

Figure 3. Crystal reacted with potassium at 925 °C for 15 min, showing approximately 13-Å fringes thought to be TTB (lower left) and tungsten trioxide fringes.

the carbon film that supports the crystal seriously reduces the quality of the image.

There is also clear evidence of the formation of tungsten bronze crystals by a vapor reaction. Needlelike or prismatic crystals are found among the tungsten trioxide fragments in the ratio of about 1:100, in a sample heated to 480 °C for 69 h. High-resolution transmission electron microscope images of these needles appear to be *a*-axis projections of both HTB and TTB crystals. This is a growth habit reported for TTB.¹⁴ Hexagonal potassium tungsten bronzes are more often flakes,¹⁵ though Rb_xWO_3 is prismatic.¹⁶ Since these crystals were only a few hundred angstroms wide and 1 μm long, it was not possible to orient them along other axes for an unambiguous identification. The presence of crystals of the appropriate colors and compositions for HTB and TTB in this sample was confirmed by optical microscopy and microprobe analysis.

Discussion

At least two distinct reaction mechanisms operate to produce the bronze phase. One mechanism is vapor growth of needlelike single crystals. The focus of this study is, however, on the second mechanism, a potassium vapor attack on WO_3 crystals.

The interface pictured in Figure 3 is not likely to have been formed by vapor-phase epitaxial growth of TTB on the tungsten trioxide substrate, because of the lack of a sharp crystalline interface. Assuming that the correct orientation match between the TTB and tungsten trioxide is not coincidental, the best explanation would appear to be that potassium bonded to the surface of the crystal, and diffusing from the lower left and moving right, converted the tungsten trioxide to bronze in a surface reaction. The disordered region at the interface is in transition from tungsten trioxide to bronze, as the TTB boundary moves right.

From this study it is clear that whatever process forms the bronzes is kinetically aided by the ease of penetration of potassium along {100} planes. It is also shown that a reaction that appears

to be a simple moving boundary by optical microscopy may actually be more complex.

Acknowledgment. Support by the National Science Foundation through research Grant DMR 81-08306 is gratefully acknowledged. We also thank John Holloway for the use of the optical microscope and his group for instruction in its use. Use of the high-resolution microscope facility was possible through NSF support through Grant DMR-8306501.

Registry No. K, 7440-09-7; WO_3 , 1314-35-8; K_xWO_3 , 37349-36-3.

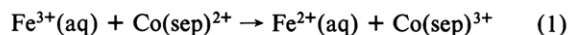
Contribution from the School of Chemical Sciences,
University of East Anglia, Norwich NR4 7TJ, England

Kinetics of the Electron-Transfer Reaction between the Hexaquoiron(III) Ion and the Cobalt(II) Sepulchrate Ion

Nigel Rudgwick-Brown and Roderick D. Cannon*

Received May 25, 1983

As part of a study of electron-transfer kinetics of polynuclear complexes, we have examined the reactions of aqueous iron(III) with cobalt(II) sepulchrate,^{1,2} with a view to detecting reaction pathways of the type $\text{Fe}_x(\text{OH})_y^{(3x-y)+} + \text{Co}(\text{sep})^{2+}$.³ In fact, reactions of hydroxo species proved to be too rapid to follow at the iron concentrations required to achieve significant polymerization. Acceptable data were however obtained for reaction 1, and these are briefly reported.



Cobalt(II) sepulchrate solutions were prepared by zinc reduction of cobalt(III) sepulchrate^{1b} in neutral aqueous solution under nitrogen and adjusted to the required acidity and ionic strength immediately before use. Measurements were made in the Aminco-Morrow stopped-flow apparatus with precautions against air oxidation.⁴ A constant ionic medium was maintained by using Cr^{3+} to balance variations in Fe^{3+} concentration and Li^+ to balance H^+ . Reactions were carried out with Co/Fe ratios initially in the range 1.25–1.67, but data were taken in the third to fifth half-lives of the reaction (absorbance change typically 0.05) and pseudo-first-order kinetics were observed. Constancy of $k_{\text{obsd}}/([\text{Co}^{II}]_0 - [\text{Fe}^{III}]_0)$ and lack of $[\text{H}^+]$ dependence (Table I) indicate the rate law⁵

$$-d[\text{Co}(\text{sep})^{2+}]/dt = k[\text{Fe}^{3+}][\text{Co}(\text{sep})^{2+}] \quad (2)$$

$k = (1.2 \pm 0.1) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 0 °C, $k = (1.75 \pm 0.2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C, and $I = 0.23 \text{ M}(\text{LiNO}_3)$.

The structure of the sepulchrate ligand ensures that reaction 1 is outer sphere. Rates of outer-sphere reactions are usually explained in terms of the Marcus equations⁸

$$\log k = \frac{1}{2}(\log k_{11} + \log k_{22} + \log K + \log f) \quad (3)$$

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

where K is the equilibrium constant of reaction 1, k_{11} and k_{22} are rate constants of the self-exchange reactions, and Z is a limiting rate constant, corresponding to a diffusion-controlled encounter

(14) Magnéli, A. *Ark. Kem.* **1949**, *1*, 213.

(15) Magnéli, A. *Acta Chem. Scand.* **1953**, *7*, 315.

(16) Wanlass, D. R.; Sienko, M. J. *J. Solid State Chem.* **1975**, *12*, 362.

(1) (a) Creaser, I. I.; Harrowfield, J. MacB.; Herlt, A. J.; Sargeson, A. M.; Springborg, J.; Geue, R. J.; Snow, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 3181. (b) Harrowfield, J. MacB.; Herlt, A. J.; Sargeson, A. M.; Del Donno, T. *Inorg. Synth.* **1982**, *20*, 85.

(2) Sargeson, A. M. *Chem. Br.* **1979**, *15*, 23.

(3) sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane.

(4) Rudgwick-Brown, N.; Cannon, R. D. *J. Chem. Soc., Dalton Trans.* **1984**, 479.

(5) Under the conditions used, not more than 0.004% of the iron(III) is present as $\text{Fe}_2(\text{OH})_2^{4+}$ (calculated from data of ref 7, Table 2).

(6) Baes, C. F.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley: New York, 1976; Table 10.18.

(7) Sillén, L. G.; Martell, A. E. "Stability Constants of Metal-Ion Complexes"; The Chemical Society: London 1964; Spec. Publ. No. 17.

(8) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

Table I. Rate Data for Reaction 1^a

$T, ^\circ\text{C}$	$a, ^\circ\text{C}$ 10^{-3} M	$b, ^\circ\text{C}$ 10^{-3} M	$[\text{H}^+],$ 10^{-3} M	no. of runs	$k_{\text{obsd}}, \text{s}^{-1}$	$k, ^d$ $10^5 \text{ M}^{-1} \text{s}^{-1}$
2.0	12.5	7.5	50.0	7	571 ± 68	1.14
2.0	12.5	10.0	50.0	9	294 ± 33	1.15
2.0	12.5	11.25	50.0	8	165 ± 14	1.32
6.0	12.5	11.25	50.0	7	162 ± 14	1.30
9.0	12.5	11.25	50.0	9	177 ± 66	1.42
20.0	12.5	11.25	50.0	9	202 ± 20	1.61
2.0	12.5	11.25	11.25	15	138 ± 16	1.10

^a $\lambda = 460 \text{ nm}$. Aqueous solution, $[\text{Fe}^{3+}(\text{aq})]_0 + [\text{Cr}^{3+}(\text{aq})] = 0.0125 \text{ M}$, $[\text{H}^+] + [\text{Li}^+] = 0.10 \text{ M}$, $[\text{Zn}^{2+}] = 0.00625 \text{ M}$, total ionic strength 0.23 M (NO_3^-). ^b $\pm 0.2^\circ\text{C}$. ^c Initial concentrations. $a = [\text{Co}(\text{sep})^{2+}]_0$, $b = [\text{Fe}^{\text{III}}]_0$. ^d $k = (k_{\text{obsd}}/(a - b))(1 + K_a/[\text{H}^+])$; $K_a = [\text{FeOH}^{2+}][\text{H}^+]/[\text{Fe}^{3+}]$; $\text{p}K_a = 3.5, 3.4, 3.2, 2.9$ at $T = 2, 6, 9, 20^\circ\text{C}$, respectively, estimated from the ionic strength dependence of ref 6 and the temperature dependence of ref 7.

without electron transfer.⁹ The value of Z is however expected to depend on the charge product of the reacting ions. At present, electron-transfer reactions of cationic complexes seem to fall into two categories. On the one hand rates of reactions mostly involving ruthenium ammines, various polypyridyl complexes, and excited-state species agree reasonably well with eq 3 and 4 when Z is estimated on the basis of the Debye equation,^{10a} with or without appropriate modifications for high ionic strength (typically $\log Z = 9\text{--}11$ at $I = 0.1\text{--}1 \text{ M}$).^{11,12} On the other hand, reactions

between two aquo or two oxo complexes or an aquo and an oxo complex are consistent with lower limiting rates, sometimes as low as $\log Z = 6$.^{13–15} It has been held that differences in the energy of cation–cation association may account for the difference in behavior,¹⁴ though there are difficulties with the ionic diffusion model,¹⁶ and more recently, factors such as nonadiabaticity have been emphasized.^{12,17–20} For the present reaction we have $\log k_{11} = 0.71$,¹ $\log k_{22} = 0.62$,²¹ and $\log K = 17.80$.²² Taking $\log Z = 10$, we obtain $\log k = 7.5$; but with $\log Z = 6$, $\log k = 5.9$, compared with the experimental value, $\log k = 5.2$. It appears therefore that this reaction of the sepulchrate ion belongs to the second group of reactions, being subject to a limiting rate similar to that of the majority of aquo ion electron transfers.

Acknowledgment is made to the Royal Society for support of this work. N.R.-B. held a Science Research Council Research Studentship.

Registry No. $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, 15377-81-8; $\text{Co}(\text{sep})^{2+}$, 63218-22-4.

- (9) More precisely, $Z = [8\pi k_B T(m_1 + m_2)/m_1 m_2]^{1/2} L r^2$, where m_1 and m_2 are the masses of the reacting species and r is the distance between them at the moment of collision.^{10b}
- (10) Cannon, R. D. "Electron Transfer Reactions"; Butterworth: London, 1980: (a) p 100; (b) p 222.
- (11) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.
- (12) Balzani, V.; Scandola, F.; Orlandi, G.; Sabbatini, N.; Indelli, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 3370.

- (13) Hyde, M. R.; Davies, R.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1972**, 1838.
- (14) (a) Ekstrom, A.; MacLaren, A. B.; Smythe, L. E. *Inorg. Chem.* **1975**, *14*, 2899. (b) *Inorg. Chem.* **1976**, *15*, 2853. (c) *Inorg. Chem.* **1977**, *16*, 1032.
- (15) Falcinella, B.; Felgate, P. D.; Laurence, G. S. *J. Chem. Soc., Dalton Trans.* **1975**, 1.
- (16) in some cases^{11,14b} ionic strength dependence of the rate is opposite to the Debye–Hückel prediction. In the case of the reaction $\text{Co}^{3+} + \text{U}^{3+}$, the rate is close to the calculated diffusion limit and the ionic strength dependence fits the modified Debye–Hückel equation, but other reactions with different charge products approach the same limit.^{14c}
- (17) Brunswig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 5798.
- (18) Newton, M. D. *Int. J. Quantum Chem., Symp.* **1980**, *14*, 363.
- (19) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 741.
- (20) Buhks, E.; Bixon, M.; Jortner, J. *J. Phys. Chem.* **1981**, *85*, 3759.
- (21) Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536. From data of: Silverman, J. W.; Dodson, R. W. *J. Phys. Chem.* **1952**, *56*, 846.
- (22) Calculated from $E^\ominus(\text{Co}(\text{sep})^{3+/2+}) = -0.30 \text{ V}^1$ and $E^\ominus(\text{Fe}^{3+/2+}) = 0.745 \text{ V}^{12}$.