Notes

Kinetics of Reduction of Tris(ethylenediamine)cobalt(III) by Ethylenediamine-*NNN'N'*-tetra-acetatochromate(II)

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The kinetics of the reduction of $[Co(en)_3]^{3+}$ (en = ethylenediamine) by $[Cr(edta)]^{2-}$ have been studied by stopped-flow methods under a variety of conditions. The reaction is first order in both reagents, with a second-order rate constant of 3.37×10^3 dm^3 mol^{-1} s^{-1} at 25 °C, pH 4.81, unit ionic strength and [edta] = 5×10^{-2} mol dm^{-3} (edta = ethylenediamine-*NNN'N'*-tetra-acetate). Activation parameters ($\Delta H^{\ddagger}$ = 56 kJ mol^{-1}, $\Delta S^{\ddagger}$ = 12 J K^{-1} mol^{-1}) are consistent with weak electrostatic attraction between the reactants. The rate shows an inverse dependence on the concentration of free edta, attributed to formation of an ion pair or hydrogen-bonded adduct with the oxidant. The pH dependence is a double sigmoid, consistent with two protonation equilibria in the reductant with pK_a values of 2.7 and 5.5, and the reaction rate increases with increasing numbers of negative donor groups in the complex.

Complexes of transition-metal ions in low oxidation states are of considerable interest as reducing agents. Most studies on electron-transfer reaction kinetics have been carried out using aqua ions as reductants, such as those of Cr^{2+} and V^{2+}, but the use of chelating ligands greatly increases both the range of electrode potentials available and the range of conditions (especially pH) under which reactions can be carried out. Areas in which this approach has been particularly fruitful include reactions with metalloproteins,[1,2] and the reductive dissolution of metal oxides. In the latter context, the reactions of a number of such reagents have been studied in detail, both with oxidants in solution and with iron-containing oxides,[3—7] and the use of tris(picolinato)vanadate(II) (picolinic acid = pyridine-2-carboxylic acid) in the decontamination of nuclear plants is well established.[8—10] However, a more powerful reductant is required to reduce chromium(III), which at present can only be dissolved from oxides by oxidative processes.[11,12] Since the electrode potential of the aqueous $Cr^{2+/3+}$ couple is −0.41 V,[13] any reductant sufficiently powerful to reduce Cr^{III} is also unstable with respect to oxidation by water. Preliminary tests with a variety of such complexes have shown that reagent decomposition tends to be the dominant reaction in most cases, but a limited chain reaction has been observed between Cr_2O_3 and chromium(II) complexes of nitrilotriacetate (nta) and ethylenediamine-*NNN'N'*-tetra-acetate (edta).[5,14] Although very strong reducing agents (E^0 *ca.* −1 V for the edta complex[15]), these complexes are stable for hours under ideal conditions,[16] but the reaction with solvent is readily catalysed, for example by metal surfaces.

A detailed study of the kinetics of reaction of the $[Cr(edta)]^{2-}$ complex with a well characterised outer-sphere oxidant was therefore undertaken as part of the programme to determine the factors controlling the rates of the electron-transfer reactions of these reductants. Very few unambiguously outer-sphere reactions of aminopolycarboxylate complexes of Cr^{II} have been studied,[17] but a single rate constant for the reduction of $[Co(en)_3]^{3+}$ (en = ethylenediamine) by $[Cr(edta)]^{2-}$ has been reported.[18] Using this value and the rate constant for reaction with $[Co(edta)]^-$,[19] a self-exchange rate constant of 6×10^{-2} dm^3 mol^{-1} s^{-1} was calculated for the chromium complex.[3]

Experimental

Reagents.—The complex $[Co(en)_3]Br_3 \cdot 3H_2O$ was prepared by air oxidation of a 1:3:3 stoicheiometric mixture of cobalt(II) chloride, ethylenediamine, and HCl in water, followed by addition of an excess of solid KBr to precipitate the product, which was recrystallized from water (Found: Co, 10.9. Calc. for $C_6H_{30}Br_3CoN_6O_3$: Co, 11.0%). Visible spectrum: $\lambda_{max.}$ 465 nm (ε 90, lit.[20] 87 dm^3 mol^{-1} cm^{-1}). $[Co(en)_3][ClO_4]_3$ was prepared similarly. Solutions of Cr^{2+} were prepared by reduction of a solution of $CrCl_3$ in HCl over zinc amalgam. All solutions were made up in triply distilled water and all reagents used were AnalaR grade. Solutions were deaerated with oxygen-free argon, and Cr^{2+} was handled using conventional syringe techniques.

Kinetic Apparatus and Procedures.—Kinetic measurements were made with a Canterbury SF-3A stopped-flow apparatus (Hi-Tech Ltd.). The photomultiplier voltage was recorded on a BBC B microcomputer *via* a Unilab 532.001 interface; 250 readings were taken for each run, and were analysed by the Guggenheim method.[21] The procedure for the kinetic runs was as follows: one reservoir was loaded with the required concentrations of both the oxidant and edta at the desired pH, plus $NaClO_4$ to give I = 1 mol dm^{-3}, and the other with Cr^{2+} also in sodium perchlorate. Reactions were monitored at 540 nm to follow the formation of the Cr^{III}–edta complex. Several replicate runs were recorded for each set of conditions to obtain a satisfactory average.

Results

Only a single exponential was observed in all cases, leading to a stable 'infinity' value, and first-order plots were linear over several half-lives: runs were monitored for 4—8 half-lives and no significant deviations were observed. Rate constants under a variety of conditions are given in Table 1.

Dependence on $[Co^{III}]$ *and Temperature.*—Keeping all other variables constant, reaction is first order in oxidant concentration over the range (5—25) × 10^{-3} mol dm^{-3}. No change in rate constant is observed on changing the initial Cr^{II} concentration from 5×10^{-4} to 1×10^{-3} mol dm^{-3}. At 25 °C, pH 4.81, and $[edta]_{total} = 5 \times 10^{-2}$ mol dm^{-3}, the mean second-order rate constant is $(3.37 \pm 0.18) \times 10^3$ dm^3 mol^{-1} s^{-1}. At these reagent concentrations the results at different temperatures give a linear Eyring plot, and an unweighted linear

Table 1. Rate constants for the reduction of $[Co(en)_3]^{3+}$ by $[Cr(edta)]^{2-}$ [a]

$10^2[Co^{III}]$/ mol dm^{-3}	T/°C	10^2[edta]/ mol dm^{-3}	$k_{obs.}$/s^{-1}	10^3 $k_{obs.}[Co^{III}]^{-1}$/ dm^3 mol^{-1} s^{-1}
0.50 [b]	25.0	5.0	17.0	3.40
1.00	25.0	5.0	34.5	3.45
1.48	25.0	5.0	53.6	3.62
2.00	25.0	5.0	63.0	3.15
2.53	25.0	5.0	82.1	3.25
0.50 [b]	30.0	5.0	27.5	5.50
0.50 [b]	37.0	5.0	47.9	9.58
0.50 [b]	44.4	5.0	68.3	13.7
1.00	25.0	0.50	42.9	4.29
1.00	25.0	1.0	42.5	4.25
1.00	25.0	2.5	38.2	3.82
1.00	25.0	7.5	28.0	2.80
1.00	25.0	10.0	21.0	2.10

[a] $[Cr^{II}] = 1 \times 10^{-3}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3} ($NaClO_4$), pH 4.81. [b] $[Cr^{II}] = 5 \times 10^{-4}$ mol dm^{-3}.

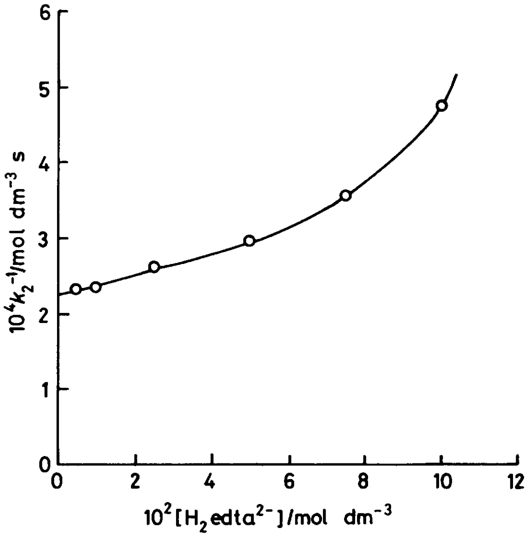

Figure 1. Dependence of second-order rate constant (k_2) on free H_2edta^{2-} concentration (T = 25 °C, pH 4.81)

regression yields activation parameters $\Delta H^{\ddagger} = 56 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = 12 \pm 8$ J K^{-1} mol^{-1}.

Dependence on [edta].—There is a significant dependence of rate on the concentration of free ligand at pH 4.8, the rate decreasing by a factor of two over the range (0.5—10) $\times 10^{-2}$ mol dm^{-3}. This is shown in Figure 1 as a plot of the reciprocal of the second-order rate constant against [edta]. This plot is clearly curved at higher concentrations, but approximates to a straight line up to about 5×10^{-2} mol dm^{-3}. At low [edta] the result is in excellent agreement with the rate constant obtained by Ogino *et al.*[18] in acetate buffer ([edta] is used here to represent all forms of the free ligand; at pH 4.8 it is essentially all present as the divalent anion).[22]

Dependence on pH.—The pH dependence is shown in Figure 2. There is a strong trend of increasing rate with increasing pH, and the results fit well to a double sigmoid. The curve plotted in Figure 2 is a computer-generated least-squares fit using the function (1). Derived values for the variable parameters are given in Table 2.

Table 2. Rate and equilibrium constants derived from the pH dependence of the rate of reduction of $[Co(en)_3]^{3+}$ by $[Cr(edta)]^{2-}$ *

k_0	5.9×10^3	dm^3 mol^{-1} s^{-1}
k_1	2.9×10^3	dm^3 mol^{-1} s^{-1}
k_2	1.1×10^3	dm^3 mol^{-1} s^{-1}
K_1	3×10^5	dm^3 mol^{-1}
β_2	1.5×10^8	dm^6 mol^{-2}

* $[Co^{III}] = 1.0 \times 10^{-2}$ mol dm^{-3}, $[Cr^{II}] = (5 - 10) \times 10^{-4}$ mol dm^{-3}, [edta] $= 5 \times 10^{-2}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3} ($NaClO_4$), T = 25.0 °C.

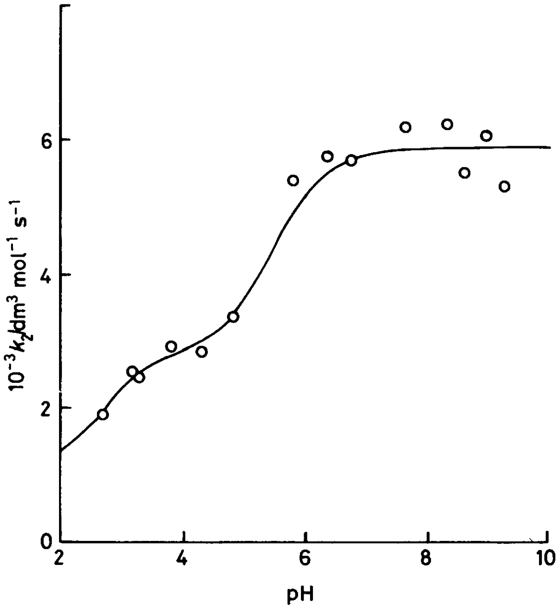

Figure 2. pH Dependence of second-order rate constant (k_2) for reduction of $[Co(en)_3]^{3+}$ by the edta complex of Cr^{II} [(T = 25 °C, I = 1.0 mol dm^{-3} ($NaClO_4$)]

$$k_{calc.} = \frac{k_0 + k_1K_1[H^+] + k_2\beta_2[H^+]^2}{1 + K_1[H^+] + \beta_2[H^+]^2} \quad (1)$$

Discussion

The Reaction Sequence.—Two reactions take place when the reagent solutions are mixed. The first is the formation of the strongly reducing chromium(II) complex, by substitution of edta on the very labile hexa-aqua ion: equation (2). The formation constant is high enough to ensure that all the chromium is present as the complex ($\log_{10} K_f = 13.6$);[15] the alternative pathway of direct reduction of the cobalt complex by the aqueous Cr^{2+} ion is far to slow to compete.[20]

$$[Cr(H_2O)_6]^{2+} + H_2edta^{2-} \longrightarrow [Cr(edta)]^{2-} + 2H^+ + 6H_2O \quad (2)$$

This is followed by the electron-transfer reaction (3), with

$$[Cr(edta)]^{2-} + [Co(en)_3]^{3+} \longrightarrow [Cr(edta)]^- + [Co(en)_3]^{2+} \quad (3)$$

subsequent aquation of the $\mathrm{Co^{II}}$ product and probable complexation by excess edta. Only reaction (3) is observed, and all the rate constants measured are for this reaction.

The Concentration Dependences.—The linear dependence of rate constant on cobalt concentration shows that the association constant for formation of the precursor is quite small, which is not unexpected at high ionic strength; a limiting value can be derived, $K_{\text{ass.}} < 8\ \mathrm{dm^3\ mol^{-1}}$, under the conditions used. The effect of the free ligand, on the other hand, may be ascribed to some form of association between it and the oxidant, reaction (4).

$$[\mathrm{Co(en)_3}]^{3+} + \mathrm{H_2edta}^{2-} \overset{K_L}{\rightleftharpoons} [\mathrm{Co(en)_3{\cdot}H_2edta}]^{+} \qquad (4)$$

The electrostatic attraction between the free ligand (predominantly a dianion at pH 4.8) and the tripositive cation may be augmented by hydrogen bonding between the carboxylates and amine hydrogens. An outer-sphere adduct or ion pair of this kind would clearly be much less reactive towards the reductant, being both larger and less highly charged than the original $[\mathrm{Co(en)_3}]^{3+}$ complex. Inhibition caused by association in this way leads to a rate expression of the form (5) where k' is the rate at zero free ligand concentration and K_L the association constant for formation of the adduct. Thus a plot of $1/k_{\text{obs.}}$ *vs.* [edta] should be linear. Figure 1 shows that this applies except at high ligand concentrations; from the intercept and slope of this line approximate values for k' and K_L can be obtained, $4.4 \times 10^3\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ and $6\ \mathrm{dm^3\ mol^{-1}}$ respectively. At high concentrations of edta, further interactions may be possible, but medium effects may also become significant.

$$k_{\text{obs.}} = \frac{k'}{1 + K_L[\text{edta}]} \qquad (5)$$

The Temperature Dependence.—The activation parameters are consistent with a weak electrostatic attraction between the reactants. At lower ionic strength, the entropy term would be expected to be large and positive, this being the dominant term in electrostatic interactions in aqueous solution. Under the conditions used here, this contribution is still large enough to cancel out any negative activation entropy of the electron-transfer step, yielding a nett value which is small and positive. The enthalpy of activation is largely that of the electron-transfer step, since electrostatic contributions to this term are small.[23]

The pH *Dependence.*—The variation in rate constant with increasing pH is consistent with two successive protonation equilibria. In the case of the chromium(III) complex, these equilibria are attributed to protonation of a pendant carboxylate group at low pH, and deprotonation of co-ordinated water at high pH.[24] Such processes can also occur with the chromium(II) complex, and the increases in reaction rate are consistent with stepwise deprotonations of the complex; the pre-association constant is expected to increase with increasing negative charge, and the electron-transfer rate should also increase as the divalent metal ion is increasingly destabilised relative to the trivalent product. It is improbable that the increase in rate at higher pH is due to deprotonation of the free $\mathrm{H_2edta}^{2-}$ ligand, since the [edta] dependence described above implies that this process would tend if anything to reduce the reaction rate: the association constant for reaction (4), K_L, must increase as the negative charge on the ligand increases.

The values of K_1 and β_2 derived from this kinetic analysis are equivalent to pK_a values of 2.7 and 5.5. The lower figure is fully consistent with protonation of a pendant carboxylate, and is in reasonable agreement with values of 3.0 and 3.5 obtained by pH titrations,[15,25] but the second value is unexpectedly low. The polarographic behaviour of chromium(II) in edta solution was interpreted on the basis of deprotonation occurring only at pH > 10,[15] and measured pK_a values for this process in edta complexes of other divalent metal ions are all >9.[22]

One possible explanation for these observations is that the low-pH form of the complex is a neutral molecule with two pendant carboxylic acid groups, $[\mathrm{Cr(H_2O)_x(H_2edta)}]$, where $x = 1$ or 2.[*] Both pK_a values can then be attributed to carboxylic acid dissociations; the values observed are much more consistent with such processes than deprotonation of co-ordinated water.

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