Kinetics of the Electron-transfer Reaction, Iodine with 'Cobalt(II) Sepulchrate' †

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The reaction $I_2 + 2[Co(sep)]^{2+} \longrightarrow 2I^- + 2[Co(sep)]^{3+}$ obeys the rate law $-d(\ln[I_2]_T)/dt = k_0[I_2][Co(sep)^{2+}] + k_I[I_3^-][Co(sep)^{2+}]$ (sep = 1,3,6,8,10,13 16,19-octa-azabicyclo[6.6.6]icosane). At 25 °C in 0.1 mol dm^{-3} KCl, $k_0 = (5.9 \pm 0.8) \times 10^4$ dm^3 mol^{-1} s^{-1} and $k_I = (3.93 \pm 0.09) \times 10^4$ dm^3 mol^{-1} s^{-1}. These values are consistent with predictions from the Marcus cross-relation.

The caged complex 'cobalt sepulchrate' {hereafter written $[Co(sep)]^{3+}$ (sep = 1,3,6,8,10,13,16,19-octa-azabicyclo[6.6.6]-icosane)} characterised by Sargeson and co-workers [1,2] is a valuable new electron-transfer reagent. The couple $[Co(sep)]^{3+/2+}$ is readily reversible, the oxidised and reduced forms have the same structure, and both are stable in aqueous solutions at low acidity ranges, in which aqua-metal ions are subject to hydrolysis and polymerisation. Herein we report the kinetics of reaction (1) in aqueous solution in the presence of iodide ion.

$$I_2 + 2[Co(sep)]^{2+} \longrightarrow 2I^- + 2[Co(sep)]^{3+} \qquad (1)$$

Experimental

Materials.—*Cobalt*(III) *sepulchrate chloride.* The products of reaction [1b,2] of tris(ethylenediamine)cobalt(III) chloride [3] with formaldehyde and ammonia were separated by ion exchange. A convenient method was to adjust the solution to pH 6—7 with HCl and pass it through a column of Amberlite IRC-50, H^+-ion form. A pink product passed through with negligible retention, and after washing through with water, the orange-yellow sepulchrate complex was eluted with 1 mol dm^{-3} hydrochloric acid. The eluate was freeze dried, then treated with a 1 : 1 mixture of ethanol and water. A brown impurity dissolved and the resultant yellow solid after filtering and drying with ethanol and diethyl ether was recrystallised from water. The visible absorption spectrum and ^1H n.m.r. spectrum (solution in H_2O, with D_2O as internal standard) agreed with those of Creaser *et al.*[1a,b] A convenient criterion of purity was the ^{59}Co n.m.r. spectrum. The cobalt(III) sepulchrate complex shows a single broad band, well separated from the band due to $[Co(en)_3]^{3+}$ (en = ethylenediamine) {δ = 6 940, and 7 155 p.p.m. respectively relative to $[Co(CN)_6]^{3-}$; widths 480 and 100 Hz, aqueous solution, 33 °C}. No band due to $[Co(en)_3]^{3+}$ could be detected in the sepulchrate samples.

Cobalt(II) sepulchrate solutions containing the required concentrations of Cl^- and I^- were prepared by dissolving $[Co(sep)]Cl_3$, KCl, and KI in water, and reducing with amalgamated zinc under a nitrogen atmosphere for 2 h, then used immediately. Reduction to $[Co(sep)]^{2+}$ is quantitative; the yellow colour of $[Co(sep)]^{3+}$ disappears completely but re-appears on exposure to air. Iodine solutions were prepared by dissolving resublimed I_2 in solutions of KCl and KI with gentle heating if necessary, and deoxygenated by bubbling N_2. To minimise the evaporation of I_2, deoxygenation time was limited to 5—10 min, and solutions were then kept tightly stoppered. Fresh solutions were prepared each day. All solutions were dispensed with hypodermic syringes, from vessels with rubber 'suba-seal' stoppers (serum caps).

Kinetic Measurements.—The Aminco-Morrow stopped flow apparatus was used, modified for temperature control of the cell compartment.[4] As an additional precaution against air-oxidation, the space around the mixing cell was flushed with nitrogen. The output was stored in a DL-901 Transient recorder, inspected visually with an oscilloscope, and transferred to a pen-chart recorder for permanent recording. For experiments at the higher iodide concentrations, wavelengths 440 and 400 nm were selected to give a convenient absorbance change ($A_0 - A_\infty \sim 0.2$). At the lower iodide concentrations, the minimum possible wavelength of 350 nm was used to give the highest possible absorbance change ($A_0 - A_\infty \sim 0.01$).

Results

In all the experiments cobalt(II) was taken in large excess over iodine. Plots of log ($A - A_\infty$) against time were linear over 3—4 half-lives indicating a pseudo-first-order rate law [equation (2)], where $[I_2]_T$ denotes the total stoicheiometric

$$-\,d[I_2]_T/dt = k_{obs.}[I_2]_T \qquad (2)$$

iodine concentration, and this was confirmed by comparison of results with initial $[I_2]_T$ = 0.1 and 0.2 mmol dm^{-3}. Values of $k_{obs.}$ are listed in the Table. The cobalt(II) dependence was found to be linear as shown in Figure 1 [equation (3)].

$$k_{obs.} = k[Co(sep)^{2+}] \qquad (3)$$

The iodide ion dependence was studied over the range 0—0.1 mol dm^{-3}. Assuming the equilibrium (4) ‡ we may express equations (2) and (3) as equation (5), giving equation (6).

$$I_2 + I^- \rightleftharpoons I_3^- \qquad (4)$$

$$-\,d[I_2]_T/dt = (k_0[I_2] + k_I[I_3^-])[Co(sep)^{2+}] \qquad (5)$$

$$k = \frac{k_0 + k_I K_I[I^-]}{1 + K_I[I^-]} \qquad (6)$$

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† (1,3,6,8,10,13,16,19-octa-azabicyclo[6.6.6]icosane)cobalt(II).

‡ The formation of I_2Cl^- is neglected.

Table. Rate constants ($k_{obs.}/s^{-1}$) of I_2 + $[Co(sep)]^{2+}$ reactions [a]

$[Co(sep)^{2+}]$ [b]/ 10^{-3} mol dm^{-3}	$[I_2]$ [b]/10^{-3} mol dm^{-3}	$[I^-]$ [b]/10^{-3} mol dm^{-3}	No. of determinations	$k_{obs.}/s^{-1}$
3.5	0.1	100	9 [c]	139.7 ± 3.5
3.5	0.2	100	8 [c]	139.0 ± 1.9
3.0	0.1	100	8 [c]	129.6 ± 5.0
3.0	0.2	100	8 [c]	127.6 ± 5.1
2.5	0.1	100	10 [c]	97.2 ± 9.0
2.5	0.2	100	10 [c]	96.1 ± 1.9
2.0	0.1	100	6 [d]	82.3 ± 1.7
2.0	0.2	100	6 [d]	73.8 ± 1.3
1.5	0.1	100	8 [d]	52.3 ± 2.4
1.5	0.05	100	5 [d]	59.0 ± 1.3
1.0	0.1	100	11 [d]	33.7 ± 4.9
1.0	0.05	100	8 [d]	45.8 ± 1.6
0.5	0.05	100	4 [d]	18.8 ± 0.4
0.5	0.05	14.3	9 [d]	20.3 ± 1.2
0.5	0.05	5.0	9 [d]	22.2 ± 1.1
0.25	0.025	3.0	6 [e]	14.3 ± 0.9
0.25	0.025	1.5	7 [e]	13.9 ± 1.1
0.25	0.025	1.0	6 [e]	15.2 ± 3.2
0.25	0.025	0.5	10 [e]	11.4 ± 1.2
0.25	0.025	0.25	6 [e]	13.1 ± 0.8
0.25	0.025	0.1	7 [e]	13.9 ± 1.7
0.25	0.025	0	8 [e]	14.8 ± 1.5
0.5	0.05	0	8 [d]	28.1 ± 5.8

[a] T = 25 °C, $[I^-] + [Cl^-] = 0.10$ mol dm^{-3}. [b] Initial total stoicheiometric concentration after mixing. [c] λ = 440 nm. [d] λ = 400 nm. [e] λ = 350 nm.

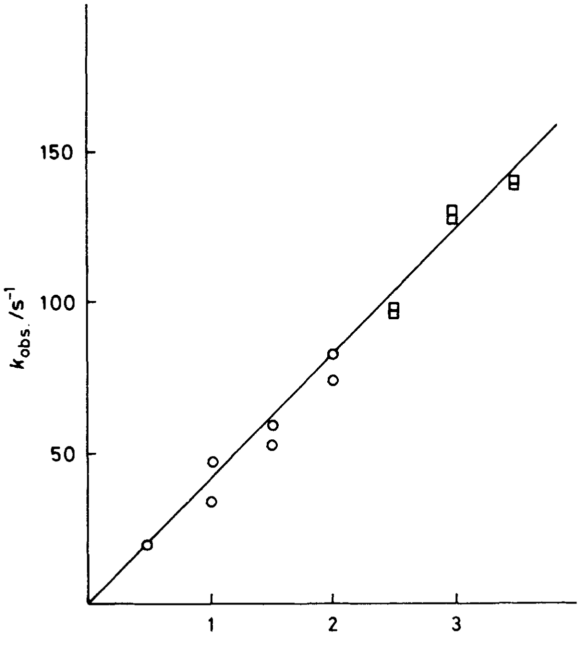

Figure 1. Cobalt(II) dependence of $k_{obs.}$; $[Co(sep)^{2+}]_0$ = initial concentration. Points are drawn from experiments at wavelength λ = 440 (○) and 400 nm (□)

Using K_I = 676 dm^3 mol^{-1},[5] a plot of $k(1 + K_I[I^-])$ *versus* $[I^-]$ is satisfactorily linear (Figure 2). Least-squares fitting gives $k_0 = (5.9 \pm 0.8) \times 10^4$ dm^3 mol^{-1} s^{-1}, and $k_I = (3.93 \pm 0.09) \times 10^4$ dm^3 mol^{-1} s^{-1}, at 25 °C and I = 0.1 mol dm^{-3} (KCl).

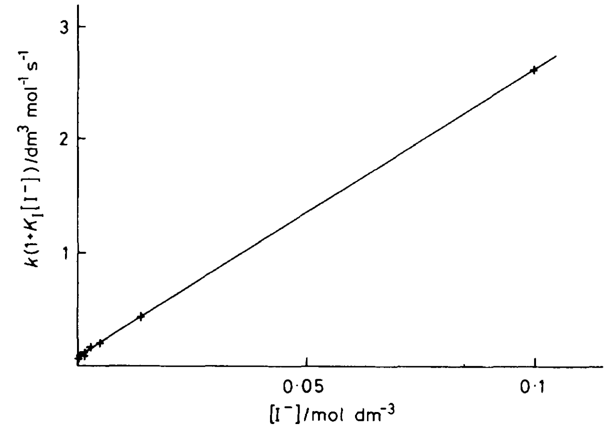

Figure 2. Iodide-ion dependence of k. The line is drawn according to equation (6) of the text with $k_0 = 5.9 \times 10^4$ dm^3 mol^{-1} s^{-1}, $k_I = 3.93 \times 10^4$ dm^3 mol^{-1} s^{-1}, and K_I = 676 dm^3 mol^{-1}

Discussion

A mechanism consistent with the rate law is given by equations (7)—(9), where steps (7) and (8) are rate-determining. The

$$I_2 + [Co(sep)]^{2+} \xrightarrow{k_0} I_2^- + [Co(sep)]^{3+} \quad (7)$$

$$I_3^- + [Co(sep)]^{2+} \xrightarrow{k_I} I_2^- + I^- + [Co(sep)]^{3+} \quad (8)$$

$$I_2^- + [Co(sep)]^{2+} \twoheadrightarrow 2I^- + [Co(sep)]^{3+} \quad (9)$$

intermediate I_2^- has been postulated in many reactions of I_2 with one-electron reductants and of I^- with one-electron oxidants.[6] An alternative to step (9) would be step (10) but

$$I_2^- + I_2^- \longrightarrow I_2 + 2I^- \quad (10)$$

this has $k = 6.7 \times 10^9$ dm^3 mol^{-1} s^{-1} at pH 6.5 [7] and in view of the low concentration of I_2^- it is probably too slow to compete. The iodine species on the right-hand sides of equations (8) and (9) are written as $I_2^- + I^-$ and $2I^-$ rather than I_3^{2-} and I_2^{2-} on the assumption that the dianions would dissociate rapidly on the time-scale of the rate-determining step. The equilibrium (11) is also attained rapidly, but it has

$$I_2^- \rightleftharpoons I^- + I \quad (11)$$

$K = 0.8 \times 10^{-5}$ mol dm^{-3},[8] and hence is displaced well to the left at all but the lowest I^- concentrations used in this work. A value of k_0 can be estimated by applying a correlation previously found by Woodruff and Margerum [6] for rate constants k_{12} of one-electron reductions of I_2 by various metal complexes, M^{III}. This may be expressed by equations (12) and (13), where k_{11} and k_{22} are self-exchange rate constants for the couples

$$\log k_{12} = \tfrac{1}{2}\log k_{11} + \tfrac{1}{2}\log k_{22} + \tfrac{1}{2}\log f + m\log K_{12} \quad (12)$$

$$\log f = (\log K_{12})^2/4\log (k_{11}k_{22}/Z^2) \quad (13)$$

$M^{III/II}$ and I_2/I_2^-, K_{12} is the equilibrium constant corresponding to k_{12}, and Z is the encounter rate constant for uncharged species. Woodruff and Margerum found m = 0.43 rather than the value of 0.5 required by Marcus' theory.[9] In the present case, taking $\log k_{11}$ = 0.71,[1] $\log k_{22}$ = 4.93,[6] $\log K_{12}$ = 6.95 {taking $E^\ominus$ for $[Co(sep)]^{3+/2+}$ = −0.30 V [1] and $E^\ominus$ for I_2/I_2^- = 0.11 V [10]} and $\log Z$ = 11.0, we have log

$f = -0.74$ and $\log k_{12} = 5.4$, as compared with the experimental value of 4.8.

The ratio k_I/k_0 found in this work may be compared with corresponding ratios for reactions with three other reducing agents, *viz.*: $[Co(edta)]^{2-}$ (edta = ethylenediaminetetra-acetate), 0.06;[6] $[Co(cdta)]^{2-}$ (cdta = *trans*-cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetate), 0.3;[6] $[Co(sep)]^{2+}$, 0.7; Fe^{2+}, 1.7.[11] The higher values for positively charged reactants could be accounted for by differences in the work terms, the reaction with I_3^- being favoured by increased stability of the M^{III}–I_3^- ion pair.

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