Inorg. Chem. **1980**, *19*, 2897–2898 **2897**

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Thermodynamics of the Formation of Tris(malonato)cobaltate(III) and Tris(carbonato)cobaltate(III)

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Received February 21, 1978

The formal oxidation–reduction potential of the couple $Co(mal)_3^{3-} + e^- = Co(mal)_3^{4-}$ was found as 0.741 V at ionic strength 1.0 M with potassium chloride as supporting electrolyte. The thermodynamics of the formation of tris(malonato)cobaltate(III) was calculated as log β_3 = 23, and the overall formation constant for tris(carbonato)cobaltate(III) was given the value log β_3 = 29.

Several values have been reported for the formal potential of the Co^{III}/Co^{II} couple in aqueous media;[1-3] the high value of 1.93 V proposed by Johnson and Sharpe is now accepted.[4] Complexing cobalt with different ligands other than water is known to lower the formal potential considerably.[3] Chadwick and Sharpe[5] have given reasons for the belief that, for the $Co(CN)_6^{3-} + e^- = Co(CN)_5^{3-} + CN^-$ system, the formal potential may be as low as −0.8 V.

In connection with our kinetic work[6] we have measured the formal potentials of the Co^{III}/Co^{II} couples as modified by the malonate and carbonate ligands and herein report the results of these experiments.

Results and Discussions

The fact that the oxidizing agents hydrogen peroxide and lead dioxide oxidize cobalt(II) to cobalt(III) in the presence of carbonate or malonate suggests that these ligands lower the standard potential of the Co^{III}/Co^{II} couple to a value of about 1.0 V or less (see eq 1–3).

$$PbO_2 + 4H^+ + 2e^- = Pb^{2+} + 2H_2O \qquad E° = 1.0\ V \qquad (1)$$

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O \qquad E° = 1.77\ V \qquad (2)$$

$$O_2 + 4H^+ + 4e^- = 2H_2O \qquad E° = 1.23\ V \qquad (3)$$

The standard potentials in eq 1–3 indicate that Co(II) in the presence of these ligands should also be oxidized to Co(III), but, as this is not observed, we suggest that kinetic factors are involved in the failure of air or pure oxygen to oxidize cobalt(II) in carbonate and malonate media.

The data in Table I demonstrate the thermodynamic tendency of some of the cobalt(III) complexes.

The result we obtained for the tris(malonato)cobaltate(III) couple is higher than that for the tris(oxalato)cobaltate(III) couple as given by Higgenson and co-workers.[7] This can be explained as the malonate ligand is less basic than the oxalate.

Table I. Formal Redox Potentials for Some Co^{III}/Co^{II} Couples[a]

oxidized form	$E°$, V	ref
$Co(mal)_3^{3-}$	0.741	this work
$Co(ox)_3^{3-}$	0.567	7
$Co(CN)_6^{3-}$	0.473	5
$Co(H_2O)_6^{3+}$	1.930	4

[a] μ = 1.0 M; T = 25 °C.

Table II

complex	overall formn const, M^{-3}	ref
$Fe(mal)_3^{3-}$	10^{16}	11
$Co(mal)_3^{3-}$	10^{23}	this work
$Co(CO_3)_3^{3-}$	10^{29}	this work
$Co(ox)_3^{3-}$	10^{31}	7
$Fe(ox)_3^{3-}$	10^{20}	12

Scheme I

$$\begin{tikzcd}
Co(H_2O)_6^{3+} + e^- \arrow[r, "E° = 1.93\ V"] \arrow[d, "K'''"] & Co(H_2O)_6^{2+} \arrow[d, "K'' = 10^3"] \\
Co(mal)_3^{3-} + e^- \arrow[r, "E° = 0.74\ V"] & Co(mal)_3^{4-}
\end{tikzcd}$$

Although the value for the Co^{III}/Co^{II} couple as modified by malonate is 0.74 V and is less than the couple in eq 4 and

$$Fe^{3+} + e^- = Fe^{2+} \qquad E° = 0.77\ V \qquad (4)$$

because ferrous ion can readily reduce cobalt(III) malonate, then it is likely that the reaction is not simply as in eq 5 but

$$Co(mal)_3^{3-} + Fe^{2+} = Co(mal)_3^{4-} + Fe^{3+} \qquad (5)$$

that the reduction of $Co(mal)_3^{3-}$ ion is similar to that of the $Co(ox)_3^{3-}$ ion. That is, one malonate ligand is transferred to the iron through the formation of a bridged intermediate. This was confirmed by the rapid formation and disappearance of iron(III) malonate (λ_{max} = 315 nm).[8] Moreover, reduction of tris(malonato)cobaltate(III) with chromium(II) and tris(oxalato)cobaltate(III) with iron(II) has been shown to occur with transfer of one malonate or one oxalate ligand to chromium(II) or iron(II), respectively.[9,10]

The reaction therefore becomes

$$Co(mal)_3^{3-} + Fe^{2+} = Co(mal)_2(H_2O)_2^{2-} + Fe(mal)^+(aq) \qquad (6)$$

and the relevant Fe^{III}/Fe^{II} couple is changed into $Fe(mal)^+ + e^- = Fe^{2+} + mal^{2-}$ which would have a small $E°$. The relationship between $E°$ for the hydrated ions and that for the malonate complexes is shown in Scheme I.

In this scheme K''' and K'' are the overall formation constants for the tris(malonato) complexes of cobalt(II) and cobalt(III), respectively. The standard free energy changes of different processes are given by

$$-\Delta G = nEF = RT \ln K = 2.3RT \log K \qquad (7)$$

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[1] Noyes, A. A.; Deahl, T. J. *J. Am. Chem. Soc.* **1937**, *59*, 1337.
[2] Lamb, A. B.; Larson, A. T. *J. Am. Chem. Soc.* **1920**, *42*, 2024.
[3] Latimer, W. M. "The Oxidation State of the Elements and Their Potentials in Aqueous Solution"; Prentice-Hall: Englewood Cliffs, N.J., 1952.
[4] Johnson, D. A.; Sharpe, A. G. *J. Chem. Soc.* **1964**, 3490.
[5] Chadwick, B. M.; Sharp A. G. *Adv. Inorg. Chem. Radiochem.* **1966**, *8*, 83, 130.
[6] Sulfab, Y.; Al-Obadie, M. S.; Al-Salem, N. A. *Z. Phys. Chem.* (*Wiesbaden*) **1975**, *94*, 77–82.
[7] Hin-Fat, L.; Higginson, W. C. E. *J. Chem. Soc. A* **1967**, 298.
[8] Al-Obadie, M. S., unpublished work.
[9] Edward, J. D.; Sulfab, Y.; Sykes, A. G. *Inorg. Chem.* **1975**, *14*, 1474.
[10] Halm, A.; Sutin, N. *J. Am. Chem. Soc.* **1966**, *88*, 5344.
[11] Schaup, W. B.; Laitinen, H. A.; Bailer, J. C., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 5868.
[12] *Chem. Soc., Spec. Publ.* **1964**, *No. 17*.

0020-1669/80/1319-2897$01.00/0

Scheme II

$$\begin{tikzcd}
\mathrm{Co(H_2O)_6}^{3+} + e^- \arrow[r, "E^\circ = 1.93\ \mathrm{V}"] \arrow[d, "K'''"] & \mathrm{Co(H_2O)_6}^{2+} \arrow[d, "K'' = 10^{13}"] \\
\mathrm{Co(CO_3)_3}^{3-} + e^- \arrow[r, "E^\circ = 1.0\ \mathrm{V}"] & \mathrm{Co(CO_3)} + 2\mathrm{CO_3}^{2-}
\end{tikzcd}$$

Thus, the change in E° gives the measure of $\log K''' - \log K''$ or

$$\Delta E^\circ = 0.059/n \log (K'''/K'') \tag{8}$$

Application of the cycle (Scheme I) would give $K''' = 10^{23}$ as the overall formation constant for the tris(malonato)cobaltate(III) anion. The value of the overall formation constant of tris(malonato)cobaltate(III) is reasonable in comparison with the constants of analogous complexes (Table II). Although it is smaller than that of $\mathrm{Co(CO_3)_3}^{3-}$ and the latter is converted into $\mathrm{Co(mal)_3}^{3-}$ by the action of malonic acid, this is probably due to the instability of H_2CO_3 with respect to water and CO_2 which is evolved.

The fact that cobalt(II) carbonate suspended in sodium bicarbonate solution is oxidized by hydrogen peroxide[13] but not by air or a current of oxygen is probably of thermodynamic origin: if so, this would require that E° for the $\mathrm{Co(CO_3)_3}^{3-} + e^- = \mathrm{CoCO_3} + 2\mathrm{CO_3}^{3-}$ system is about 1.0 V.

The value E° for this system may be related to that for $\mathrm{Co(CO_3)_3}^{3-} + e^- = \mathrm{Co}^{2+} + 3\mathrm{CO_3}^{2-}$ by the solubility product of cobalt carbonate which is approximately 10^{-13} (Scheme II). Again $\Delta E^\circ = 0.059/n \log (K'''/K'')$ as shown in eq 8 where $\log K''' - 13 = 0.93/0.059$, i.e., $K''' = 10^{29}$. This value is an approximate one since hydrolysis of the carbonate and bicarbonate has been neglected. However, the value does serve to show that $\mathrm{Co(CO_3)_3}^{3-}$ is a very stable anion with respect to the simple dissociative process $\mathrm{Co(CO_3)_3}^{3-} = \mathrm{Co}^{2+} + 3\mathrm{CO_3}^{3-}$, but it is so reactive because of the very great oxidizing power of the small amount of Co^{3+} formed on dissociation and also the ease of decomposition of carbonate in acidic solution.

Experimental Section

Potassium tris(malonato)cobaltate(III) trihydrate was prepared and purified according to our method.[14,15] Anal. Calcd for $\mathrm{K_3[Co(mal)_3]\cdot 3H_2O}$: K, 21.8; Co, 11.0; C, 20.1; H, 2.2. Found: K, 21.6; Co, 11.0; C, 19.8; H, 2.3.

Potassium tris(oxalato)cobaltate(III) trihydrate was prepared, purified, and analyzed as described by Palmer.[16] Anal. Calcd for $\mathrm{K_3[Co(ox)_3]\cdot 3H_2O}$: K, 23.73; Co, 11.92; C, 14.68; H, 0.73. Found: K, 23.3; Co, 11.8; C, 14.4; H, 0.74. Other chemicals used were of pure grade.

Measurement of the Oxidation–Reduction Potential. The measurements were made on a Cambridge pH meter used as a millivoltmeter. The cell was maintained at 25 °C and contained a bright platinum indicator electrode and a saturated calomel reference electrode. No attempt was made to remove dissolved oxygen from the cell solutions. The pH of each cell solution was measured on a Pye direct-reading pH meter. The ionic strength of all solutions was made to be 1.0 M by adding potassium chloride.

The cell was standardized by measuring the formal potential of the $\mathrm{Fe(CN)_6}^{3-} + e^- = \mathrm{Fe(CN)_6}^{4-}$ couple and also was checked by measuring the formal potential of the $\mathrm{Co(ox)_3}^{3-} + e^- = \mathrm{Co(ox)_3}^{4-}$ couple at pH 4.02. The cell solutions for the first couple were made up from solid potassium ferricyanide and potassium ferrocyanide. The cell solutions for the second couple were made up by mixing 0.001 mol of potassium tris(oxalato)cobaltate(III) trihydrate with 0.0015 mol of cobalt sulfate pentahydrate and 0.003 mol of potassium oxalate in 100 mL of 1 M potassium chloride solution. A total of 10 mL of 0.1 M potassium oxalate and 10 mL of 0.1 M potassium hydrogen oxalate was added to the solution as buffer.

Cell solutions of the $\mathrm{Co(mal)_3}^{3-} + e^- = \mathrm{Co(mal)_3}^{4-}$ couple were made by dissolving 0.001 mol of potassium tris(malonato)cobaltate(III) trihydrate and 0.0015 mol of cobalt sulfate pentahydrate in 100 mL of 1.0 M potassium chloride and by mixing them with 10 mL of 0.5 M potassium malonate. A total of 10 mL of 0.1 M potassium malonate and 10 mL of 0.1 M potassium hydrogen malonate was also added as buffer. The pH of the solution was 5.85, and the temperature was 25 °C. The value of formal potential for the $\mathrm{Co(mal)_3}^{3-} + e^- = \mathrm{Co(mal)_3}^{4-}$ couple was found as 0.741 V. Since there is no value for the stability constant of the $\mathrm{Co(mal)_3}^{4-}$ complex, we assumed it as 10^3 in the light of the first and second stability constants for mono- and bis(malonato)cobaltate(II) complexes.

Reduction of $\mathrm{Co(mal)_3}^{3-}$ with Fe^{2+}. A solution of 2.5×10^{-2} M Fe^{2+} in 1 M $HClO_4$ was reacted at 25 °C with a solution of 1.0×10^{-3} M $\mathrm{Co(mal)_3}^{3-}$ by using stopped-flow apparatus (Durrum Model 13000). The formation and disappearance of $\mathrm{Fe(mal)}^{+}$(aq) were observed at 315 nm, and also the disappearance of $\mathrm{Co(mal)_3}^{3-}$ at 615 nm was recorded.

Attempt To Oxidize Co(II) with Oxygen in Carbonate and Malonate Media. A current of pure oxygen at 1 atm pressure was passed through solutions of tris(malonato)cobaltate(II) and tris(carbonato)cobaltate(II) for several hours, but there was not any sign of oxidation of cobalt(II) in these complexes.

Registry No. $\mathrm{Co(mal)_3}^{3-}$, 22174-09-0; $\mathrm{Co(mal)_3}^{4-}$, 74176-25-3; $\mathrm{Co(CO_3)_3}^{3-}$, 15245-10-0; Fe^{2+}, 15438-31-0.

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(13) Mori, M.; Shibata, M.; Kyano, E.; Adachi, T. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 883.

(14) Al-Obadie, M. S.; Sharpe, A. G. *J. Inorg. Nucl. Chem.* **1969**, *31*, 2963.

(15) Al-Obadie, M. S. Ph.D Thesis, Cambridge University, 1970.

(16) Palmer, W. G. "Experimental Inorganic Chemistry"; Cambridge University Press: Cambridge, 1954; p 550.