Kinetics and Mechanism of the Replacement of Carbonate by Sulphite in the Tris(carbonato)cobaltate(III) Ion in Solution

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Sulphite ligands become co-ordinated to the ion $[Co(CO_3)_3]^{3-}$ in two distinct steps, without reducing the carbonate complex. The initial step is first order in the concentration of each reactant. The second substitution is not amenable to kinetic study because of slight precipitate formation, but filtration allowed the progress of the reaction to be monitored; this step is inferred to have an order of <1 in $[SO_3{}^{2-}]$. At pH <9 the rate constant for the first step is independent of pH, but increases at pH $\geqslant 9.2$. The spectra of the two products indicate that they are the mono- and bis-(sulphito)-complexes of the carbonato-species. Sulphite and oxygen have been shown to oxidise cobalt(II) in carbonate solution to $[Co(CO_3)_3]^{3-}$.

THE tris(carbonato)cobaltate(III) anion is apparently the simplest totally chelated cobalt(III) anion, occurring in the anhydrous solid.[1] It has been studied with respect to substitution by pyridine (py), ethylenediamine, and other *N*-donor ligands,[2] and also [3-6] to reduction by N_2H_4 which itself becomes co-ordinated in the process. The mechanism suggested [2] for py substitution, while not necessarily unique, has been used as a basis for rationalising the reaction with N_2H_4. In aqueous solution, tris(carbonato)cobaltate(III) may have [2] one unidentate carbonate ligand, with a water molecule possibly closing the ring by hydrogen-bonding to it. An appreciable fraction of reactant is thought [2] to be $[Co(CO_3)_2(HCO_3)(OH_2)]^{2-}$ and $[Co(CO_3)_2(OH_2)_2]^-$, both reacting with py, but the latter reacts [5] the faster with N_2H_4; $[Co(CO_3)_3]^{3-}$ itself is inferred [2,5] to be relatively unreactive. Such conclusions depend on implicit assumptions that activity coefficients are identical in solutions both of 0.8 mol dm^{-3} $[HCO_3]^-$ + 0.2 mol dm^{-3} $[ClO_4]^-$ and of 0.2 mol dm^{-3} $[HCO_3]^-$ + 0.8 mol dm^{-3} $[ClO_4]^-$. The proportions of the different carbonatocobalt(III) species were inferred to change markedly over the range of conditions studied,[2,5] and the spectra of $[Co(CO_3)_3]^{3-}$ and $[Co(CO_3)_2(HCO_3)(OH_2)]^{2-}$ are required to be virtually identical.[2]

Although the standard electrode potential for $[Co^{III}(CO_3)_3]^{3-}$—$[Co^{II}(CO_3)_3]^{4-}$ is not known, reduction by $[SO_3]^{2-}$ seemed possible, but an earlier experiment [3,4] had indicated that although colour changes occurred there was no net redox reaction. In the present work the formation of the new species, putatively the result(s) of substitution, was examined in order to establish as far as possible the mechanistic features of the reaction. A difficulty [2] is the limited stability of the anion, even when made up in the usual manner [2,5] by dissolving the sodium salt in $Na[HCO_3]$ solution. Because of the marked slowness of the overall reaction with sulphite, we used K^+ as solution cation, which allowed higher concentrations of $[Co(CO_3)_3]^{3-}$, and thus a more convenient rate: even so, runs still required up to 18 d.

Sulphite in ammine and cyano-complexes has a *trans* labilising effect, from which it has been inferred [7-9] that bonding to S is involved. *X*-Ray diffraction has established [10] that in $[Co(NH_3)_5(SO_3)]Cl$ the sulphite ligand is unidentate through S, and this is supported by i.r. and Raman results.[11] The complexes formed in the present study are thus likely to involve unidentate bonding through S.

EXPERIMENTAL

Solutions (up to 8×10^{-3} mol dm^{-3}) of tris(carbonato)-cobaltate(III) were freshly prepared for each experiment; they were found to become colloidal after 1 week. To a solution of $K[HCO_3]$ (ultimately 0.64 mol dm^{-3}) and $K_2[CO_3]$ (ultimately 0.36 mol dm^{-3}) was added the requisite dissolved cobalt(II) salt (Cl^-, $[ClO_4]^-$, or $[CO_3]^{2-}$) to give a purple solution which was oxidised with a slight excess of H_2O_2. Excess of oxygen was flushed out with nitrogen. Different $[HCO_3]^-$: $[CO_3]^{2-}$ ratios were used at lower pH. For kinetic runs, concentrated $Na_2[SO_3]$ was added and the solution made up to standard volume. Sodium sulphite solutions were made up by weight or standardised iodimetrically. The concentration of Co^{III} was checked by addition to acidified ammonium iron(II) sulphate standardised with dichromate. The molar absorption coefficients of tris(carbonato)cobaltate (III) were found to be 173 ± 2 (440 nm) and 162 ± 2 dm^3 mol^{-1} cm^{-1} (at 640 nm). These are to be contrasted with the values of 166 ± 2 and 154 ± 2 dm^3 mol^{-1} cm^{-1} respectively reported for *ca.* 0.8 mol dm^{-3} $Na[HCO_3]$ and the $[CO_3]^{2-}$ formed by dissociation.[2] The agreement is only fair, and could represent a real difference in absorption by the proposed tris(carbonato)cobaltate(III) species present in differing populations. The pH values of reaction solutions were measured on an EIL 38A pH meter standardised with borate and phosphate buffers. A Unicam SP 1800 spectrophotometer with thermostatted (25 °C) cell holder was used for recording spectra.

The investigation proceeded in four stages. (*i*) Preliminary survey. Spectra (Figure 1) were recorded after 48 h of solutions initially 2.5×10^{-3} mol dm^{-3} in Co^{III} and 0.32 or 0.65 mol dm^{-3} in $[SO_3]^{2-}$, which indicated the sequential formation of at least two products, P and Q, which were red and brick-red respectively. Assignments of spectra were made later and maxima (Figure 1) are indicated by arrows. Formation of Q was accompanied by sol then solid formation, the latter being labelled R. The fate of the $[SO_3]^{2-}$ was assessed as follows. From acidified solutions of $[SO_3]^{2-}$, attempted transfers of SO_2 by passage of nitrogen were only *ca.* 50% efficient, as indicated by the $[SO_3]^{2-}$ retained in alkaline absorber solutions. For standards, this fraction was quite reproducible. Solutions with $[SO_3{}^{2-}]$ *ca.* 6×10^{-3} mol dm^{-3} were allowed to react with tris(carbonato)cobaltate(III), then acidified, with passage of nitrogen. From the transferred SO_2 trapped as absorbed $[SO_3]^{2-}$, in comparison with the standards, most

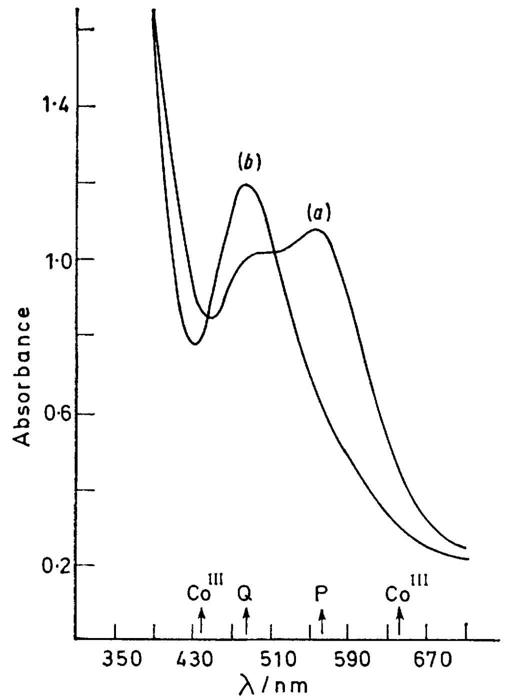

FIGURE 1 Exploratory spectra, after 48 h, of 2.5 × 10^{-3} mol dm^{-3} Co^{III} with (*a*) 0.32 mol dm^{-3} and (*b*) 0.65 mol dm^{-3} $Na_2[SO_3]$, showing (arrows) optical maxima of the products as assigned later, and maxima of $[Co(CO_3)_3]^{3-}$ in a 4-cm cell

of the original $[SO_3]^{2-}$ was shown to have survived in the reaction as such. It is an interesting observation on an unusual heterogeneous process that the cationic Co^{III} formed on acidification does not react so rapidly with $[SO_3]^{2-}$ or SO_2 as to prevent transfer of the latter, which is doubtless aided by the copious CO_2 evolution.

(*ii*) Successive spectrophotometric scans were made of three reaction solutions containing *ca.* 6 × 10^{-3} mol dm^{-3} Co^{III}, and $[SO_3^{2-}]_0$ first approximately equal in concentration (Figure 2), then ten-fold greater (Figure 3), and finally 0.325—0.65 mol dm^{-3} (Figure 4), the latter after filtering off solid R.

(*iii*) Attempts were made to analyse the small amounts of the orange solid R obtained from spent reaction solutions ($[SO_3^{2-}] > 0.1$ mol dm^{-3}) which had not already decomposed into the black-brown decomposition products [2] of the tris(carbonato)cobaltate(III) reactant.

(*iv*) Kinetic studies were performed at the stabilising $[HCO_3^-]$ and $[CO_3^{2-}]$ above (pH 9.52) by following both the disappearance of cobaltate reactant and the appearance of P, in order to establish, by the constancy of rate constant, that the same mechanism held over the wide range of $[SO_3^{2-}]_0$ and that $-d[Co(CO_3)_3^{3-}]/dt = d[P]/dt$,* when P was the predominant product. The ionic strength was 1.75 mol dm^{-3}, except for the highest $[SO_3^{2-}]_0$ when it was 2.75 mol dm^{-3}. Reactions were run in thermostatted optical cells or transferred to them from reaction vessels. Some runs were conducted at lower pH values for comparison with trends observed in the earlier investigations.[2,5]

RESULTS AND DISCUSSION

(*i*) To the species P and Q, in terms of which the main features of the reaction could be expressed, spectra were assigned as in Figure 5. The spectrum of P was obtained from a slow scan of the solution of maximum absorption in Figure 3, curve (10), where all the Co^{III} was believed to be converted into P; an apparent shoulder occurs where another maximum, subsequently assigned to Q, is found, and was excised. The spectrum of the next sequential product Q was obtained from the final 18-d old, solution of Figure 4, filtered free of the solid product R. The concentration of Q was tentatively estimated by addition of H_2O_2 which destroyed the $[SO_3]^{2-}$ and converted all the Co^{III} back into tris(carbonato)cobaltate(III), determinable spectrophotometrically.

(*ii*) Figure 2, with low $[SO_3^{2-}]_0$, shows the disappearance of the reactant cobaltate and the overlapping formation of P at $\lambda_{max.}$ 570 nm and Q at 480 nm. The crossover regions of the spectra are not isosbestic, indicating the duality of product. The fates of P and Q and not readily discerned, no solid being detected, but the later general depression of absorption might indicate the formation of species more symmetrical than P and Q.

With 0.060 mol dm^{-3} $[SO_3]^{2-}$, Figure 3, the formation of P is much more readily separated from that of Q and the crossover points are more clearly isosbestic. The

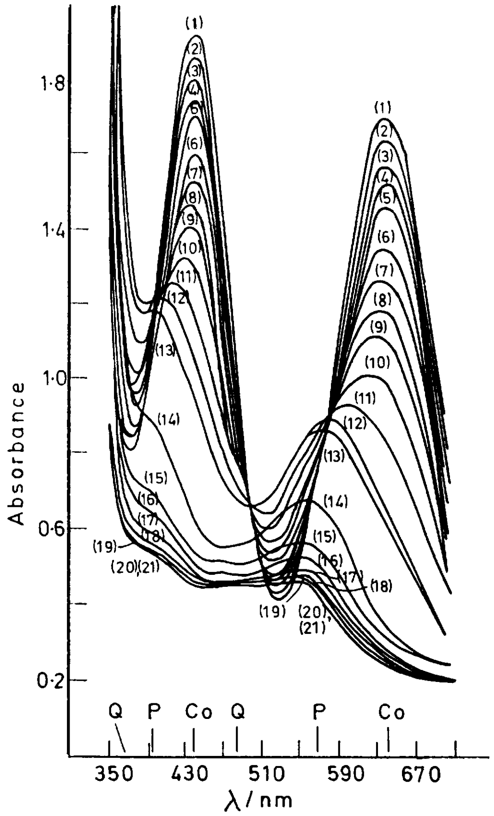

FIGURE 2 Scans with time of the reaction of 5.93 × 10^{-3} mol dm^{-3} Co^{III} and 8.82 × 10^{-3} mol dm^{-3} $[SO_3]^{2-}$ in a 2-cm cell (compositions in Table 1). Times (min) after the start of reaction from trace (1) to (21) are: 10, 15, 20, 25, 30, 41, 50, 60, 70, 90 [trace (10)], 121, 155, 170, 200, 820, 1 420, 2 240, 2 290, 4 295, 5 000 [trace (20)], 71 710 [trace (21) coincident with (20)]. Arrows denote maxima

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* $[Co(CO_3)_3^{3-}]$ is taken to represent the concentration of all the sulphite-free carbonatocobalt(III) species.

contrast in the relative rates of formation of P and Q with those in the preceding experiment can be explained if the formation rate of Q is of lower order in $[SO_3^{2-}]$ than is that of P. To anticipate, the order for P formation will be established as unity, and that for its disappearance is thus most simply assumed as zero. Support for the relative orders is obtained by contemplation of the incremental effect of $[SO_3^{2-}]_0$ at constant $[Co(CO_3)_3^{3-}]_0$ on the maximum [P] observed in Figures 2—4. Thus, most simply, at the maximum concentration of P, $[P]_{max.}$, the rate of formation of P equals its rate of removal [equation (1)]. If $n = 1$ then $\{[P]/[Co(CO_3)_3^{3-}]\}_{max.} = k_1/k_2$, *i.e.* constant, which is not the case, and $n = 2$ is similarly inapplicable. Therefore $n < 1$ and is probably zero. (The full kinetic analysis treating P as an intermediate, confirming this interim conclusion, is given in the Appendix.)

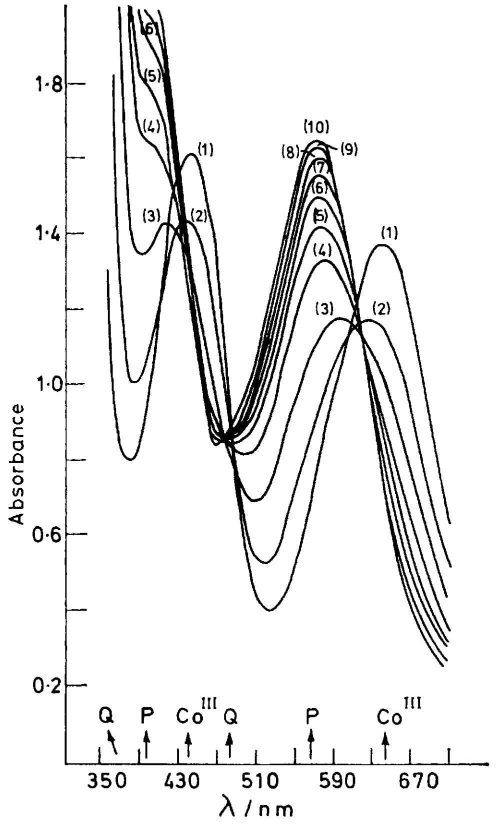

FIGURE 3 Scans with time of the reaction of 6.09×10^{-3} mol dm^{-3} Co^{III} and 0.060 2 mol dm^{-3} $[SO_3]^{2-}$ in a 2-cm cell (compositions in Table 1). Times (min) after the start of reaction are: (1) 4, (2) 6, (3) 8, (4) 10.5, (5) 12, (6) 14, (7) 16, (8) 18, and (9) 26. Finally, after 230 min, the peak at 570 nm decreased in intensity by *ca.* 10%

$$k_1[Co(CO_3)_3^{3-}][SO_3^{2-}] = k_2[P][SO_3^{2-}]^n \qquad (1)$$

In Figure 4 the very high concentration of $[SO_3]^{2-}$, 0.325 increased to 0.65 mol dm^{-3}, results in such rapid conversion into P that the reactant is not recorded at all, and the formation of Q, with R, follows.

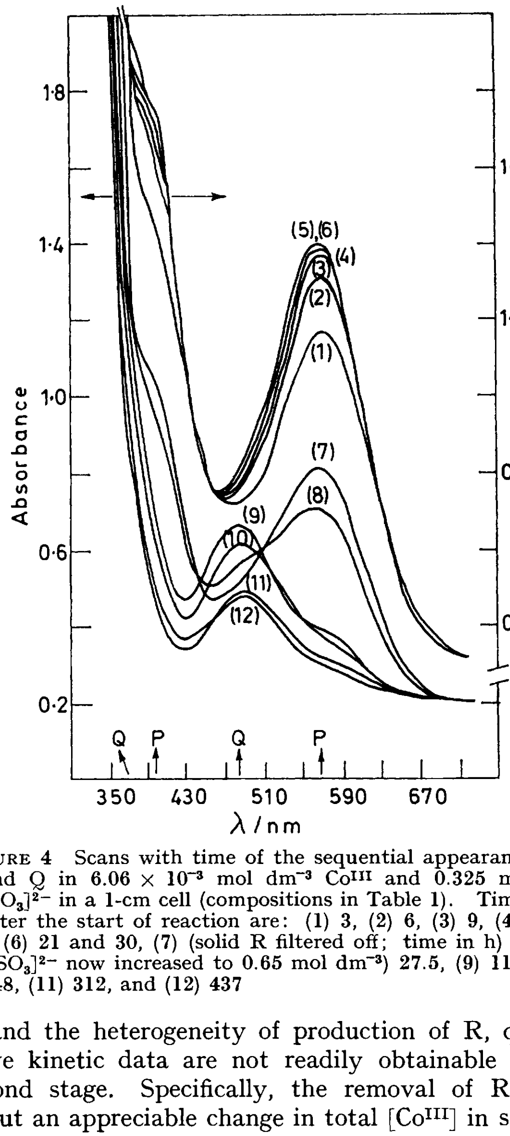

FIGURE 4 Scans with time of the sequential appearances of P and Q in 6.06×10^{-3} mol dm^{-3} Co^{III} and 0.325 mol dm^{-3} $[SO_3]^{2-}$ in a 1-cm cell (compositions in Table 1). Times (min) after the start of reaction are: (1) 3, (2) 6, (3) 9, (4) 12, (5) ≈(6) 21 and 30, (7) (solid R filtered off; time in h) 18.2, (8) ($[SO_3]^{2-}$ now increased to 0.65 mol dm^{-3}) 27.5, (9) 113.5, (10) 148, (11) 312, and (12) 437

(*iii*) Because of the extreme slowness of formation of Q and the heterogeneity of production of R, quantitative kinetic data are not readily obtainable for the second stage. Specifically, the removal of R brings about an appreciable change in total [Co^{III}] in solution. Small amounts of R retrievable from spent reactions were analysed as 7.75%, S, 4.25% C, and 0.95% H. While R may be a mixture, these figures show S:C:H = 1:1.5:4, inviting a facile assignment of R as $[Co(SO_3)_2$-

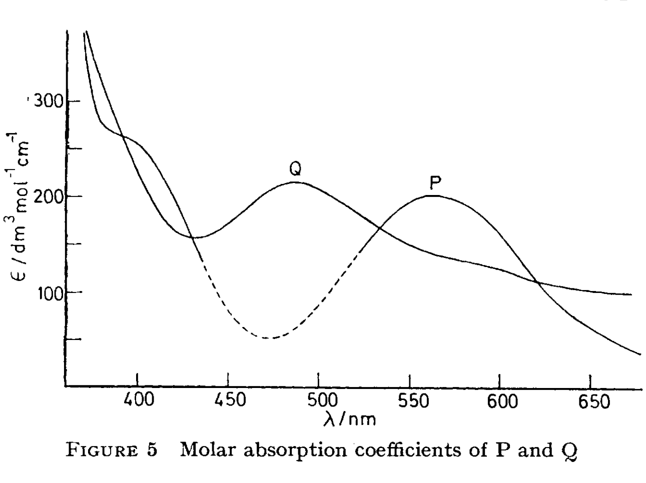

FIGURE 5 Molar absorption coefficients of P and Q

$(CO_3{}^*)(CO_3)_2]^{7-}$ ($CO_3{}^* =$ bidentate carbonate). This is a 7— anion [5— for $(HCO_3)_2$] if mononuclear, and would be slightly more acceptable if formulated as a 4— binuclear anion with bridging CO_3.

(*iv*) In establishing the kinetics of the first stage, the absorbance of tris(carbonato)cobaltate(III) (A, molar absorption coefficient ε) was followed from A_0 initially to A_t at time t, using plots against t of the second-order function $\ln\{A_t/([SO_3{}^{2-}]_0\varepsilon - A_0 + A_t)\}$, or for equal concentrations, $1/A_t$ [Figure 6(*a*) and 6(*b*)]. For excess of $[SO_3]^{2-}$, using the assumption [above, (*i*)] that when the absorption of P at 570 nm reaches its maximum, $A^{P}{}_{\text{max.}}$, all of the Co^{III} exists as P, then the gradient of the plot of $\ln(A^{P}{}_{\text{max.}} - A^{P}{}_t)$ in Figure 6(*c*) should give

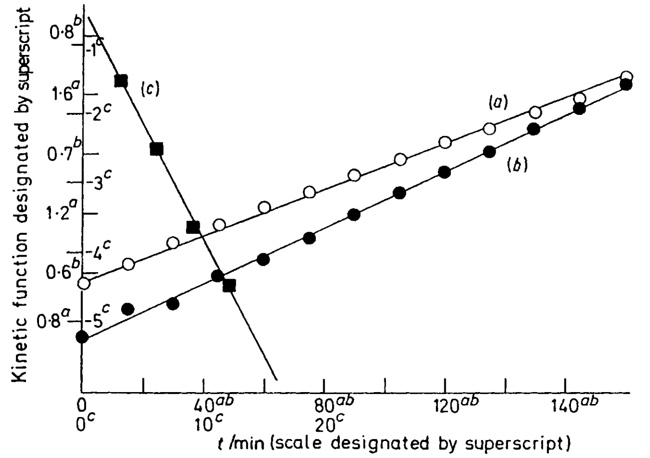

FIGURE 6 (a) A plot of $\ln\{A_t/([SO_3{}^{2-}]_0\varepsilon - A_0 + A_t)\}$ against t for 5.05×10^{-3} mol dm^{-3} Co^{III} and 3.16×10^{-3} mol dm^{-3} $[SO_3]^{2-}$. (*b*) A plot of $1/A_t$ against t, 2.7×10^{-3} mol dm^{-3} reactants. (*c*) A plot of $\ln(A^{P}{}_{\text{max.}} - A^{P}{}_t)$ against t for 6.06 $\times 10^{-3}$ mol dm^{-3} Co^{III} and 0.325 mol dm^{-3} $[SO_3]^{2-}$. Carbonate and hydrogencarbonate as in Table 1

the same rate constant as in (*a*) and (*b*), which is approximately the case (Table 1). It is necessary to emphasize that, while the plots do not give merely initial rates in the sense of being tangential to curves starting at $t = 0$, nevertheless they refer only to duration of between a quarter-life and a half-life, after which pronounced curvature sets in. The kinetics of the later fate of P are complex and no obvious rate equation can be inferred from our spectral records. It is quite possible that different final products ensue for different ranges of $[SO_3{}^{2-}]_0$.

TABLE 1

Rate constants k at 25 °C in $[HCO_3]^{-}$–$[CO_3]^{2-}$ solutions of ionic strength 1.75 mol dm^{-3} and pH 9.52 (0.64 mol dm^{-3} $K[HCO_3]$ and 0.36 mol dm^{-3} $K_2[CO_3]$)

$10^3[Co^{III}]_0$	$10^3[SO_3{}^{2-}]_0$	k
mol dm^{-3}		dm^3 mol^{-1} min^{-1}
5.05	3.16	0.95
5.07	3.03	0.92
5.13	3.07	0.92
5.55	3.05	1.3
1.64	0.99	0.92
3.56	1.97	1.16
8.04	4.01	0.87
2.84	3.79	0.82
2.82	7.39	0.88
2.88	11.53	0.85
5.19	1.45	0.88
3.84	1.98	0.94
2.69	2.71	0.89
5.93	8.82	8.80
6.06	325	0.88 *
		Av. 0.94 ± 0.13

$I = 2.75$ mol dm^{-3}.

In a brief study of the effect of pH, nine runs were performed from pH 9.32 to 8.55 (with $[CO_3{}^{2-}]$, $[HCO_3{}^{-}]$ ranging from 0.262, 0.738 to 0.057, 0.943 mol dm^{-3} respectively), giving observed k/dm^3 mol^{-1} min^{-1} decreasing from 0.5 to 0.2 ± *ca.* 10%. More specifically, at pH $\lesssim 9$ the rate constant appears to be nearly independent of pH, but at pH $\geqslant 9.2$ it increases markedly with pH. The trends with pH and $[HCO_3]^{-}$ were qualitatively as observed in the reactions with py [2] and N_2H_4.[5] For the $[HCO_3{}^{-}]$ and $[CO_3{}^{2-}]$ as in Table 1, the empirical equation established for this dependence in the py reaction [2] gives a value of k_{py} of 0.65 dm^3 mol^{-1} min^{-1}, while for N_2H_4 this procedure gives $k_{N_2H_4} = 3.83$ dm^3 mol^{-1} min^{-1}; these values are close to, and bracket, those in Table 1 for sulphite substitution. (For the py and N_2H_4 reactions the lack of any added free $[CO_3]^{2-}$ makes this comparison somewhat tentative, and in the kinetic dependences just referred to [2,5] terms in $[H^+]/[HCO_3{}^{-}]$ are kinetically indistinguishable from terms in $[CO_3{}^{2-}]^{-1}$.)

TABLE 2

Spectra of related cobalt(III) complexes: λ_1 and λ_2 are absorption maxima

Complex	λ_1/ nm	ε_1/dm^3 mol^{-1} cm^{-1}	λ_2/ nm	ε_2/dm^3 mol^{-1} cm^{-1}	Ref.
$[Co(en)_3]^{3+}$	336	65	460	76	12
$[Co(en)_2(CO_3)]^{+}$	358	120	512	127	*a*
$[Co(en)(CO_3)_2]^{-}$	390	210	570	148	*b*
$[Co(CO_3)_3]^{3-}$	440	172	640	161	*c*
$[Co(en)_2(OH_2)(SO_3)]^{+}$	360	shoulder to u.v.	465	162	*d*
$[Co(en)_2(SO_3)_2]^{-}$ *cis*			431	406	*e*
trans			440	313	*e*
$[Co(NH_3)_6]^{3+}$	338	37	471	46	12
$[Co(NH_3)_5(CO_3)]^{+}$			508	79	12
$[Co(NH_3)_5(SO_3)]^{+}$			471	141	12
$[Co(NH_3)_4(CO_3)]^{+}$	363	107	524	105	12
$[Co(NH_3)_4(SO_3)_2]^{-}$ *cis*			450	200	*f*
trans			440	500	*f*
			shoulder to u.v. tail		

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Mechanism and Probable Structures of P and Q.—Acceptance of the inferred mechanisms,[2,5] and our stoicheiometry and rate law, together with the unidentate bonding by SO_3, indicate that P is either $[Co(CO_3)_2(OH_2)(SO_3)]^{3-}$ or $[Co(CO_3)_2(HCO_3)(SO_3)]^{4-}$. The reactions of tris(carbonato)cobaltate(III) with py and N_2H_4 involve a rapid second substitution step not emulated here, possibly because of the repulsion of the 2— sulphite charge. Spectroscopic comparisons suggest that Q is a bis(sulphito)-complex; thus, in Table 2 the two visible absorption band maxima of a number of relevant complexes are listed. Comparing $[Co(en)_2(CO_3{*})]^+$ (bidentate carbonate, en = ethylenediamine) with $[Co(en)_3]^{3+}$ and $[Co(en)_2(OH_2)(SO_3)]^+$, λ increases with $[CO_3{}^{2-}]$, but any increase with $[SO_3{}^{2-}]$ is countered when *two* $[SO_3]^{2-}$ groups are inserted; furthermore, the ε values are greater for the (more hyperchromic[12]) sulphito-complexes. The same conclusion applies to the ammine complexes. Thus, replacement of $[CO_3]^{2-}$ by $[SO_3]^{2-}$ might reasonably be supposed to shorten λ and increase ε. The spectra of P and Q (Figure 5) thus predicate a sequential incorporation of sulphite, and the simplest assignment is that they are mono- and bis-sulphito-complexes respectively.

In the formation of Q the zero order in $[SO_3{}^{2-}]$ (Appendix) requires either ring opening *trans* to the first SO_3 or loss of H_2O or $[HCO_3]^-$ *cis* to it, to be rate determining.

Oxidation of Cobalt(II) *by Sulphite and Oxygen in Carbonate–Hydrogencarbonate Solution.*—In tests on solutions of Co^{II} in carbonate solutions containing $[SO_3]^{2-}$ it was observed that exposure to air generated tris(carbonato)cobaltate(III). Study of the absorbance in a solution initially 4.98×10^{-3} mol dm^{-3} in Co^{II} and 3.03×10^{-3} mol dm^{-3} in $[SO_3]^{2-}$ showed, within 20 min, a constant $[Co(CO_3)_3{}^{3-}]$ of 3.0×10^{-3} mol dm^{-3}, *i.e.* one $[Co(CO_3)_3]^{3-}$ formed per sulphite initially present. This superficially bizarre reaction occurs doubtless because O_2 oxidises sulphite to form $[HO_2]^-$ which can oxidise the Co^{II}. A formal stoicheiometry can be written

$$\begin{aligned}Co^{II} + 3[CO_3]^{2-} + [SO_3]^{2-} + \tfrac{3}{4}O_2 + \tfrac{1}{2}H_2O \longrightarrow \\ [Co^{III}(CO_3)_3]^{3-} + [OH]^- + [SO_4]^{2-} \quad (2)\end{aligned}$$

as in (2). It is interesting that little if any of the sulphito-complexes are formed.

APPENDIX

Determination of the Order n *in Sulphite in the Second Reaction Step.*—Writing $[Co(CO_3)_3]^{3-}$ for brevity as just Co^{III}, we take the simplest kinetics, for $Co^{III} \longrightarrow P \longrightarrow Q$, as being (A1) and (A2). In excess of $[SO_3]^{2-}$, $k_1[SO_3{}^{2-}]$

$$Co^{III} + [SO_3]^{2-} \xrightarrow{k_1} P \quad (A1)$$

$$P + n[SO_3]^{2-} \xrightarrow{k_2} Q \quad (A2)$$

and $k_2[SO_3{}^{2-}]^n$ are constants, k' and k'', in any one run, and if we write $[Co^{III}]_0 = a = [Co^{III}] + [P] + [Q]$, standard

$$[P] = [k'a/(k'' - k')][\exp(-k't) - \exp(-k''t)] \quad (A3)$$

kinetic analysis gives (A3). $[P]_{max.}$ occurs at $t_{max.}$, when expression (A4) is applicable;

$$\begin{aligned}d[P]/dt = k'a/(k'' - k')[k''\exp(-k''t_{max.}) - \\ k'\exp(-k't_{max.})] = 0 \quad (A4)\end{aligned}$$

whence $t_{max.} = [\ln(k''/k')]/(k'' - k')$ and $[P]_{max.} = a(k'/k'')^{k''/(k''-k')}$.

The relative magnitudes of k' and k'' are paramount in determining the sign of the dependence of $[P]_{max.}$ on $[SO_3{}^{2-}]_0$, *i.e.* for $n = 0$, whether $k_1[SO_3{}^{2-}] < k_2$ or $>k_2$. Knowing k_1, the former relation can be refuted by our experiments with excess of $[SO_3]^{2-}$. Thus we write, still for $n = 0$, equation (A5). If x is a small fraction, as is established by

$$\begin{aligned}[P]_{max.} &= a(k_2/k_1[SO_3{}^{2-}])^{k_2/(k_1[SO_3{}^{2-}]-k_2)} \\ &\approx a(k_2/k_1[SO_3{}^{2-}])^{k_2/k_1[SO_3{}^{2-}]} \\ &\approx ax^x \quad (A5)\end{aligned}$$

the inequality applicable to our experiments, then $[P]_{max.}$ increases with $1/x$, *i.e.* with $[SO_3{}^{2-}]$, as is observed. No other value of n gives this relation in the general result (A6).

$$[P]_{max.} = a\left(\frac{k_1[SO_3{}^{2-}]}{k_2[SO_3{}^{2-}]^n}\right)^{k_2[SO_3{}^{2-}]^n/(k_2[SO_3{}^{2-}]^n - k_1[SO_3{}^{2-}])} \quad (A6)$$

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