(*Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, Australia* 5001)

SUBSTITUTION reactions of metal complexes containing *S*-bonded sulphito-ligands are remarkably rapid.[1] We report some substitution reactions of sulphito-complexes whose fast rates arise from abnormally low enthalpies of activation [see (2) below]. This suggests that the weakening of the ligand bond *trans* to the *S*-bonded sulphite-ligand is a prime cause of the *trans*-labilizing effect of this ligand. This lability is also manifested in solid-state reactions [see (3) below]. We also report the ability of the sulphite anion to substitute rapidly on co-ordinated aquo-ligands [see (1) below], and show in (4) that sulphito-ligands can undergo an unusual mutual redox reaction with a cobalt(III) centre with the production of sulphite radical anions.

(1) *The rapid addition of sulphite ion to* trans-Co en_2OH,OH_2^{2+}

When aqueous solutions containing *trans*-Co en_2OH,OH_2^{2+} and SO_3^{2-} are mixed in the molar ratio 1 : 2 at pH 7·5 and 25°, *trans*-Co $en_2(SO_3)_2^-$ is formed quantitatively (half-time 0·7 sec.). In an equimolar mixture of the reactants, all the sulphite becomes initially bound in *trans*-Co $en_2(SO_3)_2^-$ (half-time 0·7 sec.). The resultant solution which still contains 50% unreacted *trans*-Co en_2OH,OH_2^+, is then transformed quantitatively (half-time 6·2 sec.) to the final product *trans*-Co $en_2SO_3OH_2^+$. This unusual sequence of reactions arises because, as is shown in (2) below, the *trans*-Co $en_2SO_3OH_2^+$ is much more labile to sulphite substitution than the reactant *trans*-Co en_2OH,OH_2^+.

Reaction half-times for

$$trans\text{-Co } en_2OH,OH_2^{2+} + SO_3^{2-} \rightarrow trans\text{-Co } en_2SO_3OH_2^+$$

increase sharply above and below pH 7·5 where optimum concentrations of both reactive species are established. Both *cis*- and *trans*-Co $en_2(OH)_2^+$ undergo sulphite substitution at pH >12, with half-times of 10—100 hr. Their relative inertness to sulphite substitution compared to *trans*-Co en_2OH,OH_2^+ is analogous to the much faster isomerization and water-exchange reactions of the hydroxo-aquo-complex,[2] but the sulphite addition reaction is at least 20 times faster than these other reactions. Since rapid substitution of SO_3^{2-} only occurs in cobalt(III) complexes with aquo-ligands, it is suggested that substitution proceeds *via* addition to the oxygen of the aquo-ligand followed by rapid intramolecular rearrangement of the *O*-bonded sulphito-complex to the *S*-bonded form. We have not detected the *O*-bonded intermediate.

(2) *Rapid substitution reactions of* trans-Co en_2SO_3,OH_2^+

Experiments using $H_2{}^{18}O$ have shown that the aquo-ligand of *trans*-Co en_2SO_3,OH_2^+ exchanges completely with the solvent within 45 sec. at pH 6·5 and 32°. Under the same conditions, the half-time for exchange of the oxygen atoms of the sulphito-ligand is >15 hr., very much slower than that of the free sulphite anion.

Stopped-flow measurements show that sulphite substitution of *trans*-Co en_2SO_3,OH_2^+ proceeds with half-times in the msec. range by a dissociative mechanism:

$$\text{(I) } trans\text{-Co } en_2SO_3,OH_2^+ \rightleftarrows \text{Co } en_2SO_3^+ + OH_2 \quad (k_{-OH_2}, k_{OH_2})$$

$$\text{(II) Co } en_2SO_3^+ + SO_3^{2-} \rightleftarrows trans\text{-Co } en_2(SO_3)_2^- \quad (k_{SO_3}, k_{-SO_3})$$

For this reaction scheme, the rate constant for aquo-release is $k_{-OH_2} = 13·2 \pm 0·9$ sec.$^{-1}$ at 25° with $\Delta H^\ddagger_{-OH_2} = 15·9 \pm 1·0$ kcal. mole^{-1} and $\Delta S^\ddagger_{-OH_2} = 0·2 \pm 4$ e.u., whilst for sulphite release from *trans*-Co $en_2(SO_3)_2^-$, $k_{-SO_3} = 0·111 \pm 0·004$ sec.$^{-1}$ at 25° with $\Delta H^\ddagger_{-SO_3} = 20·4 \pm 0·8$

kcal. mole^{-1} and $\Delta S^{\ddagger}_{-\mathrm{SO_3}} = 6 \pm 3$ e.u. These activation enthalpies are much lower than those normally observed for substitution on cobalt(III) complexes.[3]

The relative reactivity of water and sulphite ion towards the intermediate Co $\mathrm{en_2SO_3^+}$ is $k_{\mathrm{OH_2}}[\mathrm{H_2O}]/k_{\mathrm{SO_3}} = 6 \times 10^{-3}$. Azide ion and hydrogen sulphite ion also compete efficiently with water for the intermediate, and the same limiting rate constant for substitution at high nucleophile concentration is observed for $\mathrm{N_3^-}$ (12·9 ± 0·9 sec.$^{-1}$) as for $\mathrm{SO_3^{2-}}$ (13·2 ± 0·9 sec.$^{-1}$). Above pH 12, hydroxide ion competes very efficiently with $k_{\mathrm{SO_3}}/k_{\mathrm{OH}} = 1{\cdot}1 \times 10^{-2}$. Sulphite substitution of Co $\mathrm{en_2SO_3OH}$ therefore involves an equilibrium

$$\text{(III) } trans\text{-Co en}_2\mathrm{SO_3OH} + \mathrm{SO_3^{2-}} \rightleftarrows trans\text{-Co en}_2(\mathrm{SO_3})_2^- + \mathrm{OH^-}$$

with $K_{\mathrm{III}} = 0{\cdot}385 \pm 0{\cdot}018$ at 25°. Again a dissociative mechanism operates with $k_{-\mathrm{OH}} > 2$ sec.$^{-1}$.

(3) *Dehydration of solid* trans-[Co $\mathrm{en_2SO_3OH_2}$]$\mathrm{ClO_4,H_2O}$

In the solid state, brown crystalline *trans*-[Co $\mathrm{en_2SO_3OH_2}$]$\mathrm{ClO_4,H_2O}$ is transformed to a red amorphous powder of empirical composition Co $\mathrm{en_2SO_3ClO_4}$ with the loss of 2·0 moles of water. The reaction, detectable even at room temperature, is readily followed by mass spectrometry near 100°, where 10 min. is sufficient for complete reaction. The rate of loss of the aquo-ligand is at least 10^3 times faster than that in *cis*-[Co $\mathrm{en_2SO_4,OH_2}$]$\mathrm{ClO_4}$ which forms [Co $\mathrm{en_2SO_4}$]$\mathrm{ClO_4}$.[4] Thus a marked *trans*-labilizing effect of the sulphito-ligand operates also in the solid state.

The u.v.-visible reflectance spectrum of red [Co $\mathrm{en_2SO_3}$]$\mathrm{ClO_4}$ is consistent with an *O*-bonded sulphito-ligand. Although a bidentate sulphito-structure is one possibility suggested by the i.r. spectrum, a polymeric structure based on the unit [. . Co en$_2$–O–SO–O • •] seems more probable.[5] Isotopic enrichment studies with $\mathrm{H_2{}^{18}O}$ show that, before the aquo-ligand is eliminated, one oxygen of the sulphito-ligand becomes nonequivalent to the other two; this would suggest the intermediate formation of *trans*-Co $\mathrm{en_2OSO_2,OH_2^+}$ before polymer formation. The slow dissolution of Co $\mathrm{en_2SO_3ClO_4}$ in dilute $\mathrm{HClO_4}$ yields the *S*-bonded *trans*-Co $\mathrm{en_2SO_3,OH_2^+}$ ion.

(4) *Internal oxidation–reduction in* trans-Co $\mathrm{en_2SO_3OH_2^+}$ *in perchloric acid*

The *S*-bonded sulphito-ligand is very inert to both acid and base hydrolysis but at elevated temperatures and in perchloric acid media ranging from 0·01–7 M, *trans*-Co $\mathrm{en_2SO_3OH_2^+}$ quantitatively forms $\mathrm{Co_{aq}^{2+}}$ and dithionic acid. Radical scavengers like $\mathrm{Fe^{2+}}$ and $\mathrm{O_2}$ reduce the $\mathrm{H_2S_2O_6}$ yield but do not affect the rate of $\mathrm{Co^{2+}}$ formation. The reaction can therefore be written:

$$\text{(IV) } trans\text{-Co en}_2\mathrm{SO_3OH_2^+} + 5\mathrm{H^+} \rightarrow$$

$$\mathrm{Co_{aq}^{2+}} + \mathrm{HSO_3} + 2\,\mathrm{enH_2^{2+}} \quad \text{(slow)}$$

$$2\mathrm{HSO_3} \rightarrow \mathrm{H_2S_2O_6} \quad \text{(fast)}$$

At 73°, $k_{\mathrm{IV}} = 3{\cdot}2 \times 10^{-4}$ sec.$^{-1}$ with $\Delta H^{\ddagger}_{\mathrm{VI}} = 32{\cdot}8 \pm 0{\cdot}5$ kcal. mole^{-1} and $\Delta S^{\ddagger}_{\mathrm{IV}} = 20 \pm 2$ e.u. Check experiments have verified that, in sealed vessels, there is no measurable concentration of $\mathrm{Co_{aq}^{2+}}$ produced in acid solutions of $\mathrm{SO_3^{2-}}$ and *cis*- and *trans*-Co $\mathrm{en_2(OH_2)_2^{3+}}$ which are possible intermediates in this decomposition. Reaction IV is therefore an example of an inner-sphere redox reaction. The alternative acid hydrolysis of *trans*-Co $\mathrm{en_2SO_3OH_2}$ only becomes detectable in 8—11M-$\mathrm{HClO_4}$ media.

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