Confirmation of the Non-existence of Polymeric Species in Aqueous Perchloric Acid Solutions of the Hexa-aquocobalt(III) Ion

By **Geoffrey Davies,** Department of Chemistry, Northeastern University, Boston, Massachusetts 02115, U.S.A.
Björn Warnqvist,* Department of Inorganic Chemistry, Royal Institute of Technology KTH, S–10044 Stockholm 70, Sweden

The use of Ag^{I} as a potential mediator in potentiometric measurements of the Co^{III}–Co^{II} couple in aqueous perchloric acid solutions of the hexa-aquocobalt(III) ion does not invalidate the conclusion that the cobalt(III) species present are monomeric and behave as one-equivalent oxidants. Evidence from isotope distribution and kinetic studies is reviewed and shown to support this conclusion.

EVIDENCE for the presence of polymeric species in aqueous solutions of the hexa-aquocobalt(III) ion in perchloric acid has recently been reviewed.[1] The question of the existence of such species can best be approached by (i) studies of oxygen–isotope distribution in the hexa-aquocobalt(III) ion oxidation of ^{18}O-enriched solvent water [2,3] and (ii) accurate potentiometric measurements of the cobalt(III)–cobalt(II) couple.[4] A reinvestigation [3] of (i) indicates that the product of oxidation has the same isotopic composition as the solvent, which is consistent with either (*a*) complete equilibrium between the solvent and the cobalt(III) centre or (*b*) production of oxygen entirely from unco-ordinated solvent. The concentrations of hexa-aquocobalt(III) ions in the isotope studies [2,3] were much higher than those generally employed in kinetic investigations,[1,5,6] where an independence of kinetic parameters on the stoicheiometric cobalt(III) ion concentration suggests that an equilibrium involving monomeric and dimeric cobalt(III) species is not significant, *i.e.* hexa-aquocobalt(III) ions are present in one form, either monomeric or polymeric.

A distinction between conclusions (*a*) and (*b*) in the isotope-exchange studies can be made from estimates of the rate of solvent exchange in the Co^{3+}(aq) ion and its conjugate base, $CoOH^{2+}$(aq). An estimate of the rate of water exchange in Co^{3+}(aq) in 6M-perchloric acid has been made [7] but, unfortunately, the presence of a high concentration of Co^{2+}(aq) ions in these solutions provides a means for very rapid solvent exchange on Co^{2+}(aq) through the Co^{III}–Co^{II} electron-exchange reaction.[1] However, some complexation [1,8,9] and substitution-controlled [5] redox reactions involving hexa-aquocobalt(III) ions at lower concentrations also exhibit an independence of the rate of the reaction on the concentration of Co^{II}, indicating that solvent-exchange rates for the cobalt(III) species themselves are sufficiently rapid to allow complete equilibration with solvent water throughout the course of the hexa-aquocobalt(III)–water reaction. This conclusion suggests that the oxygen produced in the latter reaction is derived from co-ordinated solvent having essentially the same isotopic composition as that of the experimental medium, and precludes the existence of any species which is kinetically inert, which is the essential feature of the mechanism proposed by Anbar and Pecht.[2]

Potentiometric measurements of the Co^{III}–Co^{II} couple enable a determination of the importance of the monomer–dimer equilibrium (1). Unfortunately, the establishment of equilibrium between Co^{III} species and suitable redox electrodes such as Pt or Au is sufficiently slow

$$2Co^{III} \underset{}{\overset{K_D}{\rightleftharpoons}} (Co^{III})_2 \qquad (1)$$

---

[1] G. Davies and B. Warnqvist, *Co-ordination Chem. Rev.*, 1970, **5**, 349.

[2] M. Anbar and I. Pecht, *J. Amer. Chem. Soc.*, 1967, **89**, 2553.

[3] R. K. Murmann, *Inorg. Chem.*, 1971, **10**, 2070.

[4] B. Warnqvist, *Inorg. Chem.*, 1970, **9**, 682.

[5] G. Davies and K. O. Watkins, *J. Phys. Chem.*, 1970, **74**, 3388; *Inorg. Chem.*, 1970, **9**, 2735.

[6] R. C. Thompson and J. C. Sullivan, *Inorg. Chem.*, 1970, **9**, 1590.

[7] H. L. Friedman, H. Taube, and J. P. Hunt, *J. Chem. Phys.*, 1950, **18**, 759.

[8] J. Hill and A. McAuley, *J. Chem. Soc.* (*A*), 1968, 1169, 2405.

[9] G. Davies, unpublished work.

to create analytical problems because of simultaneous reduction of hexa-aquocobalt(III) ions by water.[4,10] However, the addition of traces of Ag^I to these solutions greatly increases the rate of equilibration with the electrode through reactions (2) and (3). Wells and Husain[11]

$$Co^{III} + Ag^{I} \underset{\text{fast}^{1}}{\rightleftharpoons} Co^{II} + Ag^{II} \qquad (2)$$

$$Ag^{II} + e^{-} \underset{\text{fast}}{\rightleftharpoons} Ag^{I} \qquad (3)$$

have criticized this approach[4,10] by suggesting that the use of Ag^I as a potential mediator invalidates the potentiometric method as a means of distinguishing between mono- and poly-meric cobalt(III) species in solution.

Considering the case in which equilibrium (1) is rapid, equation (4) pertains and thus (5) can be obtained where

$$[(Co^{III})_2] = K_D[Co^{III}]^2 \qquad (4)$$

$$\begin{aligned}[Co^{III}]_T &= [Co^{III}] + 2[(Co^{III})_2] \\ &= [Co^{III}] + 2K_D[Co^{III}]^2 \qquad (5)\end{aligned}$$

$[Co^{III}]_T$ is the stoicheiometric cobalt(III) ion concentration. The real root of quadratic equation (5) is (6).

$$[Co^{III}] = \frac{(1 + 8K_D[Co^{III}]_T)^{\frac{1}{2}} - 1}{4K_D} \qquad (6)$$

The overall measured potential, E, for reactions (7) and (8) is given by equation (9). Since the equilibrium

$$\left.\begin{aligned}(Co^{III})_2 + e^{-} &\rightleftharpoons Co^{II},Co^{III} \qquad (7) \\ Co^{II},Co^{III} &\rightleftharpoons Co^{II} + Co^{III} \qquad (8)\end{aligned}\right\} Q$$

$$E = E_0 + \frac{RT \ln 10}{F} \log \frac{[(Co^{III})_2]}{[Co^{II}][Co^{III}]} \qquad (9)$$

constant Q is defined by (10), equation (9) can also be

$$Q = \frac{[(Co^{III})_2]}{[Co^{II}][Co^{III}]} = \frac{K_D[Co^{III}]}{[Co^{II}]} \qquad (10)$$

expressed as in (11), where $E_0' = E_0 + \frac{RT \ln 10}{F} \log K_D$.

$$\begin{aligned}E &= E_0 + \frac{RT \ln 10}{F} \log \frac{[Co^{III}]}{[Co^{II}]} + \frac{RT \ln 10}{F} \log K_D \\ &= E_0' + \frac{RT \ln 10}{F} \log \frac{[Co^{III}]}{[Co^{II}]} \qquad (11)\end{aligned}$$

Inserting (6) into (11) we obtain equation (12) which is

$$E = E_0' + \frac{RT \ln 10}{F} \log \frac{(1 + 8K_D[Co^{III}]_T)^{\frac{1}{2}} - 1}{4K_D[Co^{II}]} \qquad (12)$$

that of (2) in ref. 4; it refers to *any* one-equivalent electrode reaction.

If K_D in equation (4) is so large that $[Co^{III}]_T \approx 2[(Co^{III})_2]$, then it can easily be shown that, for the electrode reaction (13), the measured potential is given

$$(Co^{III})_2 + 2e^{-} \overset{E_0''}{\rightleftharpoons} 2Co^{II} \qquad (13)$$

$$E = E_0''' + \frac{RT \ln 10}{2F} \log \frac{[Co^{III}]_T}{[Co^{II}]^2} \qquad (14)$$

by equation (14) (where $E_0''' = E_0'' - \frac{RT \ln 10}{2F} \log 2 = E_0' - \frac{RT \ln 10}{2F} \log 2K_D$) which is that of (2*a*) of ref. 4.

Equation (14) is thus the limiting case of (12); it, together with (12), is deduced whether the potential, E, is regarded as being determined by the electrode reactions (7), (13), or (3) (see below), assuming that any one of these, and all other reactions in the solution, are reversible.

If the redox potential, E, is considered to be determined by the couple Ag^{II}–Ag^{I} [equation (3)], then equation (15) is applicable. If a dimeric species were

$$E = E_0(Ag) + \frac{RT \ln 10}{F} \log \frac{[Ag^{II}]}{[Ag^{I}]} \qquad (15)$$

to be involved {equilibria (16) and (17), where $R = [Ag^{II}][Co^{III}][Co^{II}]/[(Co^{III})_2][Ag^{I}]$}, then we would obtain

$$\left.\begin{aligned}(Co^{III})_2 + Ag^{I} &\rightleftharpoons Co^{II},Co^{III} + Ag^{II} \qquad (16) \\ Co^{II},Co^{III} &\rightleftharpoons Co^{II} + Co^{III} \qquad (17)\end{aligned}\right\} R$$

equation (18) and substitution into equation (15) would give (19) where $E_0'(Ag) = E_0(Ag) + \frac{RT \ln 10}{F} \log R = E_0$. Equation (19) is comparable to (11); both equa-

$$[Ag^{II}]/[Ag^{I}] = R[(Co^{III})_2]/[Co^{III}][Co^{II}] \qquad (18)$$

$$\begin{aligned}E &= E_0(Ag) + \frac{RT \ln 10}{F} \log \frac{R[(Co^{III})_2]}{[Co^{II}][Co^{III}]} \\ &= E_0'(Ag) + \frac{RT \ln 10}{F} \log \frac{K_D[Co^{III}]}{[Co^{II}]} \qquad (19)\end{aligned}$$

tions yield a Nernst slope corresponding to one-electron reduction and, when expressed in terms of $[Co^{III}]_T$, result in equation (12), *etc.* The only difference between equations (11) and (19) is that in the former the electrode is assumed to donate an electron to Co^{III}, whereas in the latter the electron donor is Ag^I.

Experimental conditions for representative studies of the hexa-aquocobalt(III) ion in acidic perchlorate solutions

Investigation	$[Co^{II}]_0$ [a] M	$[Co^{III}]_0$ [a] M	$[HClO_4]$ [b] M	Ref.
Isotope distribution	0·003—0·393	0·052—0·703	2·3—5·81	3
Potentiometry	0·02—0·05	0·0005—0·005	0·5—3·0	4
Kinetic	0·00002—0·087	0·00002—0·006	0·05—3·0	5
		0·0007—0·001	1·04—5·01	6

[a] Represents a *ca.* 10^4-fold range of concentration for all studies. [b] Represents a *ca.* 120-fold range of concentration for all studies.

The above considerations show that the use of Ag^I as a potential mediator in potentiometric measurements of the Co^{III}–Co^{II} couple in aqueous perchloric acid solutions of the hexa-aquocobalt(III) ion does not invalidate the conclusion[4] that the cobalt(III) species present are

---

[10] A. A. Noyes and T. J. Deahl, *J. Amer. Chem. Soc.*, 1937, **59**, 1337.

[11] C. F. Wells and M. Husain, *Trans. Faraday Soc.*, 1971, **67**, 760.

monomeric (K_D *ca.* 0), since the conclusion is made[4] on the basis of logarithmic terms in equations (12) and (14); these equations obtain whether (3), (7), or (13) is assumed to establish the electrode potential. This result, taken together with the evidence from measurements over a very wide range of cobalt(III) ion concentrations (Table), indicates that hexa-aquocobalt(III) ions are essentially monomeric under these experimental conditions.

[2/1806 *Received*, 31*st July*, 1972]