i.e.*, $\Delta G_t(Ph_4P^+) = \Delta G_t(Ph_4B^-)$.[15,16]

[¶] The standard Gibbs transfer functions for the transition state were calculated as $\Delta G_t(TS) = \Delta G_t(IS) + \Delta G_t^{\neq}$, where $\Delta G_t(IS) = \Delta G_t([Co(en)_2SCH_2CH(COO)NH_2]^+) + \Delta G_t(S_2O_8^{2-})$ and $\Delta G_t^{\neq} = RT\ln(k_w/k_x)$, k_w and k_x are the rate constants of peroxodisulfate oxidation in water and aqueous methanol, respectively.

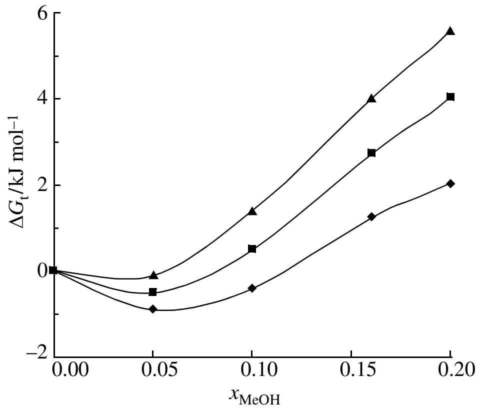
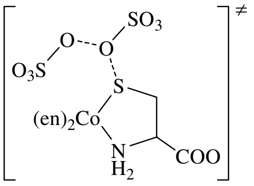


Figure 2 Gibbs free energies of transfer from water to aqueous methanol for cysteinatobis(ethylenediamine)cobalt(III) cation (◆), initial state (■) and transition state (▲) of the reaction at 298.15 K.

It holds a negative charge and has a larger molar volume than $[Co(en)_2SCH_2CH(COO)NH_2]^+$.



Scheme 1

In conclusion, the preferential solvation of solutes can be an important issue in an overall solvent effect on the rate of chemical reaction. A solvation shell around the complex cation is rearranged when peroxodisulfate approaches the thiolato sulfur atom.

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