The oxidation of ligands by Co^{III}_{aq} and $Co^{III}OH^-_{aq}$ ions in aqueous perchlorate media — an overall isokinetic relationship and its mechanistic interpretation

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Abstract

The variation of the enthalpy of activation, ΔH^*, with the entropy of activation, ΔS^*, has been investigated for the oxidation of a wide range of substrates by both Co^{III}_{aq} and $Co^{III}OH^-_{aq}$. It is found that, for all substrates, excluding possibly propan-2-ol, benzene and formic acid, irrespective of differing mechanistic detail, such as the detection or not of intermediate complexes, the variation of ΔH^* with ΔS^* occurs on the same linear plot for both oxidants in aqueous perchlorate media. A unifying mechanism is discussed, involving differential effects of solvation on the initial and transition states, with compensating contributions to ΔH^* and ΔS^*. It is suggested that the above possible exceptions may modify the solvent structure of the aqueous perchlorate media sufficiently to produce a different variation of ΔH^* with ΔS^*, similar to the operation of the Barclay–Butler relationship for ΔH° and ΔS° for gas solubilities in solvents with differing structures.

Davies has attempted to classify oxidisable ligands reacting with $Co^{III}OH^-_{aq}$ ions into two categories: either no penetration of the aqua-sheath continuous with Co^{III}, or, the replacement of an H_2O in the contiguous aqua-sheath is the rate-determining process [1]. In support of this, the enthalpy ΔH^* and the entropy ΔS^* of activation of a genuine rate-determining substitution by chloride ions into the inner coordination sphere of $Co^{III}OH^-_{aq}$ has been compared with a linear variation of ΔH^* with ΔS^* for the oxidation of selected ligands by $Co^{III}OH^-_{aq}$ [1]. Unfortunately, the selection of ΔH^* and ΔS^* used for the redox reactions with $Co^{III}OH^-_{aq}$ contains only a few of the collected data available [2] together with some new data for carboxylic acids and amino acids [1]. As plots of ΔH^* against ΔS^* can be used as a criterion for the unity of mechanism in a series of related reactions [3], it is instructive to compare plots of ΔH^* against ΔS^* for the oxidation of *all* ligands [2] by $Co^{III}OH^-_{aq}$ with ΔH^* and ΔS^* for the substitution of Cl^- into $Co^{III}OH^-_{aq}$ and also to compare a plot of ΔH^* against ΔS^* for the oxidation of all ligands by Co^{III}_{aq} [2] with ΔH^* and ΔS^* for the substitution of Cl^- into Co^{III}_{aq}.

Overall values for ΔH^* and ΔS^* have been used for these oxidations, as before [2], except that errors in Table 5 of ref. 2 for HN_3, H_2O_2 and benzene

have been corrected by reference back to the original data. The observed rate constant k_{obs} usually varies with $[H^+]$ according to eqn. (1).

$$k_{obs} = a + b[H^+]^{-1} \qquad (1)$$

ΔH^*_a and ΔS^*_a from the temperature variation of a include a contribution for the oxidation of the substrate by Co^{III}_{aq} and also a contribution from any rapid preliminary complexation of Co^{III}_{aq} with the ligand. ΔH^*_b and ΔS^*_b from the temperature variation of b all include a contribution for the oxidation of the substrate by $Co^{III}OH^-_{aq}$ and ΔH°_h and ΔS°_h for the hydrolysis (2)

$$Co^{III}_{aq} \rightleftharpoons Co^{III}OH^-_{aq} + H^+_{aq} \qquad (2)$$
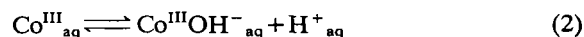
together with a contribution from any preliminary rapid complexation between $Co^{III}OH^-_{aq}$ and the ligand.

Figure 1 shows a plot of ΔH^*_b against ΔS^*_b using the collected data [2] (as corrected) for the oxidation of all ligands by $Co^{III}OH^-$ with the addition of the new data [1] of Davies for the oxidation of carboxylic acids and amino acids (circles and triangles) and the data for the substitution of Cl^- into $Co^{III}OH^-_{aq}$ (square) [6]. Before discussing this plot, some comments are necessary about the data. Firstly, for the oxidation of H_2O_2, the data used are those where
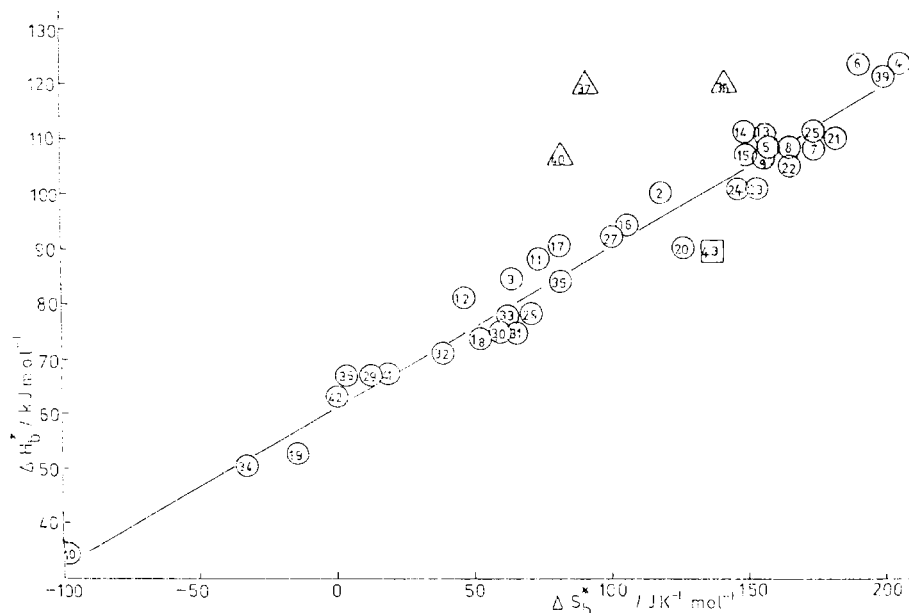
Fig. 1. Plot of the overall enthalpy of activation ΔH_b^* against the overall entropy of activation ΔS_b^* for the oxidation of substrates ($\odot$ and $\triangle$) by $Co^{III}OH^-$ and for the substitution of Cl^- into $Co^{III}OH^-$ ($\square$). Substrate ligands are as follows: 1, propionic acid [1]; 2, oxalic acid [4]; 3, malonic acid [1]; 4, 2-ethylmalonic acid [1]; 5, glycium cation [1]; 6, α-alanium cation [1]; 7, β-alanium cation [1]; 8, $HC_2O_4^-$ [4]; 9, SCN^- [5]; 10, H_2O_2 [7]; 11, Br^- at $I = 2.00$ mol dm^{-3} [10]; 12, Br^- at $I = 0.5$ mol dm^{-3} [9]; 13, Br^- at $I = 3.00$ mol dm^{-3} [5]; 14, HN_3 at low $[HN_3]/[Co^{III}]$ [11]; 15, H_2O_2 at $[Co^{III}] < 7 \times 10^{-5}$ mol dm^{-3} [8]; 16, ClO_2 [13]; 17, HNO_2 [5]; 18, catechol or adrenalin [14]; 19, I^- at $I = 2.00$ mol dm^{-3} [2]; 20, I^- at $I = 3.00$ mol dm^{-3} [5]; 21, $(NH_2)_2CSH^+$ [15]; 22, $(MeNH)_2CSH^+$ [15]; 23, $(MeNH)(NH_2)CSH^+$ [15]; 24, $(EtNH)_2CSH^+$ [15]; 25, $(CH_2NH_2)_2CSH^+$ [15]; 26, hydroquinone [5]; 27, hydroquinone [16]/ 29, 1-MeO-4-HO-benzene [16]; 30, 3-Me-1,2-diHO-benzene [14]; 31, 4-Me-1,2-diHO-benzene [14]; 32, 2,3-diHO-benzoic acid [14]; 33, 3,4-diHO-benzoic acid [14]; 34, 3,4-diHO-benzonitrile [14]; 35, 2-Me-1,4-diHO-benzene [16]; 36, 1-EtO-4-HO-benzene [16]; 37, benzene [18]; 38, propan-2-ol [19]; 39, molecular bromine [20]; 40, $HCOO^-$ [21]; 41, 2-Cl-1,4-diHO-benzene [16]; 42, 1,4-diHO-benzene-2-sulfonic acid [16]; 43, Cl^- (substitution) [22, 25].

it is known that a source of inhibitor-free H_2O_2 was used: although not specified, it appears likely that the data of Davies and Watkins [5] were obtained using a source of H_2O_2 containing inhibitor, which, as designed, will influence rates of reactions involving free radicals as intermediates. Secondly, the data of Jijee and Santappa [23] for hydroxylamine and hydrazine have not been used, as sulfate ions were present in these oxidations in sufficient quantity to influence considerably the rates of the reactions of aquacobalt(III) ions in aqueous perchlorate media [8, 24]. Thirdly, also included are $\Delta H_b^{*\prime}$ and $\Delta S_b^{*\prime}$ for the oxidation of Br_2 by hydrolysed Co^{III}_{aq} where eqn. (3) is obeyed [20].

$$k_{obs} = b'[H^+]^{-2} \qquad (3)$$

For the thioureas, the final values given by the experimentalists involved are used [15].

It seems clear from Fig. 1 that all the circles lie on the linear plot of ΔH_b^* against ΔS_b^*. Although the square for the substitution of chloride ions,

calculated from ΔH^* and ΔS^* for the rate constants determined for eqn. (4) added to ΔH_h° and ΔS_h°

$$Co^{III}OH^-_{aq} + Cl^-_{aq} \longrightarrow Co^{III}OH^-Cl^- \qquad (4)$$
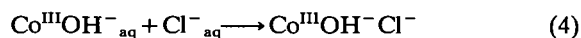
found [25] for the hydrolysis (2), appears to deviate a little from this line, the deviation is no greater than that found for the oxidation of iodide ions using the data of Davies and Watkins [5] obtained at $[ClO_4^-] = 3.00$ mol dm^{-3}. The triangle for the oxidation of benzene, must be considered a deviant from the line drawn through the circles, and those for the oxidations of formate ions and propan-2-ol may also be deviants.

Figure 2 shows a similar plot of ΔH_a^* against ΔS_a^* for the oxidation of the same substrates by unhydrolysed Co^{III}_{aq}. Again, all the circles lie on a linear plot, which appears also to include the square for the substitution of Cl^- (taken directly from ΔH^* and ΔS^*) [22]. Here, as before, although the triangle for propan-2-ol lies within the ambit of the line, the triangles for the oxidation of both benzene and formic acid seem to be deviants.
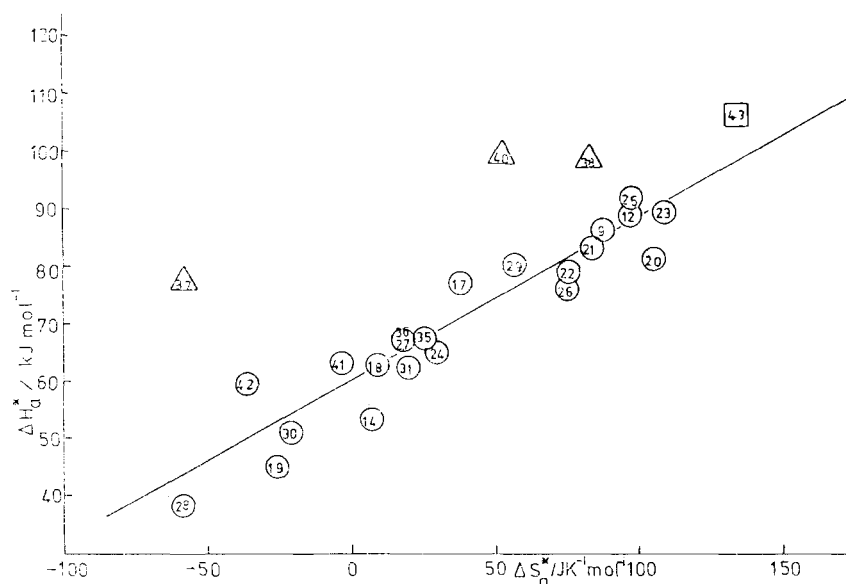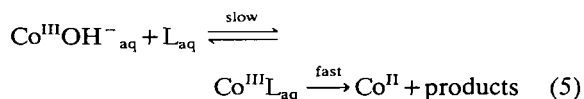
Fig. 2. Plot of the overall enthalpy of activation ΔH_a^* against the overall entropy of activation ΔS_a^* for the oxidation of substrates (○) and (△) by Co^{III}_{aq} and for the substitution of Cl^- into Co^{III}_{aq} (□). Assignment of ligands as in Fig. 1 except for: 14, HN_3 at high $[HN_3]/[Co^{III}]$ [12]; 28, hydroquinone [17]; 40, HCOOH [21].

A comparison of Figs. 1 and 2 suggests that all the circles for ΔH_a^* and ΔS_a^* and for ΔH_b^* and ΔS_b^* may lie on the same linear plot and this is confirmed by the slopes of these plots. The slope of the line in Fig. 1 is 295 K and that of the line in Fig. 2 is 281 K. The squares for the substitution of chloride ions into $Co^{III}OH^-_{aq}$ and Co^{III}_{aq} agree with these linear plots in Figs. 1 and 2, at least as good as the circles for the oxidation of iodide ions [2, 5] or of hydroquinone [17]. Davies has suggested [1] that the linearity of a similar plot to Fig. 1, using a more limited set of data, showed that all such oxidations on his plot must conform to a rate-determining subtitution, as in eqn. (5).

$$Co^{III}OH^-_{aq} + L_{aq} \xrightarrow{\text{slow}}$$

$$Co^{III}L_{aq} \xrightarrow{\text{fast}} Co^{II} + \text{products} \quad (5)$$

However, Davies also states [1] that the oxidations of I^- and of hydroquinone proceed without preliminary substitution of the substrate into the inner sphere of $Co^{III}OH^-_{aq}$ and excludes the data for these two reactions from his plot. Nevertheless, Figs. 1 and 2 show that ΔH^* and ΔS^* for both these oxidations do lie on the linear plots, with agreement at least as good as that found for the substitution of Cl^-. Moreover, the observation [26] of rapid transient colour changes at the high ionic strength of 8.00 mol dm^{-3} when I^- is mixed with solutions

containing Co^{III}_{aq} and $Co^{III}OH^-_{aq}$ in aqueous perchlorate media suggests that intermediate $Co^{III} + I^-$ complexes may be involved, formed rapidly in a pre-equilibrium to the oxidation in these conditions. For the oxidation of Br^-, also, rapid colour changes and the kinetic behaviour at high ionic strengths suggest that intermediate complexes formed in rapid pre-equilibria are involved in this reaction [10, 26]. For the oxidation of inhibitor-free hydrogen peroxide, two investigators separated in time by about twenty years [7, 8, 24], show the involvement of an intermediate $Co^{III} + H_2O_2$ complex formed in a rapid pre-equilibrium to the rate-determining oxidation. In the first of these [8, 24], both spectroscopic and kinetic results obtained using a conventional spectrophotometer show the existence of the pre-equilibrium at high initial ratios of $[H_2O_2]/[Co^{III}]$ using Co^{III}_{aq} in aqueous perchlorate media at 0 and 12.5 °C formed by removing all sulfate ions as solid $BaSO_4$ from cobalt(III) sulfate with Wells as experimentalist [24]. In the second, using a stopped-flow spectrophotometer [7], Husain [27] showed kinetically the involvement of this complex at high $[H_2O_2]/[Co^{III}]$ ratios at 16–42 °C using Co^{III} prepared electrolytically from Co^{II} in aqueous perchlorate media. The involvement of an intermediate complex was also shown spectroscopically for the oxidation of molecular bromine by Co^{III} [20].

We conclude, therefore, that, for the lines in Figs. 1 and 2, there is a gradation of mechanism from

rate determining oxidation in the outer sphere to rate determining oxidation in the inner sphere, encompassing also the extreme of rate-determining substitution into the inner sphere.

Mechanism for the oxidation by Co^{III}_{aq} and $Co^{III}OH^{-}_{aq}$

To correlate all the circles and the squares in Figs. 1 and 2 it is important to realise that all these oxidations and the substitution occur in the same medium, aqueous perchlorate mixtures. As perchlorate ions have a structure-breaking effect on water [28], this medium will not be the same as pure water but will have less structure. The first involvement of aquacobalt(III) ions $(Co^{III}S_{w})_{aq}$ (where $S = H_2O$) with the oxidisable ligand L will be the diffusion controlled formation of an outer-sphere complex $(Co^{III}S_{w}L)_{aq}$, process I in Fig. 3. After some subsequent slight re-arrangement of the solvation shell involving compensating contributions to ΔH^{*} and ΔS^{*} with $u \sim w$, electron tunnelling may then occur, as in process II.

Alternatively, if the attraction between Co^{III} and the charged or dipolar L is sufficient to modify further the outer-sphere complex before the electron transfer occurs, this rapid re-arrangement in (Co-
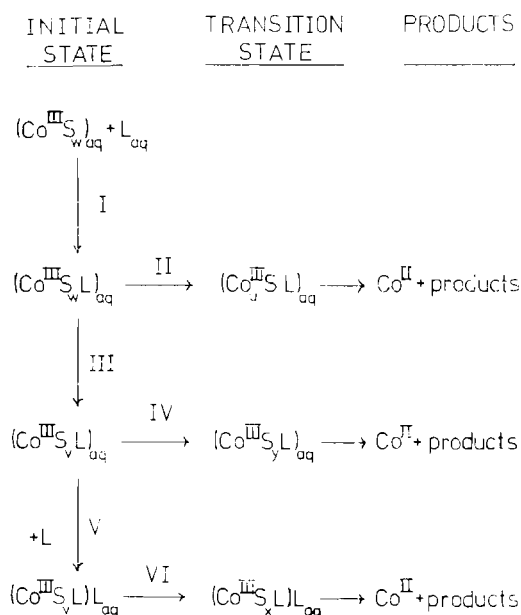
$^{III}S_{w}L)_{aq}$ to give $(Co^{III}S_{v}L)_{aq}$ with $v < w$, as in process III, may be followed by a transfer to the transition state $(Co^{III}S_{y}L)_{aq}$ with $y \neq v$ as in IV, where electron tunnelling can occur. Compensating changes in ΔH^{*} and ΔS^{*} will accompany these changes in solvation. If the proportion of the total Co^{III} present in these initial complexes is low, the complexes will not be detectable kinetically: clearly, in some cases, the amount of complex and its lifetime are sufficiently great to become kinetically detectable. Whether the complex is detectable spectroscopically will depend on the size of v in $(Co^{III}S_{v}L)_{aq}$ and the lifetime of the latter: it is not known what limiting separation of Co^{III} and L is needed to modify the energy levels of Co^{III} and, although this will occur when Co^{III} and L are contiguous, some changes will occur with larger separations. Of course, if ΔH^{*} for IV is high, III will result in a complex $(Co^{III}S_{v}L)_{aq}$ with a long lifetime, as occurs with Cl^{-} ions: in this case, the substitution kinetics have been investigated [22, 29].

If $(Co^{III}S_{v}L)_{aq}$ is relatively stable to oxidation, a further molecule of L may attach itself in a diffusion controlled formation of an outer-sphere complex, as in V, followed by changes in solvation to produce a situation in VI where electron tunnelling can occur, as found with HN_3 at high initial $[HN_3]/[Co^{III}]$ ratios.

Although the assignment of individual oxidisable ligands to each category is open to speculation in some cases [2], it is clear that the major contribution to all the enthalpies and entropies of activation are changes in solvation, irrespective of the cobalt(III) being Co^{III}_{aq} or $Co^{III}OH^{-}_{aq}$, and hence the coincident linear plots in Figs. 1 and 2 with compensating contributions to ΔH^{*} and ΔS^{*}, similar to those found in the Barclay–Butler rule for the solvation of gaseous molecules in a particular solvent [28, 30].

Although this mechanism in Fig. 3 unifies all the circles in Figs. 1 and 2 and probably includes the squares also, with ΔH^{*} and ΔS^{*} all determined in aqueous perchlorate media, there remains the deviant triangles in Figs. 1 and 2 for the oxidation of benzene and those for the possible deviants propan-2-ol and $HCOO^{-}$. Although there is some uncertainty concerning the consumption ratio $|\Delta[Co^{III}]|/|\Delta[benzene]|$ which will affect the numerical value for ΔS^{*}, a ratio of 12 is assumed here [18]; a variation from between 2 and 12 does not appreciably alter the deviation of this reaction in Figs. 1 and 2. Essentially, these three oxidations are similar to all those represented by the circles in Figs. 1 and 2, with the charge changes requiring adjustment of the solvation before the electron tunnelling occurs. However, the reason for their deviation may lie in the effect of these particular oxidisable ligands on the solvent in the concentrations employed. Relatively high concentrations of propan-2-ol are used and the physical

Fig. 3. Changes in solution for the process initial state going to transition state for alternative mechanisms for the oxidation of ligands by Co^{III}_{aq} or $Co^{III}OH^{-}_{aq}$ producing compensating changes in ΔH^{*} and ΔS^{*}.

evidence for water + propan-2-ol mixtures, such as the structural contribution to the change in the temperature of maximum density of water [31], the sharp minimum in the relative partial molar volume of propan-2-ol, $\bar{V}_2 - V_2^\circ$ [32], the maximum in the ultrasonic absorption [33], the maximum in the viscosity [34] and the deviation of the minimum in the excess enthalpy of mixing from a mole fraction of propan-2-ol = 0.5 [35], all indicate that even small additions of propan-2-ol to water increase the extent of the formation of structure in the solvent. Therefore, with this particular substrate, the medium differs, probably considerably, from the broken-down structure present in the aqueous perchlorate media [28] used for the reactions in the circles. Even very small additions of benzene increase the amount of structure in water [36, 37], so again we conclude that a different medium is used. It also seems likely that the relatively high concentrations of formic acid used will also modify the solvent structure. Thus, although one set of conditions in Fig. 3 applies in a fixed medium, like the aqueous perchlorate media used for the circles and squares in Figs. 1 and 2, with a change in the medium, induced by the particular substrate, another set of conditions will apply in Fig. 3, causing a deviation from the linear plot found in the aqueous perchlorate media. This can be compared with the differing slopes found for the Barclay–Butler relationship for gas solubilities in solvents with differing degrees of association [28, 30].

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