

Kinetics of Iron(II) Reduction of *cis*-Bis(iminodiacetato)- cobaltate(III) & Bis(Malonato)- ethylenediaminecobaltate(III) in Methanol-Water Mixtures

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The kinetics of Fe(II) reduction of *cis*-bis(iminodiacetato)cobaltate(III) has been studied in aqueous perchlorate medium at $I = 1.00 \text{ mol dm}^{-3}$ (LiClO_4) and 30°C in the $[\text{H}^+]$ range $0.1\text{--}0.7 \text{ mol dm}^{-3}$. The reaction is found to be second order and independent of $[\text{H}^+]$. In methanol-water mixtures, the rates of iron(II) reduction of *cis*-bis(iminodiacetato)cobaltate(III) and bis(malonato)ethylenediaminecobaltate(III) increase with increase in the mol fraction of methanol, probably as a result of structural changes in the inner sphere of Fe(II) or/and an increase in the Fe(II)-complex precursor equilibrium constant in methanol, besides the increased $[\text{H}^+]$ -assisted generation of the aquomalonato species.

It has been observed that the reductions of carboxylato complexes of cobalt(III) exhibit acid independent, retarded, and catalysed pathways¹⁻⁵. Numerous literature reports over the last two decades are available on electron transfer reactions between metal ions in solution⁶. However, very few papers have appeared on reactions between different metal ions in nonaqueous solvents⁷⁻⁹. Watts *et al.*⁹ have reported on the Fe(II) reduction of halogenopentamminecobalt(III) complexes in aprotic solvents. However, no systematic comparison has been made on the $[\text{H}^+]$ effects on reduction rates in mixed solvents. The effect of $[\text{H}^+]$ on Fe(II) reduction rates has been investigated in this laboratory^{4,10,11} and the title investigation is in continuation of such studies.

dl-Sodium bis(malonato)ethylenediaminecobaltate(III) monohydrate, $\text{Na}[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$ and *cis*-(N)-sodium bis(iminodiacetato)cobaltate(III), $\text{Na}[\text{Co}(\text{NH}(\text{CH}_2\text{CO}_2)_2)_2]$, were prepared and purified by literature methods^{12,13} and their purity confirmed by UV-vis, IR and conductivity measurements and elemental analyses. $\text{Fe}(\text{ClO}_4)_2$ was prepared by the method used by Wada *et al.*¹⁴ and stored under nitrogen.

Kinetic studies were carried out with 20-fold and 5-fold excess of Fe(II) in water and in methanol-water mixtures, respectively. Preequilibrated solutions of the reactants were mixed under oxygen-free conditions and the cells used were carefully sealed using serum caps and flushed with nitrogen. Reactions were followed spectrophotometrically at 540 nm for the malonato complex and at 560 nm for the *cis*-bis(iminodiacetato) complex employing a Carl-Zeiss UV-vis recording spectrophotometer. Reactions were carried out in perchlorate medium and the ionic strength was adjusted to 1.00 mol dm^{-3} with lithium perchlorate.

Pseudofirst order rate constants for the kinetic runs in aqueous medium were calculated from the slopes of $\log(A_t - A_\infty)$ versus time plots, where A_t and A_∞ are the absorbances at time t and after completion of reaction. Excellent linear plots were obtained for at least three half-lives. Second order rate constants were calculated as $k_{\text{obs}}[\text{Fe(II)}]^{-1}$. Rate constants in methanol-water mixtures were calculated using the equation $kt = (a - b)^{-1} \ln b(a - x)a^{-1}(b - x)^{-1}$ where $a = [\text{Fe(II)}]$, $b = [\text{Complex}]$, $b - x = [\text{unreacted complex}]$ and $a - x = [\text{unreacted Fe(II)}]$.

The stoichiometry of the reactions were established spectrophotometrically by determining Fe(III) and Co(II) present in the reaction mixture after completion of the reaction. Cobalt(II) was estimated as CoCl_4^{2-} in the presence of excess of HCl ¹⁵. The ratio of Fe(III) to Co(II) was found to be 1 : 1, indicating a stoichiometry of 1 : 1.

The k values for the Fe(II) reduction of Co(ida)_2^- at 30°C and $I = 1.00 \text{ mol dm}^{-3}$ in the $[\text{H}^+]$ range of $0.1\text{--}0.7 \text{ mol dm}^{-3}$ in water medium show little dependence on $[\text{H}^+]$ (Table 1). The activation parameters are: $\Delta H^\ddagger = 58.9 \pm 4.1 \text{ kJ mol}^{-1}$; and $\Delta S^\ddagger = -122.0 \pm 15.2 \text{ JK}^{-1} \text{ mol}^{-1}$. The k values for the Fe(II) reduction of $[\text{Co(ida)}_2]^-$ and $[\text{Co(en)(mal)}_2]^-$ in methanol-water mixtures in the $[\text{H}^+]$ range of 0.1 to 0.5 mol dm^{-3} and in $0.40n$ ($n = \text{mol fraction}$) methanol, and the k values at $[\text{H}^+] = 0.5 \text{ mol dm}^{-3}$ in $0.10\text{--}0.51n$ methanol at 30°C and $I = 1.00 \text{ mol dm}^{-3}$ are presented in Table 2. The rate constant for the malonato complex at $[\text{H}^+] = 0.50 \text{ mol dm}^{-3}$ increases in the range of 0.67×10^{-2} to $8.91 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ with increase in mol fraction of methanol from 0.10 to 0.51 . The corresponding increase, for bis(iminodiacetato)cobaltate(III) at $[\text{H}^+] = 0.5 \text{ mol dm}^{-3}$ is from 3.11×10^{-3} to $11.95 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. In $0.40n$ methanol and in the range $0.1 < [\text{H}^+] < 0.5 \text{ mol dm}^{-3}$, the rate constants increase from 1.30

Table 1—Rate Constants for Fe(II) Reduction of $\text{Co}(\text{ida})_2^-$ and $\text{Co}(\text{en})(\text{mal})_2^-$ in Water at Different $[\text{H}^+]$

$[I = 1.0 \text{ mol dm}^{-3}$; temp. = $30 \pm 0.1^\circ\text{C}$]

$[\text{H}^+] \times 10^4$ mol dm^{-3}	$10^3 k$ $(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ $[\text{Co}(\text{ida})_2^-]^a$	$10^4 k$ $(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ $[\text{Co}(\text{en})(\text{mal})_2^-]^b$
1.0	1.47	4.64
2.0	1.40	8.54
3.0	1.54	13.25
4.0	—	17.02
5.0	1.62	18.84
6.0	1.97	—
7.0	1.97	—
0.5	2.41 ^c , 3.41 ^d , 5.19 ^e , 7.12 ^f , 10.21 ^g , 15.10 ^h	

^a $[\text{Co}(\text{ida})_2^-] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{Fe}(\text{II})] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$; ^b $[\text{Co}(\text{en})(\text{mal})_2^-] = 7.8 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{Fe}(\text{II})] = 1.57 \times 10^{-1} \text{ mol dm}^{-3}$; (^{c-h}) 35, 40, 45, 50, 55 and 60°C respectively.

Table 2—Rate Constants for Fe(II) Reduction of $\text{Co}(\text{ida})_2^-$ and $\text{Co}(\text{en})(\text{mal})_2^-$ in Methanol-Water Mixtures at Different $[\text{H}^+]$

$[I = 1.0 \text{ mol dm}^{-3}$; temp. = $30 \pm 0.1^\circ\text{C}$;

$[\text{Complex}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$;

$[\text{Fe}(\text{II})] = 5.5 \times 10^{-2} \text{ mol dm}^{-3}$]

$[\text{H}^+] \times 10^4$ mol dm^{-3}	n^a	$10^3 k$ $(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ $[\text{Co}(\text{ida})_2^-]$	$10^2 k$ $(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ $[\text{Co}(\text{en})(\text{mal})_2^-]$
1.0	0.4	4.10	1.30
2.0	0.4	4.19	1.39
3.0	0.4	5.82	2.46
4.0	0.4	6.33	3.38
5.0	0.1	9.51	4.20
5.0	0.10	3.11	0.67
	0.16	3.58	—
	0.23	4.81	1.72
	0.31	6.61	2.35
	0.40	9.45	4.25
	0.46	—	7.31
	0.51	11.95	8.91

^a n —mol fraction of methanol.

$\times 10^{-2}$ to $4.20 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the malonato and from 4.10×10^{-3} to $9.51 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the bis(iminodiacetato) complex. The rates of Fe(II) reduction in methanol-water mixtures are in the order $\text{Co}(\text{en})(\text{mal})_2^- > \text{Co}(\text{ida})_2^- > \text{Co}(\text{ida})_2^-$, while the order is reversed in water medium, at $[\text{H}^+] \leq 0.3 \text{ mol dm}^{-3}$.

The second order rate constants, k , for the Fe(II) reduction of *cis*-bis(iminodiacetato)cobaltate(III) show only a slight $[\text{H}^+]$ -dependence in the $[\text{H}^+]$ range of 0.10–0.70 mol dm^{-3} . These reactions are expected to proceed through the formation of an inner sphere

precursor between the oxidant and the reductant. The protonation of $\text{Co}(\text{ida})_2^-$ is unlikely as the rate is $[\text{H}^+]$ -independent. The values may be compared with the value for Fe(II) reduction of $\text{Co}(\text{edta})^-$ (edta = ethylenediaminetetraacetato), which at 25°C is found to increase from 8.0×10^{-4} to $3.6 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ as $[\text{H}^+]$ is increased from 0.1 to 1.0 mol dm^{-3} (ref. 16). This direct $[\text{H}^+]$ dependence is accounted for in terms of a side reaction in which $\text{Co}(\text{edta})^-$ is protonated to yield $[\text{Co}(\text{edtaH})\text{H}_2\text{O}]$ which oxidises Fe(II) more rapidly. As $\text{Co}(\text{ida})_2^-$ and $\text{Co}(\text{edta})^-$ are structurally similar, this difference in reactivity may be a result of the greater basicity of the carboxylato groups in the latter.

Iron(II) reduction of both the complexes occurs more rapidly in methanol-water mixtures than in water (Table 1). At $[\text{H}^+] = 0.5 \text{ mol dm}^{-3}$ the reduction of the malonato complex in 0.51 *n* methanol is 50 times faster than its reduction in water. Under identical conditions $\text{Co}(\text{ida})_2^-$ is reduced 7.5 times faster in aqueous methanol than in water. The steady increase in rate of reduction with increase in mol fraction of methanol in the reaction medium may be due to successive replacement of water molecules from the fast coordination sphere of iron(II) by methanol molecules, leading to the formation of mixed ligand complexes⁷.

Besides, the Fe(II)-Co(III) precursor formation should be more favourable with increase in methanol content of the medium as the solvent dielectric constant decreases. At $[\text{H}^+] = 0.50 \text{ mol dm}^{-3}$, $k(\text{malonato})/k(\text{ida})_2$ values in 0.51 *n* methanol and in water alone are 7.5 and 1.1 respectively. As has been observed earlier, the protonation of $\text{Co}(\text{en})(\text{mal})_2^-$ is more significant in methanolic solvent leading to a 20-fold increase in rate from water to 0.40 *n* methanol and a 50-fold increase in 0.51 *n* methanol; while the increase in rate under similar conditions is relatively insignificant for $\text{Co}(\text{ida})_2^-$. The $[\text{H}^+]$ -catalysis is due to the generation of the highly reactive oxidant species, $\text{Co}(\text{en})(\text{mal})(\text{H}_2\text{O})(\text{OOCCH}_2\text{COOH})$ (ref. 4), and the MeOH catalysis is due to extensive protonation in methanolic solvent.

References

- 1 Ohashi K, *Bull chem Soc Japan*, **49** (1976) 1006.
- 2 Hwang C & Haim A, *Inorg Chem*, **9** (1970) 500.
- 3 Ohashi K, *Bull chem Soc Japan*, **45** (1972) 3093.
- 4 Viswanathan R & Vijayaraghavan V R, *Indian J Chem*, (in Press).
- 5 Sulfab Y & Al-Obadie M S, *Polyhedron*, **1** (1982) 149.
- 6 Haim A, *Progress in Inorganic chemistry*, **30** (1983) 273.
- 7 Ohashi K, Yamamoto K, Hirako I & Kurimura Y, *Bull chem Soc Japan*, **45** (1972) 1712.
- 8 Ohashi K, Yamamoto K, Suzuki T & Kurimura Y, *ibid.*, **44** (1971) 3363.
- 9 (a) Matthews B A & Watts D W, *Inorg Chim Acta*, **11** (1974) 127.
(b) Matthews B A & Watts D W, *Aust J Chem*, **29** (1976) 97.
(c) Matthews B A, Turner J V & Watts D W, *ibid.*, **29** (1976) 551.

- (d) Beckham K R & Watts D W, *ibid*, **32** (1979) 1425.
- (e) Wescot T J & Watts D W, *ibid*, **32** (1979) 2139.
- (f) Spiccia L & Watts D W, *ibid*, **32** (1979) 2275.
- 10 Balasubramanian P N & Vijayaraghavan V R, *Inorg Chem Acta*, **38** (1980) 49.
- 11 Balasubramanian P N & Vijayaraghavan V R, *Inorg Chim Acta*, **53** (1981) 1209.
- 12 Dwyer F P, Reid I K & Garvan F L, *J Am chem Soc*, **83** (1961) 1285.
- 13 Mori M, Shibata M, Kyuno E & Okubo Y, *Bull chem Soc Japan*, **31** (1958) 940.
- 14 Wada G & Reynolds W, *Inorg Chem*, **5** (1966) 1354.
- 15 Kitson R E, *Anal Chem*, **22** (1950) 664.
- 16 Wood P B & Higginson W C E, *J Chem Soc*, (1965) 2116.