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ASPECTS OF THE CHEMISTRY OF COBALT(III) IN AQUEOUS PERCHLORATE SOLUTION*

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CONTENTS

ABBREVIATIONS

phen = 1,10-phenanthroline
cphen = 5-chloro-1,10-phenanthroline
mphen = 5-methyl-1,10-phenanthroline
nphen = 5-nitro-1,10-phenanthroline
bipy = 2,2′-bipyridyl
terpy = 2,2′,2″-terpyridyl
tmp = 3,5,6,8-tetramethyl-1,10-phenanthroline

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A. INTRODUCTION

The chemistry of cobalt(III) has played a very important part in the development of our knowledge of the properties and reactions of inorganic compounds. For example, the kinetic inertness of compounds of the type $Co(NH_3)_5X^{2+}$ (where $X = Cl^-, Br^-, F^-$, *etc.*) led to the first important distinction[1] between inner- and outer-sphere mechanisms for inorganic oxidation–reduction reactions, a distinction which has greatly accelerated the progress of this particular area of investigation[2].

By contrast, the study of the chemistry of the cobalt(III) species present in weakly-complexing acid perchlorate solution is comparatively modern: it has suffered from considerable uncertainty because of the inherent high chemical reactivity of cobalt(III) (aq.) towards the solvent water molecules. Indeed, the discrepancies in the results of several investigations[3–7] of this latter reaction prompted us in the first instance to examine the available data critically with the object of clarifying the situation. Of particular interest at the present time are the following questions.

(1) To what extent does dimerization occur in aqueous perchloric acid solutions? If dimers and higher polymers exist, are they in labile equilibrium with monomeric species?

(2) To what extent does hydrolysis (acid-dissociation of coordinated water molecules) occur? Are hydrolyzed species labile or inert?

(3) Why do reactions of cobalt(III) proceed at rates which are often several orders of magnitude slower than those predicted by theoretical approaches which have been used with success for reactions involving other first-row trivalent transition metal ions?

In attempting to answer some of these questions we have reviewed the current literature of cobalt(III) chemistry and have also used some information from other systems as a means of classification of some of the reactions under consideration.

B. METHODS OF PREPARATION

Solid salts of cobalt(III) are most often prepared by reaction at low temperatures: an example of this is the preparation of $Co(NO_3)_3$ by reaction between cobaltic trifluoride and dinitrogen pentoxide[8]. The green hygroscopic crystals rapidly evolve oxygen in water leaving a pink acidic solution containing three nitrate anions per cobalt(II) ion. In general, solutions of cobalt(III) become increasingly unstable as the acidity is lowered or the temperature is raised, and so most preparations are carried out at moderately high acidities (typically 3M $HClO_4$) and at temperatures near 0°. The two most common modes of oxidation of cobalt(II) to the trivalent state are by ozonolysis[9] or by anodic oxidation[6,10,11]. Grey-blue crystals of the salt $Co_2(SO_4)_3 \cdot 18H_2O$ are produced in maximum yield by electrolysis for four hours of a saturated solution of cobalt(II) sulphate in 5M sulphuric acid at 0.05 amp $\cdot$ cm^{-2} and 5–10° (Ref. 11). The crystals may be stored for some days in a refrigerator over a sulphuric acid desiccant[6,11]. The precipitation of solid material during this procedure is reminiscent of the appearance of a solid manganese(III) sulphate during electrolysis of manganese(II) in 7–8M H_2SO_4* (Ref. 12).

The direct electrolytic preparation of dilute cobalt(III) solutions by oxidation of cobalt(II) perchlorate ($\sim 5 \times 10^{-2}$M) in perchloric acid solution has been used for some years. Low current densities ($\sim$0.002 amp $\cdot$ cm^{-2}), high acidities ($\sim$3M) and an operating temperature near 0° give cobalt(III) solutions with reproducible kinetic and spectral properties. It is sometimes necessary to carry out a preliminary electrolysis to eliminate traces of oxidizable impurity. We have found the salt $Co(ClO_4)_2 \cdot 6H_2O$ (G. Frederick Smith Chemical Company, Columbus, Ohio, U.S.A.) to be a suitable starting material**. Under the above conditions a maximum yield of *ca.* 70% (based on the initial cobalt(II) concentration) is obtained in about 7 hours. The solutions are moderately stable ($t_{\frac{1}{2}} \sim 30$ days) at 0°. Use of higher current densities in an attempt to accelerate the rate of electrolysis leads to solutions containing cobalt(III) species with properties which are appreciably different from those prepared as outlined above[16]. Similarly, the employment of lower acidities in the mixture to be electrolyzed seems to yield solutions with different (and not always reproducible) spectral and kinetic properties from those prepared after dilution of solutions obtained under the recommended conditions[16,17]. No solid material precipitates even from the preparation of a 0.6M solution of cobalt(III) in 6M perchloric acid at 0° (Ref. 7).

C. ANALYTICAL METHODS

Since cobalt(III) is a strong oxidant and is usually present at comparatively high concentrations in stock solutions almost any back-titration method is applicable for its estimation. Amongst methods which might be mentioned are addition of an aliquot to excess oxalate and back-titration with permanganate[11c] and

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* It is perhaps unfortunate that some early studies of reactions of cobalt(III) were carried out in sulphuric acid mixtures[3] in view of the complexity of the equilibria involved[13,14]. Of particular concern is the use of the solid sulphate hydrate as a starting material for the preparation of comparatively concentrated cobalt(III) solutions in perchloric acid media[6]. It is known to be difficult to remove the last traces of mother liquor (*i.e.* sulphuric acid) from the crystals[11c], which probably accounts for the necessity of using an excess of barium perchlorate to precipitate "all the sulphate"[6] (see section D)

** The dissolution of metallic cobalt in perchloric acid tends to produce traces of chloride even at 0° (Ref 15) addition to excess iron(II) and back-titration with cerium(IV) (ferroin indicator)[15] or dichromate (diphenylamine indicator).

More dilute solutions may be estimated by direct or indirect spectrophotometric methods. Suitable wavelengths for direct spectrophotometry of perchlorate solutions are at 605 nm ($\varepsilon_{605}^{\mathrm{Co^{III}}} = 35.3 \pm 0.1$)[*,18] or at 250 nm [$\varepsilon_{250}^{\mathrm{Co^{III}}} = (2.89 \pm 0.03) \times 10^3$, (Ref. 6)]. Indirect methods include addition to an excess of iron(II) [$\varepsilon_{260}^{\mathrm{Fe^{III}}} = (2.88 \pm 0.03) \times 10^3$, (Ref. 19)], *p*-hydroquinone (ε_{250} for *p*-benzoquinone is $(2.11 \pm 0.04) \times 10^4$, (Ref. 20) or hydrogen peroxide (estimated as the $\mathrm{Ti^{IV}}$ complex, $\varepsilon = 731$ at 415 nm, (Ref. 21)).

D. THE SPECIES PRESENT IN ACIDIC PERCHLORATE SOLUTION

There is some disagreement about the species existing in cobalt(III) perchlorate solutions, and a paucity of good equilibrium data. This is largely a consequence of experimental difficulties due to the instability of cobalt(III) in such solutions.

(*i*) *Extent of dimerization* (*polymerization*)

It seems to be well established that some binuclear and/or polynuclear hydrolyzed complex(es) form at relatively high concentrations, $[\mathrm{Co^{III}}] > (10^{-3} - 10^{-2}\mathrm{M})$ and at low acidities, $[\mathrm{H^+}] < 0.4\mathrm{M}$, at temperatures greater than about 10°. The evidence for this comes mainly from spectrophotometric measurements[4,6,17] (see Figs. 1 and 2, which are reproduced from Ref. 17). Of particular note is a strong absorption, compared to that of monomeric cobalt(III), at 330 nm[4,17]. The observed extinction coefficient, ε_{330}, is cobalt(III) concentration-dependent[17], and inversely acid concentration-dependent[4,17].

Weiser[4] made a detailed study of the absorption spectrum in the range 220–900 nm for cobalt(III) perchlorate solutions at various acidities, (0.002–7M $\mathrm{HClO_4}$), at 25°. According to his results solutions containing $[\mathrm{Co^{III}}] = (0.5-3) \times \times 10^{-3}\mathrm{M}$ were practically all polymeric (perhaps dimeric) at acidities less than about 0.02M, whereas at $[\mathrm{Co^{III}}] = 1 \times 10^{-3}\mathrm{M}$ and $[\mathrm{H^+}] = 0.4\mathrm{M}$ it was found that <0.5% was polymeric (dimeric). An estimate of 15% cobalt(III) as a dimeric species at $[\mathrm{Co^{III}}] = 3 \times 10^{-3}\mathrm{M}$ and $[\mathrm{H^+}] = 0.14\mathrm{M}$ is an example of his results from intermediate acidities. At 0°, cobalt(III) was found to be all monomeric, $\mathrm{Co_{aq}}^{3+}$, down to $[\mathrm{H^+}] = 0.1\mathrm{M}$.

In general, "dimeric" cobalt(III) seems not to be in rapid equilibrium with monomeric cobalt(III)[4,17]. As a consequence polymers may persist at low total

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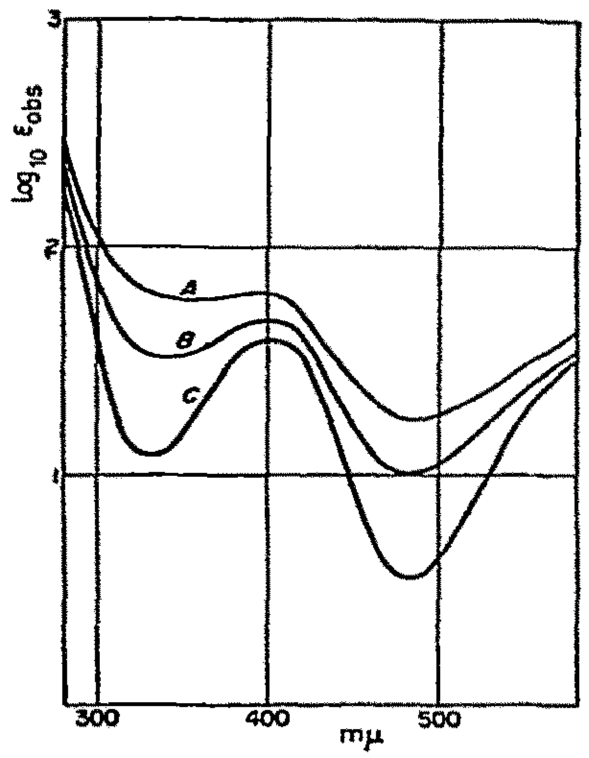
[*] There have been several estimates of $\varepsilon_{605}{}^{\mathrm{Co(III)}}$ reported in the literature: they range from 33.0 to 39.0. We recommend the value $\varepsilon_{605}{}^{\mathrm{Co(III)}} = 35.3 \pm 0.1$, which is in good agreement with the measurements of Weiser[4].



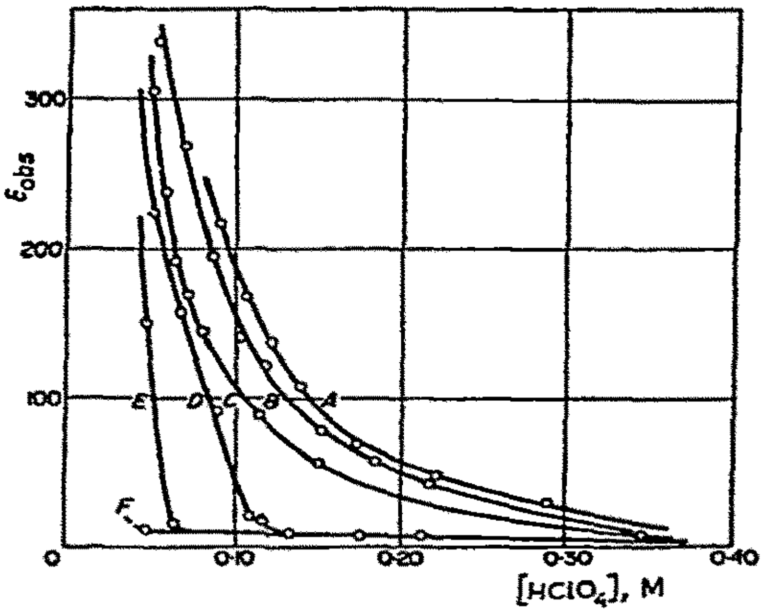


Fig 1 Absorption spectra of cobaltic perchlorate solutions at 20 00°, [HClO$_4$] = 0 34M and ionic strength 1 1M The concentrations of cobalt(III) are· A = 18 6 × 10^{-3}M, B = 9 2 × 10^{-3}M, C = 2 5 × 10^{-3}M, from Ref. 17 (reproduced by permission of the copyright owner, Pergamon Press)

Fig 2 Variation of the observed extinction coefficient at 330 nm with acidity; temperatures· A = 32 00°, B = 28 00°, C = 24 00°, D = 20 00°, E = 16 00°, F = 12 00°; ionic strength, 1 0M; Co(III) concentration, 2 7 × 10^{-4}–10 4 × 10^{-4}M; from Ref 17 (reproduced by permission of the copyright owner, Pergamon Press)

cobalt(III) concentrations in solutions prepared by dilution[17], after lowering the temperature to 0° (Refs. 4, 17), and after electrolytic preparation at a high current density[16]; in other words, it is hard to prepare "dimeric" cobalt(III) solutions reproducibly.

Wells[22] has suggested, on the basis of various kinetic studies[6,7,23,24] that cobalt(III) is predominantly dimeric, not only in the high cobalt(III)–low acidity range discussed above, but also at [cobalt(III)] $\sim 1 \times 10^{-3}$M and at high acidities. The main evidence for this conclusion comes from the work on the cobalt(III)–water reaction[6], where a rate law involving a single term with 3/2 order in cobalt(III) was found. The reaction mechanism given to explain this rate law involved postulating that cobalt(III) exists mainly as a dimer, in rapid equilibrium with monomeric cobalt(III). However, the slowness and virtual irreversibility of the association reaction(s)[4,17] noted above casts some doubt on the proposed mechanism[5,6]. In addition, the possible influence of sulphate impurity* cannot be ruled out in this work: thus, a reaction order of $\sim 3/2$ in [Co^{III}] was also found to hold in a sulphuric acid medium.

As observed by Taube[5], the common features of other studies[3,4] on the cobalt(III)–water reaction seem to be:

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* See first footnote on p. 351.

(*a*) a (reproducible) term in the rate law second-order in [cobalt(III)] and proportional to $[H^+]^{-2}$, (according to Weiser[4], proportional to $[H^+]^{-1}$ at high acidity);

(*b*) another term approximately first order in [cobalt(III)], which seems to be irreproducible, and to depend on the history of the solution[4]. The former, main term of the rate law can be explained by a rate-determining step involving two monomeric cobalt(III) species, *e.g.* two $CoOH^{2+}$ ions, as well as by a binuclear complex It should be pointed out that a comparison with the photo-activated reaction[4] between cobalt(III) and water indicates that the OH radical is not involved in the mechanism of the thermal reaction. Thus, the rate of the photo-induced reaction is retarded by cobalt(II), presumably due to the competing oxidation of Co^{2+} by OH[4]. The rate of the thermal reaction, on the other hand, is independent of the cobalt(II) concentration[3,4,6].

The kinetics of the oxidation of benzene by cobalt(III)[23] do not necessarily require a dimeric cobalt(III) species, as pointed out by the author.

As for the work on the Co^{III}–bromine reaction[24], we feel that the cobalt(III) concentration range and the fraction of the reaction followed may both have been too small to establish the reaction order with certainty. Furthermore, the dependence on the hydrogen ion concentration may be somewhat uncertain due to medium effects at the ionic strength used (5M).

The evidence to be discussed below, in addition to the spectrophotometric results noted above, indicates that cobalt(III) exists in monomeric form at concentrations $\lesssim 10^{-2}$M in highly acidic perchlorate media

In their ^{18}O distribution study Anbar and Pecht[7] found "<3.1% dimeric cobalt(III)" at $[Co^{III}] = 0.6$M in 6M $HClO_4$ at room temperature. This corresponds to an overall dimerization quotient, K_D, of $\leq 0.03M^{-1}$ for the equilibrium

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

K_D may be a function of acidity and ionic strength, but if neither dimeric nor monomeric cobalt(III) hydrolyzes appreciably in the acidity range 0.1–6M[22], then K_D will be within an order of magnitude of the above-mentioned maximum value. If this is the case, then less than 1% cobalt(III) would be dimeric at $[Co^{III}] = 3\times10^{-3}$M and $[H^+] \approx 0.1$M. An increase in K_D proportional to the inverse of the square of the hydrogen ion activity would give $K_D \lesssim 2\times10^2M^{-1}$ at $[H^+] \approx 0.1$M, which corresponds to $\geq 60\%$ monomeric Co^{III} at $[Co^{III}] = 3\times10^{-3}$M. In short, Anbar's and Pecht's findings hardly furnish quantitative support for the idea that cobalt(III) would exist, at equilibrium, mainly as a dimer in highly acidic perchlorate solutions.

The conclusion that cobalt(III) in acid perchlorate solutions is mainly monomeric is supported by Warnqvist's[25] potentiometric measurements with the Co^{III}/Co^{2+} redox electrode. His results established an upper limit for K_D of 10–20M^{-1} at 3° with $[HClO_4] = 0.05$–3M at ionic strength 3M, and at 23° with

$[HClO_4] = 3M$. This corresponds to less than 10 percent of dimeric cobalt(III) species at $[Co^{III}] \leq 3\times10^{-3}M$. At 23°, 0.5M $HClO_4$, and ionic strength 3M, lower accuracy due to the rapid reduction of cobalt(III) by water gave[25] an upper limit for K_D of *ca.* $500M^{-1}$, which corresponds to less than 40% dimeric cobalt(III) at $[Co^{III}] = 1\times10^{-3}M$. A plausible maximum dimerization enthalpy of about +20 kcal gives an upper limit for K_D of 250–500 M^{-1} in the acidity range 0.05–0.5M H^+ at 25°, based on the K_D limit at 3°. This estimate is probably too high[4] (see also the kinetic results of Ref. 18).

We conclude from the above considerations that the diamagnetism of cobalt(III) perchlorate solutions (*ca.* 0.1(?)M in 4M $HClO_4$ at 1°)[26] can be explained in terms of a low spin ($t_{2g}{}^6$) electronic configuration for monomeric hexaaquocobalt(III) ions.

(ii) *Hydrolysis of $Co^{3+}(aq)$*

Published values for the equilibrium constant of the reaction

$$Co_{aq}{}^{3+} \rightleftharpoons CoOH_{aq}{}^{2+} + H_{aq}^{+} \qquad (K_h) \qquad (1)$$

range from $0.22M^{27}$ to $<3\times10^{-3}M^{4}$ at 25°. Spectrophotometric measurements have in general yielded estimates close to the lower end of this range[4,6,28], whereas estimates from kinetic studies have tended to give values of the order of $10^{-1}M$[27,29]. Considering the nature of the kinetic analysis one would be inclined to regard K_h values obtained from kinetic studies less reliable than more direct spectrophotometric determinations. Indeed, when these high estimates of K_h are used in kinetic equations some inconsistencies are evident (see Section E).

In view of the general similarities between the equilibria and kinetics of complexation of $Fe_{aq}{}^{3+}$ and $Co_{aq}{}^{3+}$, it seems reasonable to expect similar values of K_h for the two ions. If so, K_h would be $\sim 10^{-3}M$ at 25° and 3M ionic strength[30]. It is interesting to note that if the linear free-energy relationship for the 1:1 complexes of trivalent first-row transition metal ions with OH^- and F^- demonstrated by Rosseinsky[31] is accepted to be closely valid for $Co_{aq}{}^{3+}$, then a value for $K_h = (2 \pm 1)\times10^{-3}M$ (at 25°, $\mu = 1M$) is obtained This result comes from a relationship with the corresponding ΔG values for the ions Fe^{3+} and Cr^{3+}, for which it has been possible to obtain accurate hydrolysis data. In addition, this value for K_h is in line with spectrophotometric estimates[4,6], and is consistent with many kinetic results[18] (see section E). Hence, we believe this to be the best estimate for K_h available, and it will be used throughout our discussion in section E.

Sutcliffe and Weber[28] estimated ΔH_h for the hydrolysis reaction to be $+10 \pm 2$ kcal · mole^{-1}. This agrees quite well with the corresponding ΔH_h values for Fe^{3+} [32] and Cr^{3+} [33], and itself suggests a small hydrolysis constant if the entropies of hydrolysis in the series are, in fact, similar. From the estimates of K_h and ΔH_h one may compute $\Delta S_h = +(22 \pm 8)$ cal · degree^{-1} · mole^{-1} at 25°.

It should be pointed out that these values for ΔH_h and ΔS_h are in line with those of other trivalent ions in terms of the trends noted by Wells[34], although the relatively large error in the entropy makes the argument somewhat uncertain for cobalt(III).

(iii) *The equilibrium* $Co^{III}+e^- \rightleftharpoons Co^{II}$ *in acid perchlorate solution: standard electrode potentials for the* Co^{III}/Co^{II} *couple*

There has been a paucity of standard potential (E°) data for the $Co_{aq}^{3+}/Co_{aq}^{2+}$ couple in non-complexing aqueous solutions. For a long time the E°-values measured by Noyes and Deahl[35] in nitric acid media were generally quoted (*e g.*, 1.842 V in 3M HNO_3, 1.850 V in 4M HNO_3 at 25°). However, these values may be somewhat affected by complex formation. Warnqvist[36] has determined a value $E^\circ = (1.92 \pm 0.02)$ V from EMF measurements in 4M $HClO_4$ at 25°. Like Noyes and Deahl he used a gold foil as the inert electrode (found to reach equilibrium much more rapidly than platinum), and added silver ion as a potential mediator. The value of the equilibrium constant for the reaction, $Co^{III}+Ag^I \rightleftharpoons Co^{II}+Ag^{II}$, obtained kinetically[36b], is $2\,3 \times 10^{-2}$ in 4M $HClO_4$ at 25°. This corresponds to $E^\circ = 1.90$ V for the $Co_{aq}^{3+}/Co_{aq}^{2+}$ couple (for Ag^{II}/Ag^+, $E^\circ = 2.00$ V)[37]. Johnson and Sharpe[38] have given an estimate, (1.93 ± 0.10) V at 15° [$(1.95 \pm 0\,10)$ V at 25°] in 4M $HClO_4$, based on thermochemical data for the reaction of Co_{aq}^{3+} with Fe_{aq}^{2+}. More recently, Warnqvist[25] made further EMF measurements with the Co^{III}, $Co_{aq}^{2+}/Au(s)$ electrode in 3M (Na^+, H^+)ClO_4^- media. He obtained the following values for E° at 23°: (1.86 ± 0.02) V at $[H^+] = 3M$, and (1.85 ± 0.02) V at $[H^+] = 0\,5M$; and at 3°: (1.83 ± 0.02) V at $[H^+] = 3M$, $(1.83 \pm 0\,01)$ V at $[H^+] = 0.05$ and 0.5M, (1.82 ± 0.01) V at $[H^+] = 0.1M$. Uncertainties in liquid junction potentials are the major contributors to the error estimates. The net sign of the liquid junction potentials may in fact have been such that the actual E°-values are closer to the upper limits quoted.

E. SOME KINETIC ASPECTS OF COBALT(III) REACTIONS

In the previous section we indicated the conditions under which hexaaquocobalt(III) exists as a monomeric species in rapid equilibrium with hydroxopentaaquocobalt(III). We shall now examine some kinetic results foi reactions involving cobalt(III) under these conditions. An attempt will be made to classify the reactions in terms of current ideas concerning mechanism. In particular, we shall be searching for evidence to distinguish between inner- and outer-sphere reaction pathways.

After considering reactions which might be expected to be outer-sphere we shall go on to discuss reactions involving "simple" metallic reductants. Complex formation and the kinetics of reactions with non-metallic reductants will then be reviewed and some conclusions concerning the mechanisms of cobalt(III) reactions will be presented.

Sutin and his coworkers[39] have been eminently successful in applying the ideas of Marcus[40] to reactions which might be expected to have outer-sphere mechanisms: examples of these are the reactions of cerium(IV)[41] and manganese(III)[42] with substituted phenanthroline complexes of iron(II). By contrast, application of the Marcus theory to reactions involving aquocobalt(III) ions has invariably yielded predicted rate constants which are up to five orders of magnitude greater than those found experimentally[39,41,42].

While the majority of cobalt(II) complexes are in the spin-free $t_{2g}{}^5e_g{}^2$ state[43], monomeric hexaaquocobalt(III) exists as a low-spin, diamagnetic complex in strongly acid solution[26] and in solid salts (*e.g.*, $CO_2(SO_4)_3 . 18H_2O$ and $CsCo(SO_4)_2 . 12H_2O$ (Refs. 44, 45). It would appear that this difference in spin state is important in determining the rate of transfer of an electron to a low-spin cobalt(III) ion, and the recent work of Farina and Wilkins[43] casts some new light on this question. A comparison between observed and calculated (Marcus[40]) rate constants for electron exchange involving some cobalt(III) oxidants is given in Table 1. It will be seen that agreement is good when the reactants are the pairs $Co(bipy)_3{}^{3+}$/$Co(terpy)_2{}^{2+}$, $Co(terpy)_2{}^{3+}$/$Co(bipy)_3{}^{2+}$ and $Co(phen)_3{}^{3+}$/$Co(terpy)_2{}^{2+}$: these reactions would be expected to have an outer-sphere mechanism. However, agreement between observed and calculated rate constants becomes much poorer as the chelated ligands are progressively replaced by water molecules, and it is worthwhile to consider in general terms what effects might be expected as the ligands are replaced.

Metal ions which carry coordinated ligands are believed to undergo water-exchange at a higher rate than do the unsubstituted aquo-ions[48]. This conclusion comes, in part, from the observation that the rate of formation of a disubstituted complex is often higher than the rate of formation of the monocomplex from which it is derived[48]. It might be argued, therefore, that an inner-sphere mechanism is able to offer an energetically favorable pathway for reaction, for example, when the oxidant is substitution-labile $Co(bipy)^{3+}$ or $Co(phen)^{3+}$ (Table 1), and agreement between observed and calculated (Marcus) rate constants might not be good for these oxidants[43]. An interesting result of Farina and Wilkins[43] is the agreement between observed and calculated (Marcus) rate constants for outer-sphere reactions involving both *high-spin* [$Co(bipy)_3{}^{2+}$ and $Co(phen)_3{}^{2+}$] and *low-spin* [$Co(terpy)_2{}^{2+}$] cobalt(II) complexes[43].

The progressive replacement of ligands by water molecules in cobalt(III) complexes increases the overall free energy change, $\Delta G°$, and the rates of reaction with a given cobalt(II) reductant generally increase through the series (Table 1)[43]. This argues for a predominantly outer-sphere mechanism for the "mixed" cobalt(III) complexes, a conclusion borne out by the observation[43] of

TABLE 1

THE RATE CONSTANTS OF SOME REACTIONS INVOLVING COBALT(III) COMPLEXES

Oxidant	*Reductant*	$k_{obs}{}^{a}$	$k_{calc}{}^{a,b}$	*Ref*
$Co(bipy)_3{}^{3+}$	$Co(terpy)_2{}^{2+}$	$64^{c\ d}$	32	43
$Co(terpy)_2{}^{3+}$	$Co(bipy)_3{}^{2+}$	$27^{c\ d}$	14	43
$Co(phen)_3{}^{3+}$	$Co(terpy)_2{}^{2+}$	$280^{c,d}$	110	43
$Co(tmp)_3{}^{3+}$	$Co(terpy)_2{}^{2+}$	$68^{c\ e}$		43
$Co(bipy)_2{}^{3+}$	$Co(terpy)_2{}^{2+}$	$13000^{c,d}$		43
$Co(phen)_2{}^{3+}$	$Co(terpy)_2{}^{2+}$	$3000^{c,d}$		43
$Co(bipy)^{3+}$	$Co(terpy)_2{}^{2+}$	$680^{c\ d}$	64000	43
$Co(phen)^{3+}$	$Co(terpy)_2{}^{2+}$	$1400^{c\ d}$	64000	43
$Co_{aq}{}^{3+}$	$Co(terpy)_2{}^{2+}$	$74000^{c,f}$	2×10^{10}	43
$Co_{aq}{}^{3+}$	$Fe_{aq}{}^{2+}$	$43^{f\ g}$	2×10^{7}	46
$Co_{aq}{}^{3+}$	$Fe(mphen)_3{}^{2+}$	$15000^{g\ h}$	$1\ 3\times10^{9}$	47
$Co_{aq}{}^{3+}$	$Fe(phen)_3{}^{2+}$	$14000^{g\ h}$	$8\ 8\times10^{8}$	47
$Co_{aq}{}^{3+}$	$Fe(cphen)_3{}^{2+}$	$5020^{g\ h}$	$4\ 6\times10^{8}$	47
$Co_{aq}{}^{3+}$	$Fe(nphen)_3{}^{2+}$	$1490^{g,h}$	$1\ 0\times10^{8}$	47

[a] Units are $M^{-1}\ sec^{-1}$. [b] Calculated from the equation $k_{calc} = (k_1k_2K_{12}f)^{1/2}$, where k_1 and k_2 are the rate constants for exchange of the reactant couples (*e g* the rate of the Co^{3+}–Co^{2+} exchange reaction is $7M^{-1}\ sec^{-1}$ at 25° (Ref. 52)), K_{12} is the equilibrium constant for the redox reaction ($\log K_{12} = 16\ 9\ \Delta E_0$ at 25°) and $\log f = -(\log K_{12})^2/88 \log (k_1k_2)$. [c] Temperature = 0°. [d] Ionic strength = 0 05M. [e] Ionic strength = 0 02M [f] Ionic strength = 1 0M [g] Temperature = 25°. [h] Ionic strength 3 0M ($HClO_4$)

small effects of acidity and of the spin state of the cobalt(II) reductant with oxidants such as $Co(bipy)_2(H_2O)_2^{3+}$.

The observed second-order rate constant for the exchange reaction between the aquo cobalt(III) and cobalt(II) ions takes the form[49,50]

$$k_{obs} = k_1 + k_2K_h/[H^+] \tag{2}$$

corresponding to the reactions

$$Co_{aq}{}^{3+} + Co_{aq}{}^{2+} \overset{k_1}{\rightleftharpoons} Co_{aq}{}^{2+} + Co_{aq}{}^{3+} \tag{3a}$$

$$CoOH_{aq}{}^{2+} + Co_{aq}^{2+} \overset{k_2}{\rightleftharpoons} Co_{aq}{}^{2+} + CoOH_{aq}^{2+} \tag{3b}$$

This type of rate law is common to many reactions of cobalt(III). An important point to be made here is that it is a special case of the more general rate law[51]

$$k_{obs} = (k_1 + k_2K_h/[H^+])/(1 + K_h/[H^+]) \tag{4}$$

with $K_h \ll [H^+]$, a condition which is usually fulfilled in the experimental acidity range (see previous Section). The observed values of k_1 and k_2 are collected in Table 2, and the appropriate activation parameters are given in Table 3 The rate constants increase with increasing ionic strength and the activation parameters are not appreciably sensitive to a change of medium from $HClO_4/NaClO_4$ to $HClO_4/LiClO_4$ mixtures. At 25° and ionic strength 1M we find that $k_2/k_1 \approx 1.6\times10^2$. The corresponding ratio for the iron(III)–iron(II) exchange reaction is *ca.* 7.5×10^2 at 25° (Refs. 50, 52). Both of these exchange reactions are catalyzed by anions

TABLE 2

KINETIC DATA FOR THE COBALT(III)–COBALT(II) EXCHANGE REACTION

Temperature (°C)	*Ionic strength (M)*	$k_1{}^a$	$10^{-2}k_2{}^a$
0.15	0.5	0.42 ± 0.01	1.11 ± 0.05
10.6	0.5	0.88 ± 0.05	1.92 ± 0.13
18.35	0.5	1.53 ± 0.11	2.62 ± 0.24
0.15	1.0	0.58 ± 0.05	1.78 ± 0.19
10.6	1.0	1.43 ± 0.10	2.47 ± 0.26
18.35	1.0	2.38 ± 0.18	3.25 ± 0.16
0.15	3.0	0.97 ± 0.03	4.17 ± 1.39
10.6	3.0	3.05 ± 0.50	4.36 ± 1.80

[a] Units are M^{-1} sec^{-1}, the data are from Ref 49.

such as sulphate[49,53] (but not low concentrations of nitrate[50]) and the energetics of reaction in the two systems are strikingly similar (Table 3)[49]. However, despite the fact that there is a great deal of information available on the iron(III)–iron(II) reaction[53] the mechanism is still in doubt[54], and thus we are unable to assess the importance of spin-multiplicity in the cobalt exchange reaction[54,55]. It is in this exchange reaction that we first encounter the possibility of spin-multiplicity as an important factor in the activation process for a possible inner-sphere reaction of cobalt(III).

TABLE 3

ACTIVATION PARAMETERS FOR ELECTRON EXCHANGE REACTIONS BETWEEN COBALT(III) AND COBALT(II), AND IRON(III) AND IRON(II)[a]

Reactants	$\Delta H_1^{\neq b,c}$	$\Delta S_1^{\neq b,d}$	$\Delta H_2^{\neq c,e}$	$\Delta S_2^{\neq d,e}$	*Ref.*
$Fe_{aq}{}^{3+}$, $Fe_{aq}{}^{2+}$	10.5	−21	–	–	52
$Co_{aq}{}^{3+}$, $Co_{aq}{}^{2+}$	10.3	−21	11.8	−17	49
$FeOH_{aq}{}^{2+}$, $Fe_{aq}{}^{2+}$	8.4	−14	–	–	50
$CoOH_{aq}{}^{2+}$, $Co_{aq}{}^{2+}$	8.5	−21	5.3	−28	49
$FeSO_{4aq}{}^{+}$, $Fe_{aq}{}^{2+}$	8.4	−19	13.2	−3	55, 56
$CoSO_{4aq}{}^{+}$, $Co_{aq}{}^{2+}$	14.2	−3	–	–	49

[a] Parameters corresponding to reactions involving hydrolyzed species have been corrected by subtraction of the appropriate enthalpies and entropies of hydrolysis [b] Ionic strength 0.50M [c] Units are kcal $mole^{-1}$ [d] Units are cal deg^{-1} $mole^{-1}$. [e] Ionic strength 1.00M

The reaction between cobalt(III) and iron(II) has been studied by Bennett and Sheppard[46] using a titrimetric method. The reaction rate is first-order in each reactant and the rate law[46] is consistent with the mechanism

$$Co_{aq}{}^{3+} + Fe_{aq}{}^{2+} \xrightarrow{k_1} Co_{aq}{}^{2+} + Fe_{aq}{}^{3+} \tag{5}$$

$$CoOH_{aq}{}^{2+} + Fe_{aq}{}^{2+} \xrightarrow{k_2} Co_{aq}{}^{2+} + FeOH_{aq}{}^{2+} \tag{6}$$

with $k_1 = (42.6 \pm 10) M^{-1} \cdot sec^{-1}$ and $k_2 = (2.4 \pm 0.9) \times 10^5 M^{-1} \cdot sec^{-1}$ at 25° and ionic strength 1M. The ratio $k_2/k_1 \approx 5 \times 10^3$, is considerably larger than the value found for the corresponding ratio for the exchange reaction, $k_2/k_1 \approx 1.6 \times 10^2$, see Table 3. The observation that the reaction is first-order in both reactants indicates that the rate-determining step is not the conversion of the low-spin form of cobalt(III) to some high-spin form, since such a process would be independent of $[\mathrm{Fe^{II}}]$ The concentration of cobalt(III) was varied over a wide range in this study and the simple kinetics which are observed argue against contributions from polymerized cobalt(III) species. The reaction is catalysed by sulphate, and the rate constant for the reaction between $\mathrm{CoSO_4}^+$ and Fe^{2+} has been found to be $4.9 \times 10^3 \mathrm{M}^{-1} \cdot \mathrm{sec}^{-1}$ at 0° and 1M ionic strength[46].

Conocchioli, Nancollas and Sutin[57] have studied the effect of added chloride on the reaction with iron(II). The rapid appearance of FeCl^{2+} was observed at 336 nm when a solution containing $[\mathrm{Co^{III}}] = 9.6 \times 10^{-4}\mathrm{M}$, $[\mathrm{Co^{II}}] = 2.9 \times 10^{-2}\mathrm{M}$, $[\mathrm{Cl}^-] = 4.0 \times 10^{-3}\mathrm{M}$ and $[\mathrm{HClO_4}] = 3.0\mathrm{M}$ was mixed with one containing $[\mathrm{Fe^{II}}] = 9\,2 \times 10^{-2}\mathrm{M}$ and $[\mathrm{HClO_4}] = 2\,7\mathrm{M}$. The rate of aquation of the product was found to be identical to that of FeCl^{2+} under the same conditions. If the same experiment is repeated with chloride added to the iron(II) solution instead of to the cobalt(III) solution, then the formation of FeCl^{2+} as a primary product is not observed. This establishes that the reaction

$$\mathrm{CoCl}^{2+} + \mathrm{Fe}^{2+} \rightarrow \mathrm{FeCl}^{2+} + \mathrm{Co}^{2+} \tag{7}$$

proceeds by an inner-sphere mechanism in which the chloride ion forms a bridge between the reactants. These observations[57] illustrate the possibility of a distinction between inner- and outer-sphere mechanisms for reactions involving labile reactants and products.

Diebler and Sutin[42] have measured the rate of the reaction

$$\mathrm{Co^{III}} + \mathrm{Mn}^{2+} \rightarrow \mathrm{Co}^{2+} + \mathrm{Mn^{III}}$$

at 25° in 3M $\mathrm{HClO_4}$. The observed rate constant is $1\,0 \times 10^2 \mathrm{M}^{-1} \cdot \mathrm{sec}^{-1}$, which compares quite well with the calculated (Marcus) rate constant of $10\mathrm{M}^{-1} \cdot \mathrm{sec}^{-1}$ under these conditions. Other considerations[42,51] also suggest that this reaction may proceed *via* an outer-sphere mechanism. A study of the acid-dependence of the rate might be helpful in the determination of the mechanism of this reaction. Results for reactions of cobalt(III) with iron(II) and manganese(II) are collected in Table 4.

Comparison of the reactions of cobalt(III) with those of silver(II) is instructive, since the standard potentials of the $\mathrm{Co^{III}/Co^{II}}$ and $\mathrm{Ag^{II}/Ag^{I}}$ couples are similar (previous Section). Sutcliffe and his co-workers have studied the reduction of silver(II) by water[58]. The rate law in acid perchlorate solution has the form

$$-\frac{\mathrm{d}[\mathrm{Ag^{II}}]}{\mathrm{d}t} = \frac{k_{\mathrm{obs}}[\mathrm{Ag^{II}}]^2}{[\mathrm{Ag^{I}}]\,[\mathrm{H}^+]^2} \tag{8}$$

The following mechanism is consistent with this rate law:

TABLE 4

KINETIC PARAMETERS FOR REACTIONS BETWEEN COBALT(III) SPECIES AND IRON(II) AND MANGANESE(II)

Reaction	*Rate constant*[a] *at* 25°	$\Delta H^{\neq b}$	$\Delta S^{\neq c}$	*Ref*
$Co^{3+}+Fe^{2+}$	$42\ 6 \pm 10^{d}$, 3×10^{2e}	9 1	−23	46[d], 57[e]
$CoOH^{2+}+Fe^{2+}$	$(2\ 4 \pm 0\ 9)\times10^{5d}$	7 9	−17	46
$Co^{III}+Mn^{2+}$	$1\ 00\times10^{2e}$	–	–	42
$CoSO_4^{+}+Fe^{2+}$	$4\ 9\times10^{3d\ f}$	–	–	46
$CoCl^{2+}+Fe^{2+}$	$\geq 5\times10^{3e}$	–	–	57

[a] Units are M^{-1} sec^{-1}. [b] Units are kcal deg^{-1} mole^{-1} [c] Units are cal. deg^{-1}.mole^{-1}. [d] At ionic strength 1M. [e] Measured in 3M $HClO_4$ [f] Temperature is 0°

$$2Ag^{II} \rightleftharpoons Ag^{III}+Ag^{I} \qquad (K_1) \tag{9}$$

$$Ag^{III}+H_2O \rightleftharpoons AgO^{+}+2H^{+} \qquad (K_2) \tag{10}$$

$$AgO^{+} \xrightarrow{k_1} Ag^{I}+\tfrac{1}{2}O_2 \tag{11}$$

with step (11) rate-determining We then have

$$k_{obs} = k_1K_1K_2 \tag{12}$$

and from the variation of k_{obs} with temperature we obtain

$$k_1K_1K_2 = 5\times10^{13} \exp(17{,}300/RT) \tag{13}$$

The rate law for the reduction of cobalt(III) by Ag^{I} has the form[59]

$$-\frac{d[Co^{III}]}{dt} = \frac{k_{obs}[Co^{III}]^2[Ag^{I}]}{[Co^{II}]^2[H^{+}]^2} \tag{14}$$

which on comparison with Eqn. (8) suggests the additional equilibrium

$$Co^{III}+Ag^{I} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Co^{II}+Ag^{II} \tag{15}$$

and a mechanism with (11) as the rate-determining step. Combination of the results[58,59] of these two studies leads to the estimate $K_3 = k_2/k_{-2} = 1.7\times10^{-2}$ in 3M perchloric acid at 25°. This value is in good agreement with the value $K_3 = 2.3\times10^{-2}$ in 4M perchloric acid at 25° obtained by Huchital, Sutin and Warnqvist[36b].

Although the reaction between cobalt(III) and chromium(III) is very slow at room temperature the oxidation to Cr^{VI} is strongly catalyzed by silver(I). Sutcliffe *et al.*[60] measured rates of reaction in the presence of silver(I) by monitoring the appearance of chromium(VI) at 475 nm, where the absorbance of the reactants and of the intermediate Ag^{II} is small. The suggested mechanism[60] for this reaction consists of equilibrium (15) followed by the rate-determining step

$$Ag^{II}+Cr^{III} \xrightarrow{k_3} Ag^{I}+Cr^{IV}$$

and the fast steps

$$\begin{aligned} &\mathrm{Ag^{II}+Cr^{IV} \rightarrow Ag^{I}+Cr^{V}} \\ &\mathrm{Ag^{II}+Cr^{V} \rightarrow Ag^{I}+Cr^{VI}} \end{aligned} \tag{17}$$

If $\mathrm{Ag^{II}}$, $\mathrm{Cr^{IV}}$ and $\mathrm{Cr^{V}}$ are at steady-state concentrations and the concentrations of silver(I), chromium(III) and cobalt(II) are much greater than that of cobalt(III) then the rate law is

$$-\frac{\mathrm{d[Co^{III}]}}{3\,\mathrm{d}t} = \frac{\mathrm{d[Cr^{VI}]}}{\mathrm{d}t} = \frac{k_2 k_3 [\mathrm{Co^{III}}]\,[\mathrm{Ag^{I}}]\,[\mathrm{Cr^{III}}]}{3k_{-2}[\mathrm{Co^{II}}]+9k_3[\mathrm{Cr^{III}}]} \tag{18}$$

$$= k_{\mathrm{obs}}[\mathrm{Co^{III}}] \tag{19}$$

where $k_{\mathrm{obs}} = k_2 k_3 [\mathrm{Ag^{I}}]\,[\mathrm{Cr^{III}}]/(3k_{-2}[\mathrm{Co^{II}}]+9k_3[\mathrm{Cr^{III}}])$. (A stoichiometric factor 3 was omitted in the original paper[60]). Suitable plots of the kinetic data under different conditions allow the rate constant k_2 to be obtained as a function of temperature. We find that $k_2 = (35.3 \pm 4.0)\mathrm{M^{-1} \cdot sec^{-1}}$ at 25° and $[\mathrm{HClO_4}] = 3\mathrm{M}$. From the known value of K_3 we calculate $k_{-2} = (2\,0 \pm 0.2)\times 10^{3}\mathrm{M^{-1} \cdot sec^{-1}}$ under these conditions. These values should be compared with $k_2 = (37 \pm 4)$ $\mathrm{M^{-1} \cdot sec^{-1}}$ and $k_{-2} = (1.75 \pm 0.05)\times 10^{3}\mathrm{M^{-1} \cdot sec^{-1}}$ measured directly by stopped-flow spectrophotometry in 4M perchloric acid at 25° (Ref. 39b). Finally, the composite quantity k_{-2}/k_2k_3 is obtained from experimental plots of Eqn. (18), which enables values of k_3 to be obtained as a function of temperature. We find that $k_3 = 5.2\times 10^{3}\mathrm{M^{-1} \cdot sec^{-1}}$ in 3M perchloric acid at 25°. The results of this elegant series of studies[36b,58–60] are summarized in Table 5. Although the acid-dependence of these reaction rates would be of considerable interest, the interpretation of the data might be expected to be ambiguous in view of the extensive hydrolysis of the silver(II)/silver(III) system[61 62].

The kinetics of oxidation of mercury(I), vanadium(IV) and vanadium(III) by cobalt(III) have been investigated spectrophotometrically by Rosseinsky and Higginson[63]. The rate of oxidation of mercury(I) is unaffected by variations of

TABLE 5

KINETIC PARAMETERS FOR REACTIONS INVOLVING THE EQUILIBRIUM $\mathrm{Co(III)+Ag(I) \rightleftarrows Co(II)+Ag(II)}$ IN 3M $\mathrm{HClO_4}$

Parameter	*Value at 25°*	*Enthalpy kcal mole^{-1}*	*Entropy cal deg^{-1} mole^{-1}*	*Ref.*
$k_1K_1K_2$	11 6[a]	−17 3	+ 4	58
K_3	1.7×10^{-2}	3 9	+36	50[b], 59, 36*b*[c]
k_2	35 3[d]	17 3	+ 8	36*b*, 60
k_{-2}	2.0×10^{3}[d]	4 2	−28	59, 60, 36*b*[c]
k_3	$5\,2\times 10^{3}$[d]	10 8	−19	60

[a] Units are $\mathrm{M^{-2}\ sec^{-1}}$. [b] Data reported in this reference at 1M ionic strength [c] Data reported in this reference at 4M $\mathrm{HClO_4}$ [d] Units are $\mathrm{M^{-1} \cdot sec^{-1}}$.

$[Co^{II}]$, $[Hg^{II}]$ or perchlorate ion concentration at constant acidity and ionic strength 3M at 20°. The rate law for the reaction is of the form

$$k_{obs} = [Co^{III}]\,[Hg^{I}{}_2]\,(k_1+k_2K_h/[H^+]) \tag{20}$$

corresponding to the mechanism

$$Co^{3+}+(Hg^I)_2 \xrightarrow{k_1} Co^{2+}+(Hg^I+Hg^{II}) \text{ or } Hg_2{}^{3+} \tag{21}$$

$$CoOH^{2+}+(Hg^I)_2 \xrightarrow{k_2} Co^{2+}+OH^-+(Hg^I+Hg^{II}) \text{ or } Hg_2{}^{3+} \tag{22}$$

followed by faster reactions represented by (23),

$$Co^{III}+Hg^I \text{ (or } Hg_2{}^{3+}) \rightarrow Co^{II}+(2)Hg^{II} \tag{23}$$

The reaction between cobalt(III) and vanadium(IV) is unaffected[63] by additions of vanadium(V), but high concentrations of cobalt(II) catalyse the oxidation of vanadium(IV) by perchloric acid, thereby increasing the rate of reduction of cobalt(III). At low initial cobalt(II) concentrations the rate law is

$$-\frac{d[Co^{III}]}{dt} = k_{obs}[Co^{III}]\,[V^{IV}] \tag{24}$$

where $k_{obs} = k_1+k_2/[H^+]$; this rate law is predicted by the following mechanism

$$\begin{aligned} &Co^{3+}+VO^{2+} \xrightarrow{k_3} Co^{2+}+VO^{3+} \\ &CoOH^{2+}+VO^{2+} \xrightarrow{k_4} Co^{2+}+VO(OH)^{2+} \end{aligned} \tag{25}$$

$$\begin{aligned} &VO_{aq}{}^{3+} \rightleftharpoons VO(OH)_{aq}{}^{2+}+H^+_{aq} \\ &VO(OH)_{aq}{}^{2+} \rightleftharpoons VO_2{}^{+}+H^+_{aq} \end{aligned} \tag{26}$$

Here $k_1 = k_3$ and $k_2 = k_4K_h$.

The reaction between cobalt(III) and vanadium(III) produces vanadium(IV) and vanadium(V). The kinetics of this reaction are complicated by the rapid reaction

$$V^{III}+V^{V} \rightleftharpoons 2V^{IV} \tag{27}$$

The rates of oxidation of vanadium(III) and vanadium(IV) by cobalt(III) are similar and the rate law with excess of vanadium(III) is given by

$$-d\,[Co^{III}]/dt = k_5[Co^{III}]\,[V^{III}]+(k_3+k_4/[H^+])\,[Co^{III}]\,[V^{IV}] \tag{28}$$

where

$$k_5 = k_a+k_b/[H^+]+k_c/[H^+]^2 \tag{29}$$

where k_a, k_b and k_c are constants, and k_3 and k_4 are the rate constants for reactions (25). The complications caused by reaction (27) are unfortunate since the acid-dependence of k_5 is difficult to extract from the data (Table 4 of Ref. 63).

The rate constant does, however, exhibit a strong acid-dependence, and all three acid-dependent reactions could proceed *via* inner-sphere mechanisms. We calculate that the rate constant for the kinetically indistinguishable reactions

$$\mathrm{CoOH^{2+}+V^{3+}} \xrightarrow{k_1} \mathrm{Co^{2+}+VOH^{3+}} \tag{30a}$$

$$\mathrm{Co^{3+}+VOH^{2+}} \xrightarrow{k_2} \mathrm{Co^{2+}+VOH^{3+}} \tag{30b}$$

is $k_1K_h = k_2K_h' = 60\ \mathrm{sec}^{-1}$ at 25° and ionic strength 3M, where K_h' is the equilibrium constant for the reaction

$$\mathrm{V_{aq}}^{3+} \rightleftharpoons \mathrm{VOH_{aq}^{2+}+H_{aq}^{+}} \qquad (K_h') \tag{31}$$

Neptunium(VI) is the product of both the oxidation of neptunium(V) and of the complex $[\mathrm{Np^V}\cdot\mathrm{Cr^{III}}]$ by cobalt(III)[64]. The kinetics of the disappearance of the complex were followed spectrophotometrically at its maximum at 993.5 nm. The experimental rate law for the reaction is

$$-\frac{\mathrm{d[C]}}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{C}]\,[\mathrm{Co^{III}}] = k[\mathrm{C}]\,[\mathrm{Co^{III}}]/[\mathrm{H^+}] \tag{32}$$

where [C] is the concentration of complex. A plot of k_{obs} *vs.* $1/[\mathrm{H^+}]$ for data at 5° and ionic strength 2.1M is shown in Fig. 3. The same rate law holds in the temperature range 5–25° with perchloric acid concentrations between 0.46 and 2.08M. The following mechanism is consistent with this rate law

$$\mathrm{CoOH^{2+}+[Np^V\cdot Cr^{III}]} \xrightarrow{k_2} \mathrm{Co^{2+}+Np^{VI}+OH^-+Cr^{III}} \tag{33}$$

where $k = k_2K_h$ and $k_2 = 1.23\times10^4\mathrm{M}^{-1}\cdot\mathrm{sec}^{-1}$ at 25° and ionic strength 2.10M. The assignment of the acid-dependence of the rate in terms of the pair $\mathrm{Co^{3+}}/\mathrm{CoOH^{2+}}$ rather than the complex and its conjugate base is supported by the observation that the rate of dissociation of the complex appears to be acid-independent in this acidity range[65].

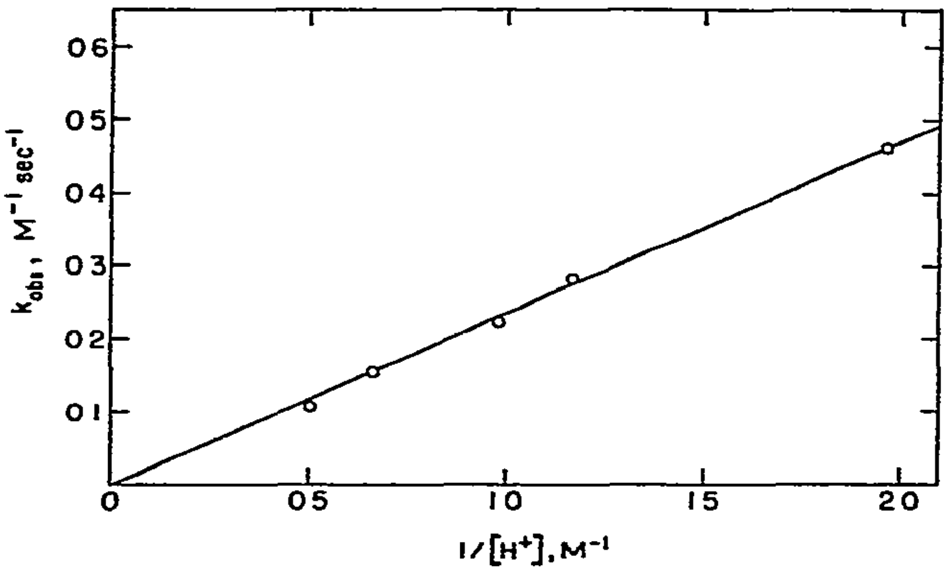

Fig. 3. Plot of k_{obs} *vs.* $1/[\mathrm{H^+}]$ for the reaction between cobalt(III) and the neptunium(V)–chromium(III) complex at 5° and ionic strength 2.10M; from the data of Ref. 64

Medium effects are usually important in reactions involving highly charged species in solution. In view of the absence of large medium effects, for example, in the cobalt(III)–cobalt(II) exchange reaction (Eqn. 5), and of the simple rate law found for the oxidation of the neptunium(V) · chromium(III) complex by cobalt(III), we feel that the rate of oxidation[64] of neptunium(V) can be fairly accurately described by the acid-independent rate constant $k_{obs} = (67.5 \pm 4.5)$ $M^{-1} \cdot sec^{-1}$ in the acidity range 0.49–2.10M $HClO_4$ at 0° and ionic strength 2.10M. At higher temperatures a small inverse acid-dependence is evident and we calculate that the rate constants k_1 and k_2 for the reactions

$$Co^{3+} + Np^{V} \xrightarrow{k_1} Co^{2+} + Np^{VI} \tag{34}$$

$$CoOH^{2+} + Np^{V} \xrightarrow{k_2} Co^{2+} + Np^{VI} + OH^- \tag{35}$$

have the values $(291 \pm 3) M^{-1} \cdot sec^{-1}$ and $(13 \pm 3) \times 10^3 M^{-1} \cdot sec^{-1}$, respectively, at 25° and ionic strength 2.10M. The similarity of these rate constants may indicate an outer-sphere path for reaction (34).

The reaction of cobalt(III) with cerium(III) in perchloric acid[28] and sulphuric acid[13] media was studied by Sutcliffe and Weber. They found that cerium(III) forms a complex, $CeClO_4^{2+}$, in perchlorate solutions (formation constant about $1.5 M^{-1}$ at 25° and ionic strength 1.14M and about $0.5 M^{-1}$ at ionic strength 5.1M). The observed second-order rate constant was found to depend on the perchlorate concentration according to

$$1/k_{obs} = b + c/[ClO_4^-]$$

and to depend on acidity according to

$$k_{obs} = a/[HClO_4]$$

where a, b, and c are constants. It was concluded from these observations that the predominant reaction is

$$CoOH^{2+} + CeClO_4^{2+} \xrightarrow{k} Co^{II} + Ce^{IV}$$

where $k = 95 M^{-1} \cdot sec^{-1}$ at 25° and ionic strength 1.03M.

The reaction is catalyzed by additions of bisulphate ions[13], and it was proposed that the complexes $CoSO_4^+$, $Co(SO_4)_2^-$ and $CeSO_4^+$ are involved. The equilibrium constants of the following equilibria were determined spectrophotometrically at 25° and ionic strength = 1 0–1 3M.

$$Co^{3+} + HSO_4^- \rightleftharpoons CoSO_4^+ + H^+ \qquad (K_1' = 2)$$

$$CoSO_4^+ + HSO_4^- \rightleftharpoons Co(SO_4)_2^- + H^+ \qquad (K_2' = 40)$$

The number of possible reactions is so large, however, that a complete kinetic analysis cannot be made. This is a common difficulty encountered in work on cobalt(III) reactions in sulphuric acid media[13,14]. A further complication is that the acidity "constant" of HSO_4^- seems to be quite sensitive to changes of the composition of the solvent medium[13], for instance, if alkali metal ions are replaced by hydrogen ions at constant ionic strength.

The reaction between cobalt(III) and thallium(I) was investigated by Ashurst and Higginson[14], mainly in perchloric acid solution. They found that the rate decreased with increasing cobalt(II) concentration and hence the following mechanism was proposed

$$Co^{3+} + Tl^{I} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co^{II} + Tl^{II}$$

$$CoOH^{2+} + Tl^{I} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Co^{II} + Tl^{II}$$

$$Co^{III} + Tl^{II} \xrightarrow{fast} Co^{II} + Tl^{III}$$

This mechanism is reminiscent of that for the iron(II)–thallium(III) reaction[66]. The rate constant k_1 was the only parameter that could be obtained with any certainty from the experimental data. At 25° and ionic strength 2.70M, k_1 is $(2.5 \pm 0.3) \times 10^{-3} M^{-1} \cdot sec^{-1}$. For the acid-dependent path, $k_2 K_h \approx 1.6 \times 10^{-4}$ sec^{-1} at 25° which gives $k_2 \approx 8 \times 10^{-2} M^{-1} \cdot sec^{-1}$. The reaction is thus very slow with an activation energy of 26 ± 2 kcal. $mole^{-1}$ for the acid-independent path. The corresponding activation entropy is +13 cal. $degree^{-1}$. $mole^{-1}$.

The reaction was found to be catalysed by sulphate ions *via* the complex $CoSO_4^{+}$. From the kinetic analysis the stability constant

$$Co^{3+} + SO_4^{2-} \rightleftharpoons CoSO_4^{+} \qquad (K_1)$$

was determined to be $K_1 = 22 \pm 7 M^{-1}$. The value for K_1' quoted previously[13] is consistent with this. From the observed rate law it was concluded that any path with an activated complex containing the bisulphate ion is negligible.

In the cobalt(III) oxidation of an organic compound, diethyl ketone[67], on the other hand, the rate decreased on addition of sulphuric acid, "owing to the formation of an inert complex, $CoSO_4^{+}$". The catalysis by sulphate of the oxidation of thallium(I) is evidently due to the involvement of a sulphate-bridged intermediate in this reaction On the other hand, the sulphatocobalt(III) complexes might be expected from energetic considerations to be less reactive towards organic molecules than are the aquocomplexes[16].

The oxidation of olefins in aqueous sulphuric acid–sodium bisulphate solution by cobalt(III) sulphate was studied by Bawn and Sharp[68]. The observed second-order rate constant was found to be practically independent of acidity and total sulphate ion concentration. This suggests that the predominant reactive cobalt(III) species is a single cobalt(III)–sulphate complex. From the stability constants given by Sutcliffe and Weber[13] (see above) it follows that $Co(SO_4)_2^{-}$ should be the major cobalt(III) species throughout the experimental range[68]. From examples like this and from other considerations discussed previously one concludes that studies in sulphate media give little information for comparisons with the nature of the oxidizing ion in noncomplexing media. On the other hand, there are a large number of studies where attention is focussed mainly on the nature of the organic substrate and of the intermediates formed. This is the case, for instance, in the series of papers by Waters and his coworkers[69]. The observation of complex formation is unusual for the slow reactions in this class: an exception is the reaction between cobalt(III) and propionic acid, where Michaelis–Menten type kinetics have been found[70].

Inner-sphere complex formation is more likely to be a feature of cobalt(III) reactions involving neutral or negatively-charged reductants than in the reactions with cationic species. Consider the reaction scheme

$$M+B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MB \tag{35}$$

$$MB \xrightarrow{k_2} \text{products} \tag{36}$$

Three cases of this general mechanism need be considered.

(1) If $k_{-1} < k_2$, then both the formation and disappearance of a complex may be observed

(2) If MB is in a steady state, then

$$k_{\text{obs}} = k_1 k_2/(k_{-1}+k_2) \tag{37}$$

and the observed activation parameters will be composite quantities.

(3) If $k_2 \gg k_{-1}$, then

$$k_{\text{obs}} = k_1 \tag{38}$$

and the rate of the oxidation–reduction process will be limited by the rate of formation of the complex

A good example of case (1) is the reaction between cobalt(III) and chloride,

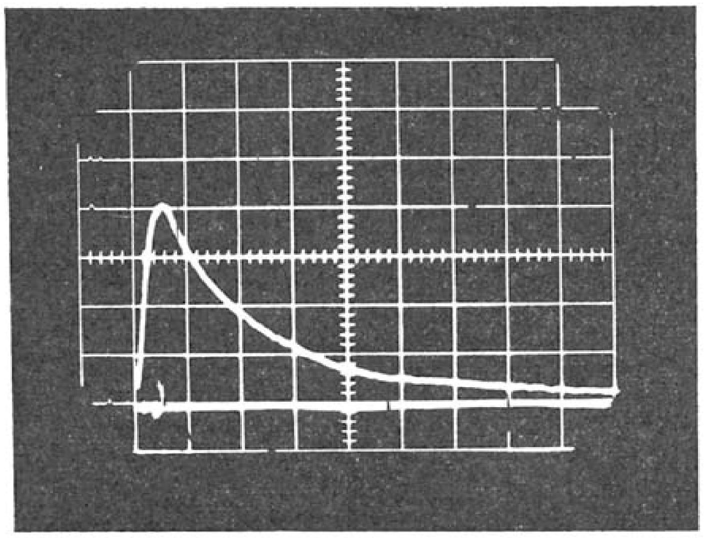

Fig 4. Stopped-flow trace showing the formation and decomposition of cobalt(III)–chloride complexes; from Ref. 27 The vertical scale is in arbitrary absorbance units and the horizontal time scale corresponds to 500 msec per division. The experimental conditions are as follows: $[Co^{III}] = 7.5 \times 10^{-5}$M, $[Co^{II}] = 2.4 \times 10^{-4}$M, $[Cl^-] = 5.0 \times 10^{-2}$M, $[HClO_4] = 1.0$M, wavelength 280 nm at 25.0° (reproduced by permission of the copyright owner, American Chemical Society)

where the formation and decay of an intermediate complex is observed under appropriate conditions (Fig. 4)[27]. Another indication that complex formation is taking place is that when reactions are run at different concentrations of (excess) reductant and the pseudo-first-order rate constants are plotted *versus* the corresponding reductant concentration then the following relation is obtained

$$k_{\mathrm{obs}} = k_{\mathrm{a}} + k_{\mathrm{b}}[\mathrm{B}] \tag{39}$$

where k_{a} and k_{b} are constants and $k_{\mathrm{a}} \neq 0$. An example of this relationship is found in Fig. 2 of Ref. 27. In the absence of cobalt(II) catalysis the following mechanism obtains[27,29]

$$\mathrm{Co_{aq}}^{3+} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\mathrm{CoB})_{\mathrm{aq}}{}^{3+} \qquad (K_1) \tag{40}$$

$$\mathrm{Co_{aq}}^{3+} \rightleftharpoons \mathrm{CoOH_{aq}}^{2+} + \mathrm{H}^+_{\mathrm{aq}} \qquad (K_{\mathrm{h}}) \tag{41}$$

$$\mathrm{CoOH_{aq}}^{2+} + \mathrm{B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (\mathrm{Co(OH)B})_{\mathrm{aq}}{}^{2+} \tag{42}$$

$$(\mathrm{CoB})_{\mathrm{aq}}{}^{3+} \rightleftharpoons (\mathrm{Co(OH)B})_{\mathrm{aq}}{}^{2+} + \mathrm{H}^+_{\mathrm{aq}} \qquad (K_3) \tag{43}$$

From this scheme we deduce the equations

$$k_{\mathrm{a}} = k_{-1} + k_{-2}K_3/[\mathrm{H}^+] \tag{44}$$

$$k_{\mathrm{b}} = [K_1/(1+K_{\mathrm{h}}/[\mathrm{H}^+])]\,(k_{-1}+k_{-2}K_3/[\mathrm{H}^+]) = (k_1+k_2K_{\mathrm{h}}/[\mathrm{H}^+])/(1+K_{\mathrm{h}}/[\mathrm{H}^+]) \tag{45}$$

It is evident from Eqn. (39) that if k_{a} is much less than $k_{\mathrm{b}}[\mathrm{B}]$ then no intercept will be observed in the plot of k_{obs} *vs.* [B]. Under these conditions it is difficult to distinguish complex formation. It follows from Eqns (44) and (45) that

$$k_{\mathrm{a}}/k_{\mathrm{b}} = 1/K_1 + K_{\mathrm{h}}/K_1[\mathrm{H}^+] \tag{46}$$

Under favorable conditions it may be possible to obtain estimates of K_1 and K_{h} from Eqn. (46). The use of this equation has the advantage that no assumptions need be made about the detailed mechanism of the reaction since Eqn. (46) depends entirely on stoichiometric considerations. However, the dependence of Eqn. (46) on ratios of intercepts to slopes makes its application susceptible to rather large errors.

An attempt has been made to obtain estimates of K_{h} by applying Eqn (46) to the reaction between cobalt(III) and chloride[27]. However, the value of K_{h} obtained there appears to be too high by at least one order of magnitude. This error probably arises from complications connected with the subsequent redox reactions which become important at lower acidities. Another example of the large error in obtaining values of an acid-dissociation constant (for $\mathrm{Mn_{aq}}^{3+}$) from graphical intercept/slope ratios has recently been discussed[71]. Similar conclusions hold for the results obtained by McAuley and his coworkers on the oxidation of malic[29] and thiomalic[29] acids by cobalt(III), where complex formation is also observed: here the uncertainty in the kinetic data is relatively large because of the narrow (typically, less than two-fold) acidity range imposed by the employment of low ionic strength. The activation parameters obtained for these reactions are also inaccurate. Results obtainable from the data for the three reactions mentioned above are summarized in Table 6.

TABLE 6

KINETIC PARAMETERS FOR REACTIONS IN WHICH COMPLEX FORMATION IS OBSERVED DIRECTLY

Reductant, B	k_1[a]	$10k_{-1}$[b]	K_1[c]	$10^{-4}k_2$[a]	$k_{-2}k_3$[d]	*Ref.*
Chloride	3	1.0	30	1.23	1.5	27[e]
Malic acid	4.6	1.6	30	0.29	0.2	29[f]
Thiomalic acid	$\lesssim 6$	$\lesssim 0.5$	≈ 120	0.76	–	29[f]

[a] Units are $M^{-1} \cdot sec^{-1}$. [b] Units are sec^{-1}. [c] Units are M^{-1} [d] Units are $M \cdot sec^{-1}$. [e] Data at 25°, ionic strength 3M [f] Data at 7°, ionic strength 0.25M

For most reactions of cobalt(III) which have been studied the kinetic traces give no indication of complex formation (Fig. 5) and the plot of k_{obs} (sec^{-1}) *vs.* [B] has no detectable intercept (Fig 6) A plot of k_{obs} *vs.* $1/(H^+]$ is a straight line, (see, *e.g.*, Fig. 7), with intercept k_1 and slope k_2K_h corresponding to the parallel slow paths

$$Co^{3+} + B \xrightarrow{k_1} \text{products}$$

$$CoOH^{2+} + B \xrightarrow{k_2} \text{products}$$

The values of k_1 are usually more uncertain than those of k_2, as noted above. We have collected values of k_1, k_2 and calculated activation enthalpies and entropies in Table 7.

After some specific points have been raised concerning particular reactions we shall go on to consider general trends in these results.

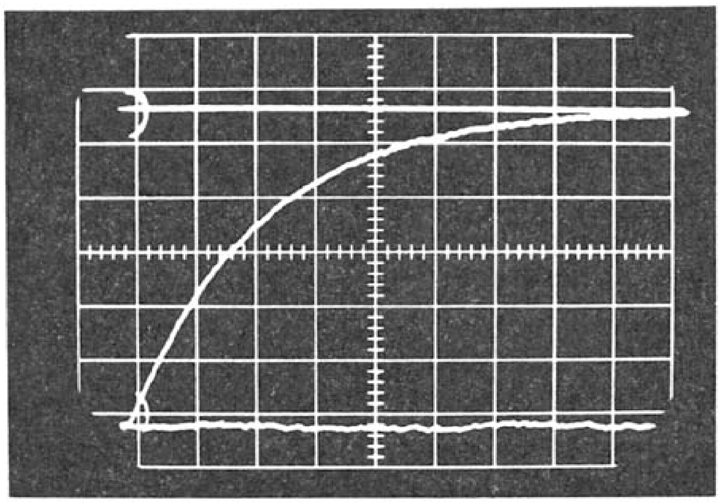

Fig. 5. Typical stopped-flow trace for a reaction in which complex formation is not observed directly. In this example the disappearance of cobalt(III) is being followed as a function of time

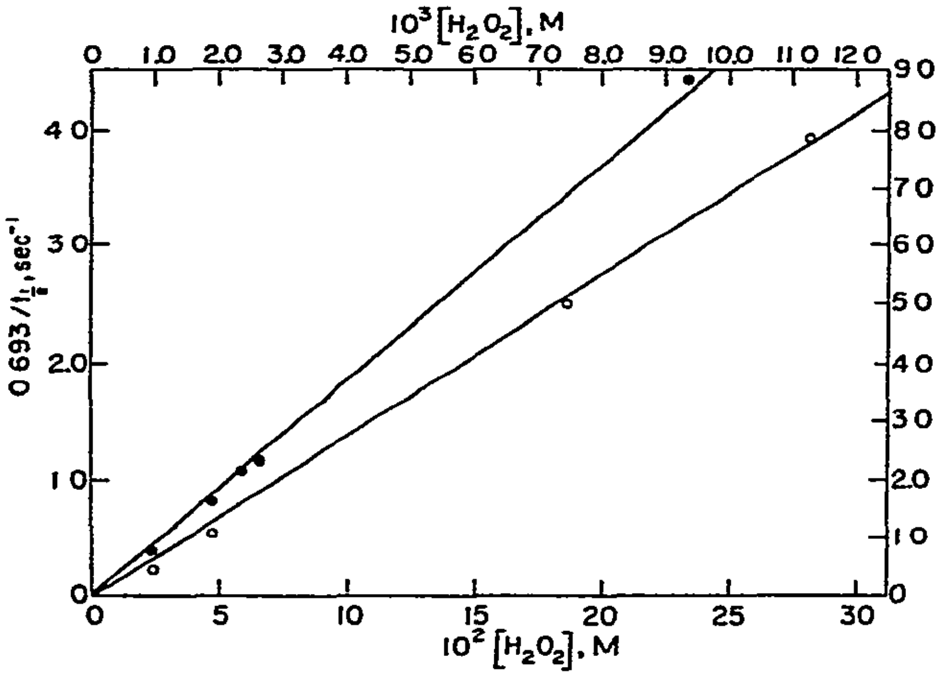

Fig 6 Plot of 0.693/$t_{\frac{1}{2}}$ vs $[H_2O_2]$ for reaction between cobalt(III) and a large excess of hydrogen peroxide at 25° and ionic strength 3M. The left and bottom axes refer to reaction in 3.0M $HClO_4$ (open circles) and the right and top axes to reaction in 0.05M $HClO_4$; from the data of Ref. 18.

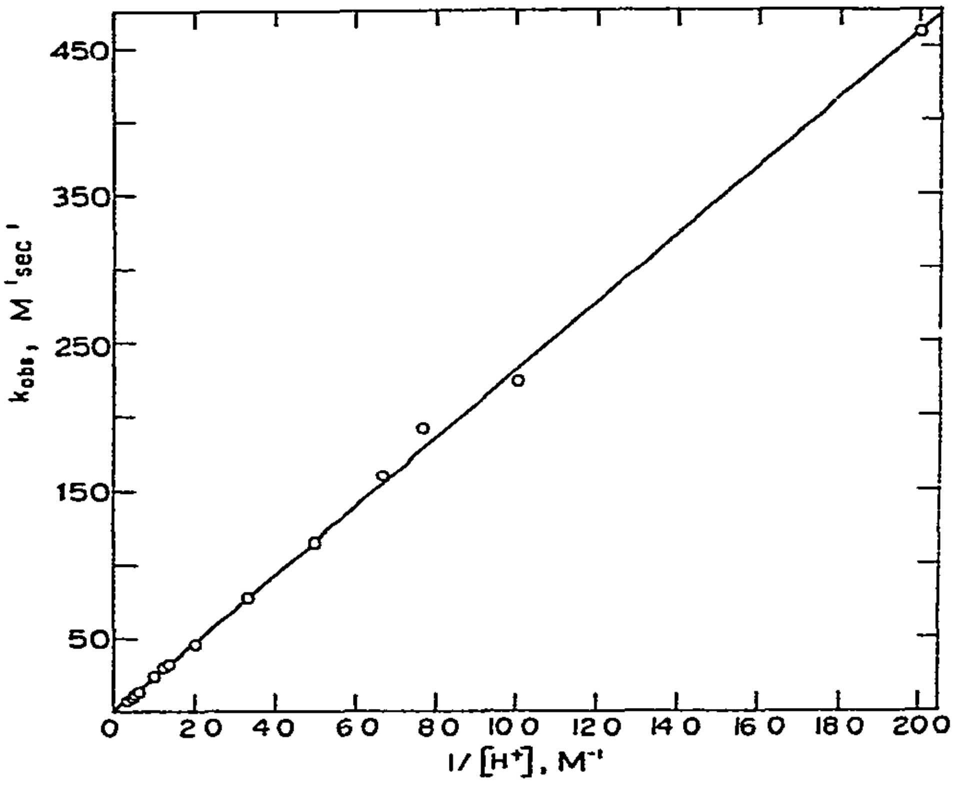

Fig. 7. Plot of k_{obs} vs $1/[H^+]$ for reaction with H_2O_2 at 25° and ionic strength 3M. A linear relationship holds over a sixty-fold acidity range under these conditions; from the data of Ref 18.

The oxidation of benzene by cobalt(III) has been studied by Wells[23]. The major reaction products are *cis-cis*-muconic acid, its lactone and *p*-benzoquinone. The experiments of Wells[23] support the reaction scheme

benzene → phenol → hydroquinone → *p*-benzoquinone
↳ catechol → *o*-benzoquinone → muconic acid (47)

The rate law for this reaction is

TABLE 7

KINETIC PARAMETERS FOR OXIDATION REACTIONS OF COBALT(III) IN ACID PERCHLORATE SOLUTION AT IONIC STRENGTH 3M

Reductant	k_1[a]	$10^{-2}k_2$[a]	$\Delta H_1^{\neq}$[b]	$\Delta S_1^{\neq}$[c]	$\Delta H_2^{\neq}$[b]	$\Delta S_2^{\neq}$[c]	*Ref.*
Ag^I	k_{obs} = 35.3		17.3[d]	+8[d]			36*b*, 60
Hg^I	6.3	160	21.5	+17	18.6	+14	63
Tl^I	2.5×10^{-3}	8×10^{-4}	26	+20	$(\Delta G_2^{\neq}$ =	19.0)	14[e]
Co^{II}	3.3	5.1	10.3	−21	11.8	−6	49, 50[f]
Fe^{II}	42.6	2400	9.1	−21	7.9	−7	46[f]
Mn^{II}	k_{obs} = 100			$(\Delta G^{\neq}$ =	14.7)		42[d]
V^{III}		300			$(\Delta G_2^{\neq}$ =	14.0)	63
$CeClO_4^{2+}$		0.95			19.0	+14	28[g]
V^{IV}	0.091	1.36×10^{-3}	21.8	−22	15.9	−5	63
Np^V	291	130	12.6	−5	(4.5)	(−25)	64[h]
$Np^V \cdot Cr^{III}$		12.3			9.0	−14	64[h]
malic acid[i]	4.6	290					29[j]
thiomalic acid[i]	$\lesssim 6$	76					29[j]
Cl^-[i]	3	123	$(\Delta G_1^{\neq}$ = 17.0)		$(\Delta G_2^{\neq}$ =	11.8)	27
NH_3OH^+		16.3			12.5	−2	78[h k]
$NH_3NH_2^+$		5.3			13.8	0	78[h,k]
thiourea (RSH^+)		260			5.7	−19	73[l]
H_2O_2	$\lesssim 2$	115			13.5	+5	18
HNO_2	18	86	18.3	+9	11.7	−1	18
HN_3	$\lesssim 2$	176			13.1	+5	74[m]
ClO_2	$\lesssim 1$	248			11.8	+1	77[h]
hydroquinone	2200	6400	18.2	+18	8.6	−3	18
Br^-	≤ 5	152			16.1	+15	18
I^-	8000	1.43×10^4	19.4	+25	11.5	+8	18
SCN^-	86.5	398	20.6	+20	15.6	+15	18

[a] Rate constants at 25°; units are M^{-1} sec^{-1} [b] Units are kcal $mole^{-1}$. [c] Units are cal deg^{-1}. $mole^{-1}$, entropies have been rounded to the nearest unit [d] Values in 3.0M $HClO_4$; activation parameters are composite and refer only to these conditions, see text [e] Ionic strength 2.7M [f] Ionic strength 1.0M [g] Ionic strength 1.0–1.14M [h] Ionic strength 2.1M. [i] The parameters refer to complex formation [j] Ionic strength 0.25M [k] Measured in nitrate media. [l] Ionic strength 0.82–1.50M; activation parameters estimated from non-linear least-squares program [m] Ionic strength 2.0M

$$-(1/n)\, d[Co^{III}]/dt = (k_1 + k_2 K_h/[H^+])\, [Co^{III}]\, [\text{ benzene}] \qquad (48)$$

where n is unknown (because of the complex nature of the products) and k_1 and k_2 are the rate constants of the reactions

$$Co^{3+} + \text{benzene} \xrightarrow{k_1} \text{products} \qquad (49)$$

$$CoOH^{2+} + \text{benzene} \xrightarrow{k_2} \text{products} \qquad (50)$$

The benzene molecule is not protonated[72] under the experimental conditions, and so the acid-dependence of the rate can be unambiguously assigned to the Co_{aq}^{3+}/$CoOH_{aq}^{2+}$ pair. By contrast, the assignment of the acid-dependence of the oxidation of alcohols, ketones and carboxylic acids, is not unambiguous since these molecules are known to be in equilibrium with protonated species in acid solution[23]. The values found[23] for nk_1 and nk_2 for the benzene reactions are $1.8 \times 10^{11} \exp(-19000/RT)\text{M}^{-1} \cdot \text{sec}^{-1}$ and $1.45 \times 10^{14} \exp(-19000/RT)\text{M}^{-1} \cdot \text{sec}^{-1}$, respectively, at ionic strength 2M. The observation that $\text{CoOH}_{\text{aq}}{}^{2+}$ is more reactive towards benzene than is $\text{Co}_{\text{aq}}{}^{3+}$ is seen to be due to the higher entropy of activation for the former reaction. This large difference in entropies might be due to a difference between spin-states for $\text{Co}_{\text{aq}}{}^{3+}$ (low-spin) and $\text{CoOH}_{\text{aq}}{}^{2+}$ (high-spin).

McAuley and Gomwalk[73] have recently reported a study of the oxidation of some thiourea derivatives by cobalt(III). This study is interesting, since the products contain sulphur–sulphur bonds. Sulphur–sulphur bonds are also formed in the oxidation of thiocyanate by cobalt(III), which produces thiocyanogen[18]. We were struck by the low activation energies reported for this series of reactions[73], and have treated the data using a non-linear least-squares program to obtain the activation parameters*. A comparison is made between the original estimates[73] and the calculated values in Table 8. No complex formation is evident in this series of reactions, nor in the case of the oxidation of thiocyanate[18], and it is not possible to get very accurate estimates of the activation parameters for reaction (51)

$$\text{Co}^{3+} + \text{RSH}^{+} \xrightarrow{k_1} \text{products} \tag{51}$$

$$\text{CoOH}^{2+} + \text{RSH}^{+} \xrightarrow{k_2} \text{products} \tag{52}$$

from the original data[73]. For this reason we compare only those for reaction (52) in Table 8. The computer calculations confirm that $\Delta H_2^{\neq}$ is small for these reactions, which are also characterized by a negative entropy of activation. We note a progressive change in activation entropy from positive to negative values in going from, say, thiocyanate (anion) to thiourea (positively charged molecule) (Table 7). In general, the entropy of activation which is observed is related to the charge

TABLE 8

RATE PARAMETERS FOR REACTION BETWEEN $\text{CoOH}_{\text{aq}}{}^{2+}$ AND SOME THIOUREA MOLECULES[a]

Reductant	$10^{-4}k_2$[b]	$\Delta H_2^{\neq}$[c d]	$\Delta H_2^{\neq}$[c e]	$\Delta S_2^{\neq}$[d f]	$\Delta S_2^{\neq}$[e f]
Thiourea	2.6	8.4 ± 0.5	5.7 ± 1.9[g]	−(22 ± 3)	−(19 ± 7)[g]
N,N′-Diethyl-thiourea	13.8	10.0 ± 0.4	6.5 ± 1.8[g]	−(12 ± 3)	−(13 ± 7)[g]
Ethylenethiourea	3.2	10.3 ± 0.5	8.3 ± 3.2[g]	−(19 ± 3)	−(10 ± 11)[g]

[a] The ionic strength varies between 0.82 and 1.70M, Ref. 73. [b] Units are M^{-1} sec^{-1} at 25°. [c] Units are kcal. mole^{-1}. [d] Estimate of McAuley and Gomwalk (Ref. 73). [e] Estimate from non-linear least squares program*. [f] Units are cal deg^{-1}. mole^{-1}. [g] Errors quoted are standard deviations

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* The computer program was based on the Los Alamos Scientific Laboratory Reports, LA 2367, by R. H. Moore and R. K. Zeigler, 1959 and LA 2367 Addenda, by P. McWilliams, 1962. This program was generously supplied by Dr. T. W. Newton. Each rate constant was weighted to the reciprocal of its square, i.e. the error in the observed rate constants[73] was assumed constant. No allowance for differences in ionic strength was made in these calculations (see Table 8).

product of the reactants. An apparent major exception to this trend is found in the reactions with cerium(III), thallium(I) and mercury(I) where the entropies are large and positive. In all these cases perchlorate complexes of the reducing ions are believed to exist[28,30].

The reaction between cobalt(III) and hydrazoic acid is first-order in both reactants[74] at acidities between 0 25 and 5M at ionic strength 2–5M in the temperature range 5–25°*. By contrast, the reaction with manganese(III) is always second-order in $[HN_3]$ even with small excesses of reductant[75a]. With greater excesses of hydrazoic acid the manganese(III) reaction becomes second-order in $[Mn^{III}]$[76b]: this is thought to be due to the availability of a formal M^{IV} oxidation state for manganese which is evidently not possible for aquo complexes of cobalt[74a,76].

Wells and Mays[75b] also examined the published data for the rates of complex formation referred to earlier (pp 367–369), and have reached a similar conclusion with regard to the magnitude of the hydrolysis constant to that which we presented in section D of this Review.

The oxidation of chlorine dioxide to chlorate has been studied by Thompson[77]. The product is inert to further oxidation, and the rate of reaction follows the familiar acid-dependent equation. The very careful experimental work and excellent kinetic data of Sullivan, Thompson and their co-workers is exemplified by an attempt to account for medium effects in terms of a Harned-type correction factor[74,77]. Fortunately, the medium effects are never large enough to cloud the true kinetic dependencies of the reactions (see above discussion and Ref. 49).

Hydrazinium is oxidized to nitrogen and ammonia[78] by cobalt(III)

$$Co^{III}+N_2H_5^+ \rightarrow \tfrac{1}{2}N_2+NH_4^++Co^{2+}+H^+ \tag{53}$$

and the major product of oxidation of hydroxylammonium is nitrogen,

$$Co^{III}+NH_3OH^+ \rightarrow \tfrac{1}{2}N_2+H_2O+Co^{2+}+2H^+ \tag{54}$$

This latter reaction is similar to that observed with cerium(IV)[79]. By contrast, nitrate is the primary product of oxidation of hydroxylammonium[80] by manganese(III), and the oxidation of hydrazinium[71] by manganese(III) does not result in the formation of nitrogen. Although all the above reactions are believed to proceed *via* free radical mechanisms, the reason for these differences is not clear.

The kinetics of the oxidation of hydrazinium and hydroxylammonium in nitric acid solution follow the inverse acid-dependent equation[78]. The reactions in sulphuric acid are more complex, however, and metal–substrate complex formation has been invoked[78] for both hydrazinium and hydroxylammonium. The conclusions to be drawn from these latter observations are somewhat tentative in view of the complicated equilibria existing in sulphuric acid media (see above discussion).

The reaction between cobalt(III) and hydrogen peroxide is of interest in

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* The rate law originally proposed by Wells and Mays[75b] which has a second-order term in $[HN_3]$ in an acid-independent rate law is inconsistent with subsequent data[74b].

view of the possibility of complex formation[51,81] in this system. The kinetics of reaction were studied by Baxendale and Wells[6], who followed the decrease of cobalt(III) concentration as a function of time at 230 nm. Although the rate of this reaction has a simple second-order concentration dependence (Fig. 6), Baxendale and Wells[6] concluded that a complex was formed between the reactants: the evidence for this came from an analysis of observed and calculated absorbancies at zero time. The kinetic range available to Baxendale and Wells[6] was restricted because of the rapidity of the reaction as followed by conventional spectrophotometry. The reaction has recently been re-investigated by Davies *et al.*[18] over much wider concentration ranges (Fig. 6) and no evidence for complex formation was observed. The reaction rate again exhibits a strong inverse acid dependence, (Fig 7).

The clear evidence for complex formation with chloride[27] is not evident in reactions with bromide[18] and iodide[18]. The ratio of rate constants k_1/k_2 (Table 7) is noticeably higher for reactions with nitrous acid, thiocyanate, hydroquinone and iodide than for the other reactions.

As more kinetic data become available it is increasingly evident that inner-sphere mechanisms are common for redox reactions involving labile reactants[39,51 82]. For cobalt(III) reactions a comparison of rate data for reactions of $CoOH_{aq}^{2+}$ is easier than for those involving Co_{aq}^{3+} since most reactions have a strongly acid-dependent character. Conclusions concerning the mechanism of oxidation reactions involving labile species can rarely be substantiated by identification of primary products, and the most detailed kinetic analysis can only give clues as to different mechanistic possibilities.

If spin-conversion were the rate-determining process in cobalt(III) reactions then the rates of oxidation would, of course, be independent of the concentration of reductant. This is contrary to the characteristic second-order rate law for these reactions. Current estimates[45] of the energy required to convert Co_{aq}^{3+} from a low spin to a high spin form are in the range 15–20 kcal.mole^{-1}. Although this is the range of observed activation enthalpies for reactions of Co_{aq}^{3+}, it seems likely from the above discussion that Co_{aq}^{3+} either reacts as a low-spin, diamagnetic species or that the energy barrier for interconversion in solution is much lower than 15 kcal.mole^{-1} (see Ref. 83). The enthalpies of activation for reactions of Co_{aq}^{3+} with nitrous acid, hydroquinone, iodide and thiocyanate are all about 20 kcal.mole^{-1}. Of these, the rapid reactions with hydroquinone and iodide are most likely to be outer-sphere, while those with thiocyanate and nitrous acid may proceed by a mechanism in which water substitution in the inner-sphere of Co_{aq}^{3+} is the rate-determining step. Clearly, more extensive data are needed for the rates of complexation reactions of Co_{aq}^{3+} before any clear mechanistic distinctions can be made for the redox reactions.

There is no direct measurement of the rate of water exchange in cobalt(III), although Friedman *et al.*[83] observed complete exchange within about two minutes in 3M perchloric acid at high cobalt concentrations. It has been suggested[16,83,84] that the water exchange is catalyzed by cobalt(II), and this is certainly possible under the conditions used.[83]

Inspection of the results in Table 7 indicates the narrow range of rate constants which characterizes the reactions of $CoOH_{aq}^{2+}$ with many different types of reductant. The free energies of activation $\Delta G^{\neq}$ of some of these reactions are compared with the overall free energy ΔG° in Table 9. The slight variation in $\Delta G^{\neq}$ for a wide range of ΔG° values is strong support for a common process in the reactions of $CoOH_{aq}^{2+}$ with Cl^-, HNO_2, H_2O_2, Br^-, HN_3, $NH_3NH_2^+$ and NH_3OH^+.

TABLE 9

FREE ENERGIES OF ACTIVATION AND OVERALL STANDARD FREE ENERGIES[a] FOR SOME REACTIONS OF $CoOH_{aq}^{2+}$

Reductant (B or HB)	$\Delta G^{\neq b}$	$\Delta G^{\circ b}$
Fe^{II}	10.1	−25
Cl^-	11.8	+9
Br^-	11.7	−3
I^-	9.0	−18
H_2O_2	11.8	−12
HNO_2	12.0	−22
hydroquinone (H_2Q)[c]	9.5	−21

[a] For the reaction: $CoOH_{aq}^{2+} + B_{aq}^{(n)+} + H_{aq}^+ \rightarrow Co_{aq}^{2+} + B_{aq}^{(n+1)+} + H_2O$; or, for "HB" ($H_2O_2$, HNO_2, H_2Q): $CoOH_{aq}^{2+} + HB_{aq} \rightarrow Co_{aq}^{2+} + B_{aq} + H_2O$ Most of the requisite ΔG° values for the reductants have been taken from W. M Latimer, *Oxidation Potentials*, 2nd edn , Prentice–Hall, New York, 1952 The ΔG° value for B(g) → B(aq) has been estimated as ≈ −0.5 kcal $mole^{-1}$ for the halogens and NO_2, by analogy with OH The standard electrode potential for Co^{III}/Co^{II} has been taken to be 1.87 V[25]. Differences in ionic strength have been ignored. [b] Units are kcal $mole^{-1}$. [c] Some requisite ΔG° data are from H Diebler, M Eigen and P. Matthies, *Z Naturforsch* , 16b (1961) 629, J. H Baxendale, H R. Hardy and L H. Sutcliffe, *Trans Faraday Soc.*, 47 (1951) 963; I. C. P Smith and A Carrington, *Mol. Phys* , 12 (1967) 434; G E Adams and B D. Michael, *Trans. Faraday Soc.*, 63 (1967) 1171

In Table 10 we have compared the ratio of rate constants for reactions of MOH^{2+} to those of M^{3+} when M is cobalt and iron, respectively. The ratios are admittedly approximate for cobalt(III) reactions, but the similarities do suggest a common rate-determining step for both complexation and oxidation reactions, and this common process is likely to be water replacement on the metal ion. The ratio of the water exchange rate in the divalent ion to that in the monohydroxy-form of the corresponding trivalent ion would then be about 30 for the elements manganese, iron and cobalt[39,51].

The interplay between a large driving force on the one hand and lability on the other makes reactions like those of cobalt(III) an interesting area of investigation. Information concerning complexation reactions should, in principle, enable the characteristics of inner-sphere reactions to be recognized, and hence lead to a more complete classification of oxidation mechanisms. Unfortunately, most of the

TABLE 10

COMPARISON BETWEEN OXIDATION AND COMPLEXATION REACTIONS AT 25°

Metal	*B*	*Process*	$\frac{10^{-3}k_2(MOH^{2+}+B)}{k_1(M^{3+}+B)}$	*Ref.*
Co	Br^-	Oxidation	3.0	18[a]
Fe	Br^-	Complexation	1.4	85[b]
Co	Cl^-	Complexation	4.1	27[a]
Fe	Cl^-	Complexation	2.4	85[b]
Co	HN_3	Oxidation	9	74[c]
Fe	HN_3	Complexation	1.7	85[b]
Co	SCN^-	Oxidation	0.46	18[a]
Fe	SCN^-	Complexation	0.08	85[b]

[a] Data at ionic strength 3M. [b] Data at ionic strength 1M [c] Data at ionic strength 2.1M

ligands which have been used to make a clear distinction in other systems[39,82,85] are oxidized by cobalt(III) with no hint of complex formation. However, enough information should eventually become available to give answers to some of the questions which have been raised.

F. SUMMARY

The equilibria and kinetics of some reactions of cobalt(III) have been reviewed. The conditions under which the concentration of polymeric species is negligible were established and the acid-dissociation constant of $Co_{aq}{}^{3+}$ was deduced from data for other tripositive ions of the first transition series. The equilibria and kinetics of complexation and some redox reactions of cobalt(III) are similar in many respects to those of iron(III), and a number of reactions of $Co_{aq}{}^{3+}$ and $CoOH_{aq}{}^{2+}$ appear to occur *via* inner-sphere mechanisms. These conclusions would be substantiated by more kinetic data for complex formation. The question of spin-states is a difficult one for cobalt(III) and kinetic data give no direct information on this point Although the $Co_{aq}{}^{3+}$ ion exists as a low-spin, diamagnetic species, it may react in a high-spin form, although the low-spin form would seem to be favored on energetic grounds. The spin-state of $CoOH_{aq}{}^{2+}$ may be high-spin in view of the similarity between some rates for the reactions of the $CoOH_{aq}{}^{2+}$ and $FeOH_{aq}{}^{2+}$ species.

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