Kinetics and Mechanism of the Reduction of Dodecatungstocobaltate(III) by Oxalate. The Catalytic Role of Alkali Metal Ions through Outer-sphere Bridging

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The kinetics of reduction of dodecatungstocobaltate(III) by oxalate follow the rate laws $k_{obs.} = 2k_1[HC_2O_4^-]$ and $k_{obs.} = 2k_2[C_2O_4^{2-}]$ at high and low hydrogen ion concentrations respectively. Both these apparent second-order rate constants (k_1 and k_2) depend on the concentration and type of cation present; k_1 and k_2 decrease in the order $K^+ > Na^+ \sim Li^+$ and $K^+ > Na^+ > Li^+$ respectively. The K^+ and Na^+ assisted paths have been studied in detail. The rate constants for these catalysed paths along with those for uncatalysed ones have been evaluated. Thermodynamic parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) associated with k_1 and k_2 have been determined. A cation-bridged outer sphere electron transfer mechanism is most likely to take place, with simultaneous generation of free radicals ($C_2O_4^{\bullet -}$).

The kinetics of the reduction of dodecatungstocobaltate(III) by some thiols [1-3] and ligands containing dihydroxyl groups[4] have been demonstrated to take place by an outer sphere mechanism, whereas the catalytic role of alkali metal ions has been encountered in the electron exchange between dodecatungstocobaltate(III), $[CoW_{12}O_{40}]^{5-}$, and dodecatungstocobaltate(II), $[CoW_{12}O_{40}]^{6-}$.[5] The absence of any data in the field of the redox interaction of this interesting tetrahedral cobalt(III) species with carboxylic acids has prompted us to undertake this study.

Experimental

Materials and Reagents.—Potassium salts of $[CoW_{12}O_{40}]^{5-}$ and $[CoW_{12}O_{40}]^{6-}$, hereafter designated as $Co^{III}M$ and $Co^{II}M$ respectively ($M = W_{12}O_{40}$), were prepared, characterised and standardised in the same way as reported earlier.[4,5] Reagent grade oxalic acid and sodium oxalate, doubly recrystallised sodium perchlorate, sodium nitrate, sodium sulphate, potassium nitrate, and lithium perchlorate were used.

Kinetic Studies.—The reaction rates were determined by observing the decrease in absorption at 388 nm. A few experiments conducted at 625 nm (which is the absorption maximum of the $Co^{II}M$ species) gave identical results. No experimental difference could be detected for parallel samples run in the presence and absence of dissolved oxygen.

Polymerisation Studies.—A series of reactions between $Co^{III}M$ and oxalic acid was carried out in deaerated vials at 28 °C in the presence of aqueous acrylonitrile (5% v/v) at pH 2.0 and 5.0 and at $[Co^{III}M] = 2 \times 10^{-4}$ mol dm^{-3} with various $[ox]_T$ (total oxalate concentration) ranging from 0.02 to 0.1 mol dm^{-3}. After 30 min mixing, an appreciable amount of precipitate was observed showing that the reaction probably proceeds through the generation of free radicals. No polymer was formed in blank experiments in which either of the reactants was absent.

Results and Discussion

The stoicheiometry of the reaction, determined by spectrophotometric titration, is as given in equations (1) and (2).

$$2Co^{III}M + HC_2O_4^- \longrightarrow 2Co^{II}M + 2CO_2 + H^+ \quad (1)$$

$$2Co^{III}M + C_2O_4^{2-} \longrightarrow 2Co^{II}M + 2CO_2 \quad (2)$$

The spectral changes observed during the reaction of $Co^{III}M$ with oxalate give a clear isosbestic point at 510 nm indicating the absence of appreciable amounts of reaction intermediates. A preliminary study of the kinetics of reactions (1) and (2) (at pH 2.0 and 5.0 respectively) shows that the pseudo-first-order rates exhibit first-order dependence on both $[HC_2O_4^-]$ and $[C_2O_4^{2-}]$.† Thus the rate laws for reactions (1) and (2) can be described by equations (3) and (4) respectively. The apparent

$$k_{obs.} = 2k_1[HC_2O_4^-] \quad (3)$$

$$k_{obs.} = 2k_2[C_2O_4^{2-}] \quad (4)$$

second-order rate constants (k_1 and k_2) at various temperatures are presented in Table 1 along with the corresponding activation parameters evaluated using the Eyring equation. These parameters, however, should be treated as composite since they take into account the contributions of both catalysed and uncatalysed paths (see below).

Since the experiments have been carried out at high cation concentrations, electron transfer *via* the formation of a bridge by the cation between the negatively charged reacting species is not unexpected.‡ To examine the possible effect of cations on the rate of this reaction, some experiments have been performed at pH 1.32 and 5.00 using salts of selective cations and anions as the supporting electrolytes and the results are shown in Table 2. It is clear from these data that at both pH's the rate largely depends on the nature of cations but is independent of that of the experimental range of anions. Thus we find cation catalytic orders $K^+ > Na^+ \sim Li^+$ and $K^+ > Na^+ > Li^+$ for $HC_2O_4^-$ and $C_2O_4^{2-}$ reductions respectively.

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† It has been experimentally recognised that at pH < 1 there is virtually no reaction which indicates that $H_2C_2O_4$ does not contribute to the redox process. The values[6] of $10^2K_1 = 6.52$ (40 °C), 5.62 (50 °C), and 4.79 (60 °C) have been used in calculating the rate parameter (k_1).

‡ We are grateful to the referees for suggesting this point.

Table 1. Kinetic and thermodynamic* parameters for the reaction of $Co^{III}M$ with oxalate at I = 1.0 mol dm^{-3} ($NaClO_4$)

Temp. (°C)	10^4k_1/ dm^3 mol^{-1} s^{-1}	10^4k_2/ dm^3 mol^{-1} s^{-1}
50	0.94 ± 0.08	22.25 ± 1.03
55	1.53 ± 0.12	31.01 ± 0.98
60	2.10 ± 0.11	47.06 ± 1.52
65		71.25 ± 2.07
70	4.23 ± 0.19	

* $\Delta H_1^{\ddagger} = 65 \pm 3$ kJ mol^{-1}, $\Delta S_1^{\ddagger} = -122 \pm 11$ J K^{-1} mol^{-1}, $\Delta H_2^{\ddagger} = 69 \pm 3$ kJ mol^{-1}, $\Delta S_2^{\ddagger} = -85 \pm 9$ J K^{-1} mol^{-1}.

Table 2. Apparent second-order rate constants in different media at 60 °C and $[ox]_T$ = 0.1 mol dm^{-3}

Medium	10^4k_1[a]/ dm^3 mol^{-1} s^{-1}	10^3k_2[b]/ dm^3 mol^{-1} s^{-1}
$LiClO_4$	2.42	2.23
$NaClO_4$	2.45	4.75
$NaNO_3$	2.49	4.76
Na_2SO_4	2.52	4.82
KNO_3	4.20	12.20

[a] $[A^+]$ = 0.9 mol dm^{-3}. [b] $[A^+]$ = 0.7 mol dm^{-3}.

The effects of K^+ and Na^+ ions on the reaction rates have also been studied individually. As expected, the rates of both reactions (1) and (2) increase with the increase in cation concentration.* Plots of both k_1 and k_2 *vs.* $[K^+]$ are linear having intercepts describing the rates of uncatalysed paths denoted by k_1^0 (3.40×10^{-5} dm^3 mol^{-1} s^{-1}) and k_2^0 (12.41×10^{-4} dm^3 mol^{-1} s^{-1}) for reactions (1) and (2) respectively. Thus the rate laws in the presence of K^+ may be written as in equations (5) and (6), where $k_{obs.}/2[HC_2O_4^-] =$

$$k_{obs.} = 2(k_1^0 + k_1'[K^+])[HC_2O_4^-] \qquad (5)$$

$$k_{obs.} = 2(k_2^0 + k_2'[K^+])[C_2O_4^{2-}] \qquad (6)$$

k_1 and $k_{obs.}/2[C_2O_4^{2-}] = k_2$. The slopes of the above mentioned plots give the K^+ ion catalysed rates, $k_1' = 4.28 \times 10^{-4}$ dm^6 mol^{-2} s^{-1} and $k_2' = 10.20 \times 10^{-3}$ dm^6 mol^{-2} s^{-1}, for $HC_2O_4^-$ and $C_2O_4^{2-}$ reduction paths respectively.

It is, however, rather surprising that the dependence of k_1 on $[Na^+]$ is not first order; a second-order behaviour with a non-zero intercept is observed and the rate law can be expressed as in equation (7). From the slope of the plot of k_1 *vs.* $[Na^+]^2$ the

$$k_{obs.} = 2(k_1^0 + k_1''[Na^+]^2)[HC_2O_4^-] \qquad (7)$$

value of k_1'' (2.16×10^{-4} dm^9 mol^{-3} s^{-1}), the Na^+ catalysed rate for $HC_2O_4^-$ reduction, is evaluated. The dependence of k_2 on $[Na^+]$ is similar to that on $[K^+]$ and the rate equation is (8).

$$k_{obs.} = 2(k_2^0 + k_2''[Na^+])[C_2O_4^{2-}] \qquad (8)$$

From the slope of the plot of k_2 *vs.* $[Na^+]$, $k_2'' = 4.90 \times 10^{-3}$ dm^6 mol^{-2} s^{-1} is determined. The k_1^0 and k_2^0 values obtained from the intercepts of these plots are in excellent agreement with the values determined experimentally in the absence of cations.†

In presence of K^+ ion the simplest reaction scheme, (9)—(14),

$$Co^{III}M^{5-} + HC_2O_4^- \xrightarrow{k_1^0} Co^{II}M^{6-} + C_2O_4^{\bullet -} + H^+ \qquad (9)$$

$$Co^{III}M^{5-} + C_2O_4^{2-} \xrightarrow{k_2^0} Co^{II}M^{6-} + C_2O_4^{\bullet -} \qquad (10)$$

$$Co^{III}M^{5-} + K^+ \overset{\text{fast}}{\rightleftharpoons} KCo^{III}M^{4-} \qquad (11)$$

$$KCo^{III}M^{4-} + HC_2O_4^- \xrightarrow{k_1'} Co^{II}M^{6-} + K^+ + C_2O_4^{\bullet -} + H^+ \qquad (12)$$

$$KCo^{III}M^{4-} + C_2O_4^{2-} \xrightarrow{k_2'} Co^{II}M^{6-} + K^+ + C_2O_4^{\bullet -} \qquad (13)$$

$$Co^{III}M^{5-} + C_2O_4^{\bullet -} \xrightarrow{\text{fast}} Co^{II}M^{6-} + 2CO_2 \qquad (14)$$

$$k_{obs.} = 2[ox]_i \frac{[H^+](k_1^0 + k_1'[K^+]) + K_2(k_2^0 + k_2'[K^+])}{K_2 + [H^+]} \qquad (15)$$

consistent with the above experimental results involves ion pairing between the polyanion and the cation in addition to the uncatalysed reaction paths. The overall rate expression for this reaction scheme is equation (15), where K_2 is the second acid dissociation constant of oxalic acid and $[ox]_i = [HC_2O_4^-] + [C_2O_4^{2-}] = [ox]_T - [H_2C_2O_4]$. At pH > 2.5, $[ox]_i = [ox]_T$. The rate-determining steps (12) and (13) may lead to identical transition states (**A**) and (**B**), in both of which the K^+ acts as a bridge.

$Co^{III}M^{5-} \cdots K^+ \cdots HC_2O_4^-$ (**A**) $Co^{III}M^{5-} \cdots K^+ \cdots C_2O_4^{2-}$ (**B**)

With Na^+ the reaction scheme is identical to that for K^+, the only exception being the second-order dependence of k_1 on $[Na^+]$ which presumably requires an activated complex of the type (**C**). Thus with Na^+ equation (12) will be replaced by

$NaCo^{III}M^{4-} \cdots Na^+ \cdots HC_2O_4^-$
(**C**)

equation (16) and the rate expression may be described as equation (17). The pH–rate profile (Figure) in $NaClO_4$ medium

$$NaCo^{III}M^{4-} + Na^+ + HC_2O_4^- \xrightarrow{k_1''} Co^{II}M^{6-} + 2Na^+ + C_2O_4^{\bullet -} + H^+ \qquad (16)$$

$$k_{obs.} = 2[ox]_i \frac{[H^+](k_1^0 + k_1''[Na^+]^2) + K_2(k_2^0 + k_2''[Na^+])}{K_2 + [H^+]} \qquad (17)$$

gives an excellent fit to equation (17) with the experimental k_1^0, k_1'', k_2^0, and k_2'' values with a value of $K_2 = (1.4 \pm 0.1) \times 10^{-4}$ mol dm^{-3} which is in good agreement with that mentioned in the literature[6–8] under comparable conditions. This type of second-order behaviour of the apparent second-order rate

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* It was not possible to hold the total ionic strength constant throughout the cation variation studies. However, we were able to do this in some experiments using a mixture of $AClO_4$ and A_2SO_4 instead of only $AClO_4$ (where A = Na or K). The results demonstrate that, except for that of cations, the effect of ionic strength on the present reaction system is either nil or negligibly small.

† It has been possible to adjust the pH at 1.32 without adding any cation in the form of base. However a small amount of alkali is required to make the pH 5.00. A dilute solution of lithium hydroxide was used for this purpose to minimise the interference due to cation, and in practice the k_2^0 value, thus determined, matches well with that obtained from the intercept.

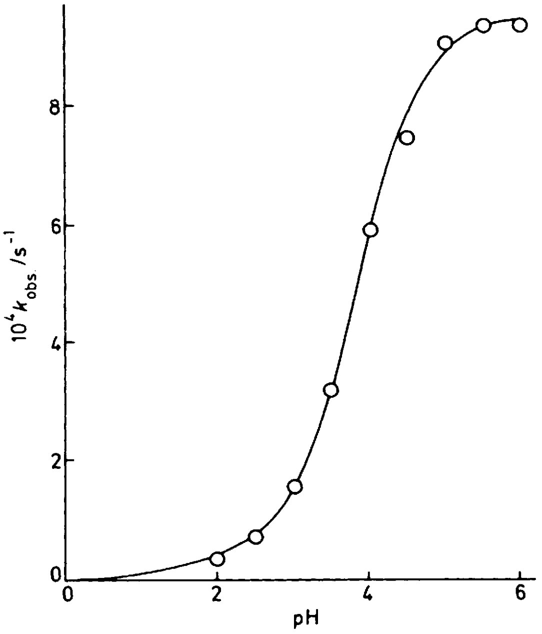

Figure. pH–Rate profile for the reduction of Co^{III}M by oxalate at 60 °C, $I = 1.0$ mol dm^{-3} (NaClO$_4$), $[ox]_T = 0.1$ mol dm^{-3}, and [Co^{III}M] = 2×10^{-4} mol dm^{-3}. The curve has been drawn through calculated values of $k_{obs.}$ obtained from equation (17) using the values of k_1^0, k_2^0, k_1'', k_2'' given in the text and considering [Na$^+$] at each pH. The circles denote experimental points

constant on sodium ion concentration and a linear dependence on [K$^+$] have also been observed by Sulfab *et al.*[9] in the oxidation of hexacyanoferrate(II) by tris(malonato)cobaltate(III) at high cation concentrations.

An interesting comparison of our results can be made with those obtained by Rasmussen and Brubaker[5] in the electron transfer between Co^{III}M and Co^{II}M. These authors noticed a first-order dependence of rate on the cation concentration for both Li$^+$ and K$^+$ and have proposed a rate equation, rate = k[A$^+$][Co^{III}M][Co^{II}M], where A = Li or K. Unfortunately the absence of data in Na$^+$ medium for the electron exchange reaction does not allow us to compare our results for Na$^+$. The faster exchange in K$^+$ medium compared to that in Li$^+$ has been suggested to be due to increased ion pairing by the larger K$^+$ ion. Judging from electrostatic considerations we can assume that larger cations such as K$^+$ are less firmly attached to the anions than are smaller cations like Li$^+$, and thus are more effective in bringing the negatively charged reacting species to a similar state. This model successfully explains the decreasing efficiency of alkali cations as catalysts in the order K$^+$ > Na$^+$ > Li$^+$. The same cation catalytic order has been observed previously in the stepwise base decomposition of dodecatungstosilicate(4−)[10] and in many other outer-sphere electron transfer processes.[11]

The redox potential values for $HC_2O_4^-$ and $C_2O_4^{2-}$, calculated using the values of $E^\circ_{H_2C_2O_4}$[12] and K_2, are −0.53 and −0.64 V respectively. Thus $C_2O_4^{2-}$ should be a better reductant than $HC_2O_4^-$, which has actually been observed.

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