Kinetics of Oxidation of Ferrocene by Tris-1,10-phenanthrolinecobalt(III) in t-Butyl Alcohol—Water and Acetone—Water Mixtures

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Abstract

Rate constants and activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) are reported for the oxidation of ferrocene by the tris-1,10-phenanthrolinecobalt(III) cation in t-butyl alcohol—water and in acetone—water solvent mixtures. Solvent effects on reactivity trends for these systems, for this same reaction in methanol—water mixtures, and for cobalt(II)-catalysed racemisation of $Co(phen)_3^{3+}$ in t-butyl alcohol—water solvent mixtures are analysed into initial state and transition state contributions. The dependences of solubilities on solvent composition for ferrocene and for $[Co(phen)_3](ClO_4)_3$ in methanol—, t-butyl alcohol—, and acetone—water mixtures are also reported; these results are needed in order to establish solvent effects on the initial states of the reactions studied.

Introduction

Previous kinetic studies of the oxidation of ferrocene by the tris-1,10-phenanthrolinecobalt(III) cation, $Co(phen)_3^{3+}$, in alcohol—water mixtures have shown that the Marcus cross-relations apply with considerable precision [1], and that pronounced solvent effects on reactivity cannot be explained by the simple continuum dielectric approach [2]. In many ways this is a very suitable reaction for probing solvation effects on redox processes. As both reactants are extremely inert to substitution the mechanism is assuredly outer-sphere, and as one reactant is uncharged there are no problems of ion-pairing between the reactants. As the Co-$(phen)_3^{3+}$ cation is large, there should also be negligible ion-pairing with large counterions such as perchlorate, introduced of necessity to maintain electrical neutrality. There are no solvent molecules in the primary coordination shell of the metal ion in either reactant, so one has only to consider secondary solvation shells. The one drawback is the very low solubility of ferrocene in water, which makes solubility measurements difficult, kinetic measurements impossible.

In the previous study [2] of solvent effects on reactivity for this reaction, which were investigated in methanol—, ethanol—, n-propanol—, and iso-propanol—water mixtures, the importance of solvent structural effects was reflected in two ways. Firstly, the effect of the alcohol on the rate constant as its mole fraction increased was greatest for the propanols, n-PrOH > i-PrOH > EtOH > MeOH, the order of decreasing effect on water structure. Secondly, there were shallow minima in plots of $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ against solvent composition for cosolvents iso- and n-propanol (though not for ethanol or methanol cosolvents) at alcohol mole fractions which corresponded to the maximum effect of alcohol on solvent structure. In the present paper we explore further the kinetics of this ferrocene—$Co(phen)_3^{3+}$ reaction in binary aqueous solvent mixtures, extending the range of cosolvents to include t-butyl alcohol and acetone. We also analyse solvent effects on rate constants into initial state and transition state contributions by use of appropriate ancillary thermodynamic data, viz. transfer chemical potentials from solubilities. We also carry out an initial state—transition state analysis of a closely related reaction, cobalt(II)-catalysed racemisation of $Co(phen)_3^{3+}$, in t-butyl alcohol—water mixtures.

Experimental

Preparations and kinetic runs were carried out as described earlier [2]. Solubilities were determined by agitating an excess of ferrocene or of $Co(phen)_3(ClO_4)_3$ with the appropriate solvent

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mixture in a darkened, thermostatted vessel. Concentrations of saturated solutions were monitored on a Unicam SP8-100 spectrophotometer, after appropriate dilution. Concentrations of ferrocene were measured at 440 nm ($\epsilon = 9.10$) [3], of Co-(phen)$_3{}^{3+}$ at 269 nm ($\epsilon = 43550$) [4].

Results

Rate constants and activation parameters for oxidation of ferrocene by Co(phen)$_3{}^{3+}$ in aqueous *t*-butyl alcohol and in aqueous acetone are given in Table I. Solubilities of ferrocene and of Co(phen)$_3$-(ClO$_4$)$_3$ in these series of solvent mixtures and in aqueous methanol, in all cases at 298.2 K, are reported in Table II. This Table also gives transfer chemical potentials, from water, for ferrocene and the cobalt(III) salt. Values of transfer chemical potentials for perchlorate, based on the single ion assumption Ph$_4$As$^+$(Ph$_4$P$^+$) $\equiv$ BPh$_4{}^-$, are available for aqueous methanol [5b], *t*-butyl alcohol [6], and acetone [7], so we have derived transfer chemical potentials for the cobalt(III) complex cation, $\delta_m\mu^\ominus$(Co(phen)$_3{}^{3+}$) (Table II).

Discussion

Figure 1 puts the solvent effects on reactivity for aqueous *t*-butyl alcohol and for aqueous acetone

into context with the earlier results [2]. As expected, *t*-butyl alcohol has the maximum effect on reactivity—at lowest mole fraction. Acetone has an effect intermediate between the two propanols. Again, *t*-butyl alcohol has the maximum effect on activation parameters, with $\Delta H^{\ddagger}$ only about 20 kJ mol^{-1} in low mole fractions of this alcohol—contrast minima of 30 to 40 kJ mol^{-1} for other alcohol—water mixtures [2]. Extrapolation of mixed aqueous $\Delta H^{\ddagger}$ values suggests an $\Delta H^{\ddagger}$ of about 45 kJ mol^{-1} in water, so *t*-butyl alcohol has a very large effect on $\Delta H^{\ddagger}$ (and on $T\Delta S^{\ddagger}$) in the composition range corresponding to its maximum structural effect. There is a less well-defined minimum for $\Delta H^{\ddagger}$ in acetone—water mixtures, but the rather shallow minimum corresponds to that found for n-propanol—water mixtures.

Table II shows that there are shallow extrema in solubilities and transfer chemical potentials at low mole fractions of organic cosolvents in several of the systems examined here, and indeed also for Fe(phen)$_3$(ClO$_4$)$_2$ in *t*-butyl alcohol—water mixtures (*cf.* below). Marked extrema in plots of enthalpies and entropies of solvation against mole fraction in alcohol—water mixtures have often been reported. Examples include PPh$_4$BPh$_4$ in methanol—water [5], lanthanide trihalides in alcohol—water [8], and Fe(phen)$_3$Cl$_2$ in methanol—water [9]. It is much rarer to find such extrema for solubilities and transfer chemical potentials.

TABLE I. Second-Order Rate Constants and Activation Enthalpies and Entropies for Oxidation of Ferrocene by the Co(phen)$_3{}^{3+}$ Cation in Binary Aqueous Solvent Mixtures[a].

	$10^3 k_2$ (M^{-1} s^{-1})			$\Delta H^{\ddagger}$ [b]	$\Delta S^{\ddagger}$ [c]
	10 °C	25 °C	40 °C	(kJ mol^{-1})	(J K^{-1} mol^{-1})
t-Butyl alcohol					
15	31	49	71	18	−94
20	25	42	64	21	−85
23	20	29	44	17	−103
27	8.6	14	23	21	−93
30	4.8	8.6	16	28	−78
40	1.5	3.5	6.0	32	−70
50	0.75	1.8	4.2	40	−49
60	0.58	1.4	3.1	39	−54
Acetone					
15	14	30	62	34	−46
20	13	25	50	30	−60
30	8.5	18	44	38	−36
40	5.1	11	22	33	−57
50	2.6	5.9	13	36	−52
60	1.2	3.1	7.1	42	−38
70	0.77	1.9	4.9	43	−37
80	0.41	1.4	3.2	48	−24

[a]Mixed solvent compositions expressed in volume percentages before mixing. [b]Standard deviations on enthalpies ±3 to 4 kJ mol^{-1}. [c]Standard deviations on entropies ±10 to 14 J K^{-1} mol^{-1}.

TABLE II. Absorbances of Saturated Solutions of Ferrocene (fc) and of Co(phen)$_3$(ClO$_4$)$_3$[a], and Derived Transfer Chemical Potentials (for Transfer from Water), for Binary Aqueous Solvent Mixtures at 298.2 K (Transfer Chemical Potentials are in kJ mol^{-1} on the Molar Scale).

Methanol (vol. %)	0	15	30	50	70	90
Abs fc	0.026	0.014	0.025	0.102	0.628	3.06
∴ $\delta_m\mu^\ominus$(fc)		+1.5	+0.1	−3.4	−7.9	−11.8
10^{-3} Abs Co(phen)$_3$(ClO$_4$)$_3$	0.188	0.149	0.259	0.512	0.585	0.624
∴ $\delta_m\mu^\ominus$(Co(phen)$_3$(ClO$_4$)$_3$)		+2.3	−3.2	−9.9	−11.3	−11.9
$3\delta_m\mu^\ominus$(ClO$_4^-$)[b]		+0.1	−0.1	0	+2.4	+12.0
∴ $\delta_m\mu^\ominus$(Co(phen)$_3^{3+}$)		+2.2	−3.1	−9.9	−13.7	−23.9

t-Butyl alcohol (vol. %)	0	10	15	20	30	40
Abs fc	0.026	0.047	0.041	0.014	0.144	0.431
∴ $\delta_m\mu^\ominus$(fc)		−1.5	−1.1	+1.5	−4.2	−7.0
10^{-3} Abs Co(phen)$_3$(ClO$_4$)$_3$	0.188	0.159	0.225	0.263	0.329	0.364
∴ $\delta_m\mu^\ominus$(Co(phen)$_3$(ClO$_4$)$_3$)		+1.7	−1.8	−3.3	−5.6	−6.5
$\delta_m\mu$(KClO$_4$)[c]		+1.4	+1.9	+2.4	+3.2	+4.0
∴ $3\delta_m\mu^\ominus$(ClO$_4^-$)[d]		−2.3	−0.5	+1.4	+6.1	+7.1
∴ $\delta_m\mu^\ominus$(Co(phen)$_3^{3+}$)		+3.9	−1.3	−4.7	−11.7	−13.6

Acetone (vol. %)	0	20	40	60	80
Abs fc	0.026	0.016	0.138	0.857	2.66
∴ $\delta_m\mu^\ominus$(fc)		+1.2	−4.1	−8.7	−11.5
10^{-3} Abs (Co(phen)$_3$(ClO$_4$)$_3$)	0.188	0.157	0.267	0.396	0.506
∴ $\delta_m\mu^\ominus$(Co(phen)$_3$(ClO$_4$)$_3$)		+1.8	−3.5	−7.4	−9.8
$3\delta_m\mu^\ominus$(ClO$_4^-$)[e]		+6.8	+11.2	+14.1	+17.3
∴ $\delta_m\mu^\ominus$(Co(phen)$_3^{3+}$)		−5.0	−14.7	−21.5	−27.1

[a]Wavelengths of maximum absorption and molar extinction coefficients are given in the text.   [b]From ref. [5b].   [c]Potassium perchlorate solubilities from ref. [5a].   [d]From ref. [6].   [e]From ref. [7].
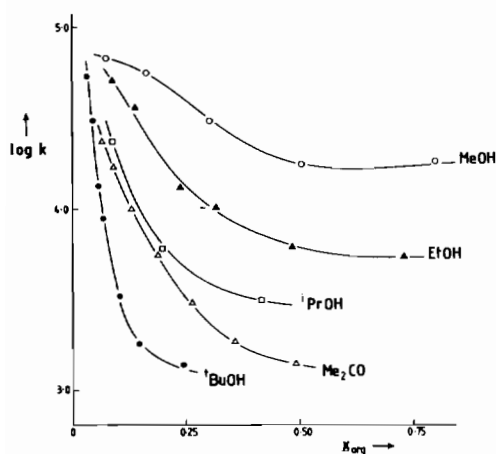

Fig. 1. Logarithms of rate constants for the ferrocene + Co-(phen)$_3^{3+}$ reaction as a function of mole fraction of organic cosolvent.

Their occurrence here shows that $\Delta H/T\Delta S$ compensation is less closely balanced than usual. These extrema do not appear in the kinetic analysis below, since the very low solubility of ferrocene in water forces us to do our transfer calculations with respect to a mixed solvent reference, which generally is beyond the extremum. While on the subject of transfer chemical potentials, it is worth noting that Co(phen)$_3^{3+}$ is more stabilised than is ferrocene by increasing the proportion of organic cosolvent, despite its 3+ charge. Clearly the electrostatic effect of this charge, attenuated as it is by the size of the complex, is masked by the greater hydrophobicity of three phenanthroline peripheries than of two considerably smaller cyclopentadienyl ligands.

Rate constants and activation parameters are composite quantities, representing differences between initial and transition states. Therefore to gain further understanding of the effects of solvents on kinetic parameters it is desirable to analyse them into initial state and transition state components, with the use of appropriate ancillary thermodynamic data for the former [10]. Such analyses have been carried out for a variety of organic and inorganic substitution reactions [11]. They are also of considerable interest in relation to redox reactions, particularly formation of the encounter complex [12], which is formally analogous to formation of an S_{N^2} or S_{E^2} transition state (*cf.* Co(NH$_3$)$_5$Cl^{2+} + Cr^{2+} and Co(NH$_3$)$_5$Cl^{2+} + Hg^{2+}).

Initial state–transition state analyses of, for example, inner-sphere reduction of $Co(NH_3)_5Cl^{2+}$ by $Fe^{2+}aq$. [13] and outer-sphere oxidations of iodide or catechol by $IrCl_6^{2-}$ [14] or of iron(II) complexes by peroxodisulphate [15, 16] show the importance of solvation changes in determining reactivity trends for these redox reactions. Our present systems extend this range somewhat, in that both reactants are markedly hydrophobic. We are restricted to solvent mixtures containing methanol, *t*-butyl alcohol, or acetone, since only in these series do we have satisfactory transfer chemical potentials for the perchlorate anion on the $Ph_4P^+(Ph_4As^+) \equiv BPh_4^-$ single ion assumption. Our initial state–transition state analyses are detailed in Table III, and the results depicted in Figs. 2–4 (all of which have the same x and y scales to facilitate comparisons). In all three cases, relatively small decreases in rate constants as the proportion of organic co-solvent increases can in general be ascribed to the small differences between large stabilisations of initial and transition states, with the former slightly the larger. Differences between solvent mixture compositions examined for the three cosolvents make intercomparisons slightly awkward, but the mole fraction dependences compared in Fig. 5 show that the relative effects of cosolvents on initial state stabilisation are in the expected order:
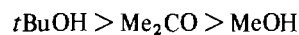
$$tBuOH > Me_2CO > MeOH$$

TABLE III. Initial State-Transition State Analysis of Reactivity Trends for $Co(phen)_3^{3+}$ Oxidation of Ferrocene in Binary Aqueous Solvent Mixtures at 298.2 K (Transfer Chemical Potentials are in kJ mol^{-1} on the Molar Scale and are for Transfer from 15% Methanol, 15% *t*-Butyl Alcohol, and 20% Acetone Respectively).

Methanol (vol. %)	30	50	70	90
$\delta_m\mu^{\ominus}(fc)$	−1.4	−4.9	−9.4	−13.3
$\delta_m\mu^{\ominus}(Co(phen)_3^{3+})$	−5.3	−12.1	−15.9	−26.1
$\therefore \delta_m\mu^{\ominus}(is)$	−6.7	−17.0	−25.3	−39.4
$\delta_m\Delta G^{\ddagger}$	+1.0	+1.8	+3.2	+2.9
$\therefore \delta_m\mu^{\ddagger}$	−5.7	−15.2	−22.1	−36.5

t-Butyl alcohol (vol. %)	20	30	40
$\delta_m\mu^{\ominus}(fc)$	+2.6	−3.1	−5.9
$\delta_m\mu^{\ominus}(Co(phen)_3^{3+})$	−3.4	−10.4	−12.3
$\therefore \delta_m\mu^{\ominus}(is)$	−0.8	−13.5	−18.2
$\delta_m\Delta G^{\ddagger}$	+0.4	+4.3	+6.5
$\therefore \delta_m\mu^{\ddagger}$	−0.4	−9.2	−11.7

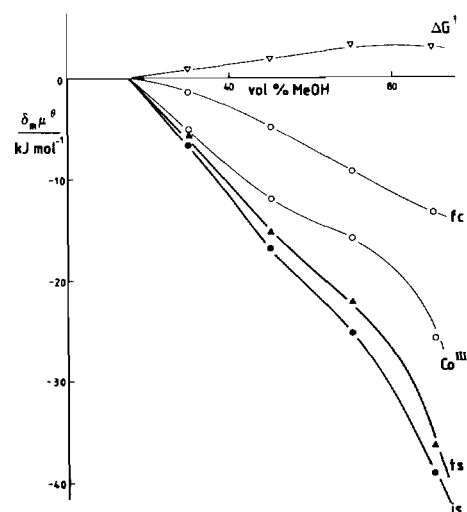| Acetone (vol. %)	40	60	80
$\delta_m\mu^{\ominus}(fc)$	−5.3	−9.9	−12.7
$\delta_m\mu^{\ominus}(Co(phen)_3^{3+})$	−9.7	−16.5	−22.1
$\therefore \delta_m\mu^{\ominus}(is)$	−15.0	−26.4	−34.8
$\delta_m\Delta G^{\ddagger}$	+2.0	+5.2	+7.1
$\therefore \delta_m\mu^{\ddagger}$	−13.0	−21.2	−27.7

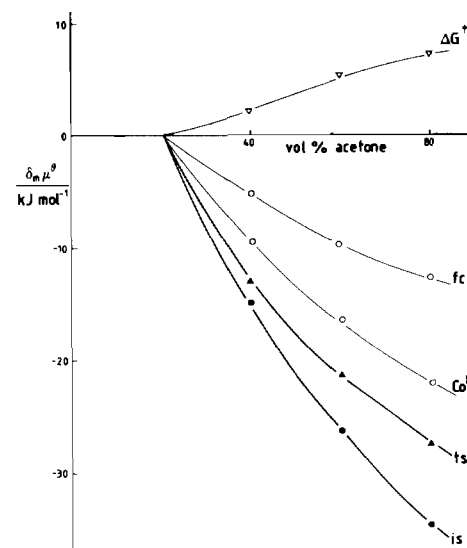Fig. 2. Initial state-transition state analysis of the ferrocene + $Co(phen)_3^{3+}$ reaction in methanol–water mixtures.

Fig. 3. Initial state-transition state analysis of the ferrocene + $Co(phen)_3^{3+}$ reaction in acetone–water mixtures.

Differences are significantly more marked on the initial state than on the transition state.

Solvent effects on reactivity for the closely related reaction of $Co(phen)_3^{2+}$-catalysed racemisation of $(+)$-$Co(phen)_3^{3+}$ in *t*-butyl alcohol–water mixtures have recently been established [17]. By taking $Fe(phen)_3^{2+}$ as a model for $Co(phen)_3^{2+}$, we have carried out an initial state–transition state analysis on this catalysed racemisation (Table IV and Fig. 4). The pattern is very similar to the ferrocene/Co-$(phen)_3^{3+}$ reaction, with the main differences being

TABLE IV. Initial State-Transition State Analysis of Reactivity Trends for Co(phen)$_3^{2+}$-catalysed Racemisation of Co(phen)$_3^{3+}$ in Aqueous *t*-Butyl Alcohol Mixtures at 298.2 K (Transfer Chemical Potentials are in kJ mol^{-1} on the Molar Scale, from Water).

t-Butyl alcohol (vol. %)	0	10	20	30	45
ln(k/M^{-1} s^{-1})[a]	3.84	3.22	2.00	1.63	1.25
∴ $\delta_m \Delta G^{\ddagger}$		+1.5	+4.6	+5.5	+6.4
$\delta_m \mu^{\ominus}$(Co(phen)$_3^{3+}$)[b]		+3.9	−4.7	−11.7	(−15)[c]
$\delta_m \mu^{\ominus}$(Co(phen)$_3^{2+}$)[d]		−1.5	−8.3	−15.6	−16.7
∴ $\delta_m \mu^{\ominus}$(is)		+2.4	−13.0	−27.3	(−32)
∴ $\delta_m \mu^{\ddagger}$		+3.9	−8.4	−21.8	(−26)

[a]From Fig. 2 of ref. [17]. [b]From Table II. [c]Extrapolated. [d]Assumes $\delta_m \mu^{\ominus}$(Co(phen)$_3^{2+}$) = $\delta_m \mu^{\ominus}$(Fe(phen)$_3^{2+}$); values for the latter from solubilities of its perchlorate (J. Burgess and C. D. Hubbard, unpublished observations, and $\delta_m \mu^{\ominus}$(ClO$_4^-$) from ref. [6]).
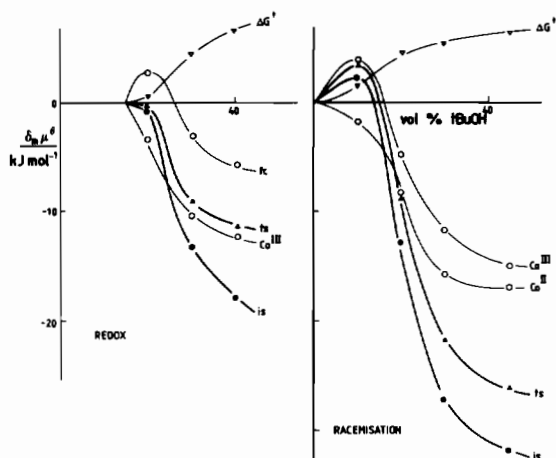

Fig. 4. Initial state-transition state analyses of the ferrocene + Co(phen)$_3^{3+}$ reaction and of Co(phen)$_3^{2+}$-catalysed racemisation of Co(phen)$_3^{3+}$ in *t*-butyl alcohol–water mixtures.
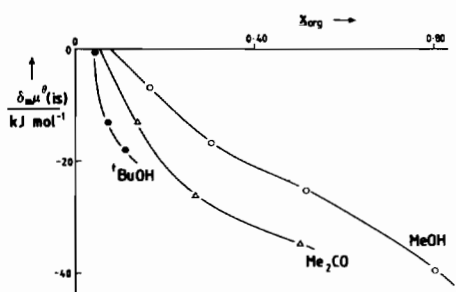

Fig. 5. Effect of solvent composition on transfer chemical potentials for the initial state of the ferrocene + Co(phen)$_3^{3+}$ reaction.

the greater effect of solvent composition on Fe(phen)$_3^{2+}$/Co(phen)$_3^{2+}$ than on ferrocene. It is interesting that the 2+ model cation is slightly more stabilised than its 3+ analogue, which difference is consistent with a limited role of electrostatics (*cf.* above).

Acknowledgements

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