Redox Decomposition of *trans*-Tetra-ammineaquosulphitocobalt(III) in Aqueous Solution

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The complex *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]^+$ decomposes to Co^{2+} in aqueous acid solution. Kinetic plots exhibit an initial period of curvature followed by a first-order process, $k_{obs} = (1\cdot14 \pm 0\cdot03) \times 10^{-4}\ s^{-1}$ at 25·0 °C, $\Delta H^{\ddagger} = 26\cdot5 \pm 0\cdot1$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 12\cdot5 \pm 0\cdot4$ cal K^{-1} mol^{-1} [I = 1·00M ($LiClO_4$)]. The rate of reaction is independent of $[H^+]$ in the range 0·01—1·00M. A mechanism is proposed relating k_{obs} to a rate-determining isomerisation to the *cis*-complex, followed by rapid conversion to the complex $[Co(NH_3)_3(H_2O)_2(SO_3)]^+$ which probably undergoes an internal redox reaction. Somewhat higher rates have been observed in the presence of molecular oxygen and evidence is presented for formation of the free radical HSO_3.

COBALT(III) complexes with oxidisable ligands are ' precursor ' species [1] capable of yielding first-order rate constants for electron transfer. Redox decomposition of the complex *trans*-$[Co(en)_2(H_2O)(SO_3)]^+$ (en = ethylenediamine) has been studied [2] but required rather drastic conditions before any redox behaviour was detected. Though the en complex is readily obtained,[3] preparation of the potentially more-reactive ammine complex proved difficult. Furthermore references in the literature [4,5] to the starting complex $[Co(NH_3)_5(SO_3)]^+$ are lacking in preparative details. A major part of this work is therefore concerned with the preparation and characterisation of the complexes $[Co(NH_3)_5(SO_3)]_2SO_4,2H_2O$ and *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]Cl$. Subsequent to the completion of our studies, Siebert and Wittke reported [6] alternative preparations of these complexes.

RESULTS

Preparation and Characterisation of Complexes.—The method of preparation of the complex $[Co(NH_3)_5(SO_3)]_2$-$SO_4,2H_2O$ was suggested by some work of Werner,[7] and details are given in the Experimental section. In view of the lability of the complex [4] in solution, it is obvious that the original [7] preparation does not yield the penta-ammine. Aspects of other studies [8-10] purporting to relate to this complex are also in error.

Visible absorption spectra. Since the ligand position *trans* to the sulphito-group is open to rapid substitution,[4] the identity of the complex in solution is defined by the medium. In addition it is only the penta-ammine (X = NH_3) in the series of complexes $[Co(NH_3)_4(X)(SO_3)]$ under investigation which is stable to redox. The spectrum in 0·1M-$HClO_4$ (X = H_2O) was only stable for *ca.* 4 min at 25 °C and in 1·0M-NaOH (X = OH), cloudiness resulted. The visible absorption spectrum in an ammonia buffer (0·5M-NH_3–0·5M-NH_4Cl) was stable for >30 min at 25 °C and is shown in Figure 1, $\lambda_{max.}$ = 456 nm (ε 147 l mol^{-1} cm^{-1}), $\lambda_{min.}$ = 397 nm (ε 45 l mol^{-1} cm^{-1}). Identical spectra were obtained irrespective of whether the complex $[Co(NH_3)_5$-$(SO_3)]_2SO_4,2H_2O$ or $[Co(NH_3)_4(H_2O)(SO_3)]Cl$ was used, and provided good evidence on the consistency of samples. This spectrum is identical with that recently reported.[6] In 0·1M-$HClO_4$ the maximum and minimum are as follows; $\lambda_{max.}$ = 472 nm (ε 159 l mol^{-1} cm^{-1}), $\lambda_{min.}$ = 400 nm (ε 27 l mol^{-1} cm^{-1}) (Figure 1) again irrespective of which complex was used. Though the position of the maximum is the same as that recently recorded by Siebert and Wittke for their complex $[Co(NH_3)_4(H_2O)(SO_3)]ClO_4$,[6] the absorption coefficient is higher by *ca.* 25% in our case.

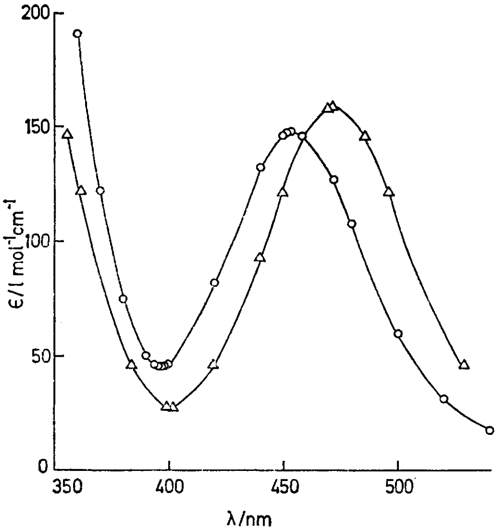

FIGURE 1 Visible absorption spectra in 0·5M-NH_3–0·5M-NH_4Cl corresponding to $[Co(NH_3)_5(SO_3)]^+$ (○) and in 0·1M-$HClO_4$ corresponding to *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]^+$ (△), at 25 °C

The spectrum described by Kiss and Czegledy,[10] with a maximum at 472 nm, was recorded in aqueous solution and does not therefore correspond to the penta-ammine but to the complex *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]^+$. A spectrochemical series [11] based on this value places SO_3^{2-} in the wrong position. By using the value reported here, one obtains the series for $[Co^{III}(NH_3)_5X]$ complexes ($\lambda_{max.}$

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[1] N. Sutin, *Accounts Chem. Res.*, 1968, **1**, 225.

[2] R. S. Murray and D. R. Stranks, *Inorg. Chem.*, 1970, **9**, 1472.

[3] K. L. Scott, R. S. Murray, W. C. E. Higginson, and S-W. Foong, *J.C.S. Dalton*, 1973, 2335.

[4] J. Halpern, R. A. Palmer, and L. M. Blakley, *J. Amer. Chem. Soc.*, 1966, **88**, 2877.

[5] A. V. Babaeva and I. B. Baranovskii, *Russ. J. Inorg. Chem.*, 1962, **7**, 404.

[6] H. Siebert and G. Wittke, *Z. anorg. Chem.*, 1973, **399**, 43.

[7] A. Werner and H. Gruger, *Z. anorg. Chem.*, 1898, **16**, 398.

[8] A. V. Babaeva, Yu. Ya. Kharitonov, and I. B. Baranovskii, *Russ. J. Inorg. Chem.*, 1962, **7**, 643.

[9] E. P. Bertin, R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1959, **81**, 3818.

[10] A. Kiss and D. Czegledy, *Z. anorg. Chem.*, 1938, **235**, 407.

[11] C. K. Jorgensen, (*a*) ' Absorption Spectra and Chemical Bonding in Complexes,' Pergamon, 1962, p. 109; (*b*) *J. Inorg. Nuclear Chem.*, 1962, **24**, 1571; (*c*) *Inorg. Chim. Acta Rev.*, 1968, **2**, 65.

in parentheses):[12] $I^-(585) < Br^-(550) < Cl^-(531) < N_3^-(516) < SO_4^{2-}(513) \sim SCN^-(512) \sim F^-(511) < NO_3^-(502) < NCS^-(497) < H_2O(492) < NH_3(476) < NO_2^-(460) < SO_3^{2-}(456) < CN^-(440)$.

The initial loss of the *trans*-ammine ligand on dissolving the complex $[Co(NH_3)_5(SO_3)]_2SO_4,2H_2O$ in 0·1M-$HClO_4$ at 25 °C was too fast to observe by conventional techniques, and the first scan (within 1 min) corresponded to the *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]^+$ complex. By precooling 0·1M-$HClO_4$ solution to 5 °C before adding the complex, it was possible to observe changes in the spectrum in accordance with Figure 1, over *ca.* 40 min at 5 °C corresponding to replacement of ammonia by water in the *trans*-position.

I.r. spectra. The i.r. spectra (KCl discs) in the range 1 350—450 cm^{-1} of the complexes $[Co(NH_3)_5(SO_3)]_2SO_4,2H_2O$ and *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]Cl$ are given in Figure 2 (for display purposes the ordinate of the latter is offset 20%). Important bands due to the sulphite ligands occur at 1 080vs (broad), 1 125vs (shoulder), 972vs, 628vs, 530w, and 512w cm^{-1} for the former complex and at 1 107vs (broad), 997vs, 984vs, 638s, 628s, and 520m cm^{-1} for the latter, in agreement with recent work of Siebert and Wittke.[6] We agree with these authors that previously published spectra of the penta-ammine complex[8,9] were carried out on samples which, from their method of preparation, could not possibly have been the penta-ammine.

Kinetic Studies.—Preliminary runs on the redox decomposition of the complex *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]^+$ to Co^{2+} gave irreproducible results. Reproducible behaviour was found when solutions were degassed and so the reaction was studied under air-free conditions. Runs were monitored spectrophotometrically by dissolving the complex *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]Cl$ in $HClO_4$–$LiClO_4$ (I = 1·00M) and following the decrease in absorption at the 472 nm maximum. Plots of $\log(OD_t - OD_\infty)$ against time showed initial curvature for *ca.* 50 min at 25·0 °C and were then linear to >94% completion of reaction (Figure 3). No difference was observed by using the complex $[Co(NH_3)_5(SO_3)]_2SO_4,2H_2O$. First-order rate constants, k_{obs}, obtained from the linear region are given in Table 1. It can be seen that k_{obs} is independent of $[H^+]$ in the range 0·01—1·00M and, at 25·0 °C, k_{obs} = (1·14 ± 0·03) × 10^{-4} s^{-1}. No difference was observed in runs also containing $CoCl_2$, Na_2SO_3, NaI, Cu^{2+}, and Fe^{3+}. Activation parameters, $\Delta H^\ddagger$ = 26·5 ± 0·1 kcal mol^{-1} and $\Delta S^\ddagger$ = 12·5 ± 0·4 cal K^{-1} mol^{-1}, were computed from an unweighted least-squares program.

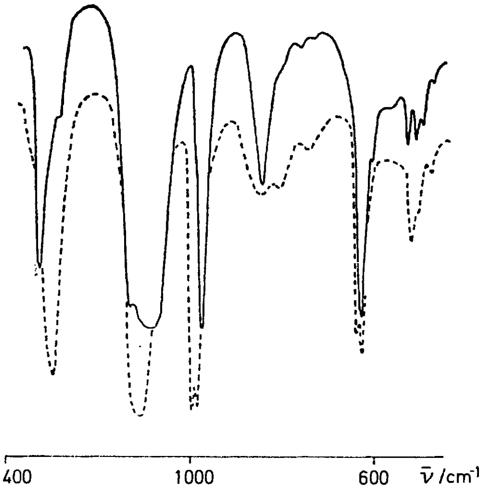

FIGURE 2 I.r. spectra (KCl discs) of the complexes $[Co(NH_3)_5(SO_3)]_2SO_4,2H_2O$ (——) and *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]Cl$ (— — —)

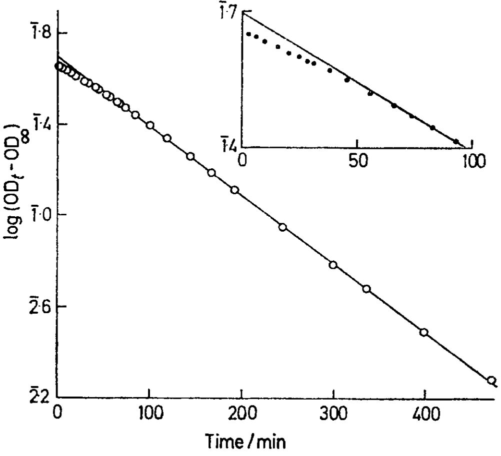

FIGURE 3 Typical first-order plot in the redox decomposition of the complex *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]^+$ (2·9 × 10^{-3}M) under air-free conditions, in 1·0M-$HClO_4$ at 25·0 °C. The early part of the reaction is shown in the inset

TABLE 1

First-order rate constants, k_{obs}, for redox decomposition of the complex *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]^+$, under air-free conditions, I = 1·00M ($LiClO_4$)

t/°C	$[HClO_4]$/M	$10^3[Co]$/M	10^4k_{obs}/s^{-1}
45	1·00	10·0	20·5
45	1·00	2·9	20·1
45	1·00	2·1	19·7
45	0·01	2·1	20·5
40	1·00	3·5	10·0
40	1·00	1·6	10·6
40	0·01	3·5	10·7
30	1·00	1·7	2·45
30	1·00	1·5	2·47
25	1·00	3·5	1·17 [a]
25	1·00	3·5	1·16 [b]
25	1·00	3·5	1·11 [c]
25	1·00	2·9	1·15
25	1·00	2·1	1·17
25	1·00	1·7	1·15
25	0·94	3·5	1·14 [d]
25	0·90	3·5	1·11 [e]
25	0·10	1·7	1·13
25	0·10	3·5	1·11 [f]
25	0·01	1·7	1·14
25	0·01	3·5	1·10 [b]
15	1·00	6·1	0·226

Solutions also contained: [a] $CoCl_2$ (3·5 × 10^{-3}); [b] NaI (8·5 × 10^{-3}); [c] Na_2SO_3 (3·5 × 10^{-3}); [d] Cu^{2+} (1·5 × 10^{-2}), [e] Fe^{3+} (8·4 × 10^{-3}); and [f] Cu^{2+} (5·9 × 10^{-3}M).

Observed rate constants, k_0, for runs carried out in the presence of an excess of oxygen are given in Table 2. For obvious reasons these are not as accurate as runs under air-free conditions, but k_0 is seen to be independent of $[H^+]$

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[12] A. W. Adamson and A. H. Sporer, *J. Inorg. Nuclear Chem.*, 1958, **8**, 214; O. J. Parker and J. H. Espenson, *J. Amer. Chem. Soc.*, 1969, **91**, 1968; G. C. Lalor and J. Lang, *J. Chem. Soc.*, 1963, 5620; D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, 1970, **9**, 655; H. Siebert, *Z. anorg. Chem.*, 1964, **327**, 63.

and of [Complex]. At 25·0 °C and I = 1·00M (LiClO$_4$), $k_0 = (1{\cdot}90 \pm 0{\cdot}06) \times 10^{-4}$ s^{-1} which can be compared with $k_{obs} = (1{\cdot}14 \pm 0{\cdot}03) \times 10^{-4}$ s^{-1}. Preliminary results with solutions that were not degassed, and which showed curvature and irreproducibility, can be understood on the basis of the dissolved oxygen being consumed. Provided the oxygen supply was maintained, the results were reproducible and not affected by using air instead of oxygen.

TABLE 2

First-order rate constants, k_0, for redox decomposition of the complex *trans*-[Co(NH$_3$)$_4$(H$_2$O)(SO$_3$)]$^+$, under excess of oxygen at 25·0 °C and I = 1·00M (LiClO$_4$)

[HClO$_4$]/M	10^3[Co]/M	10$^4k_0$/s^{-1}
1·00	0·76	1·88
1·00	0·76	1·84 [a]
1·00	0·86	2·02
1·00	1·37	1·93
1·00	1·37	1·88 [a]
0·10	1·69	1·90
0·01	1·69	1·84

[a] Air used instead of oxygen.

In the studies so far reported, plots of log(OD$_t$ − OD$_\infty$) against time exhibited initial curvature. The only runs found not to exhibit curvature were those containing Fe^{2+} at concentrations ⩾0·05M. First-order rate constants, k_f, in the presence of Fe^{2+} under air-free conditions are given in Table 3. As evidence that the increase in rate is dependent on [Fe^{2+}] and not due to a medium effect, a run with Mg(ClO$_4$)$_2$ (0·175M) in HClO$_4$ (0·48M), I = 1·00M, was carried out and gave $k_{obs} = 1{\cdot}09 \times 10^{-4}$ s^{-1}.

TABLE 3

First-order rate constants, k_f, for redox decomposition of the complex *trans*-[Co(NH$_3$)$_4$(H$_2$O)(SO$_3$)]$^+$ under air-free conditions, in the presence of Fe^{2+}, at 25·0 °C and I = 1·00M (LiClO$_4$)

10^2[Fe^{2+}]/M	[H$^+$]/M	10^3[Co]/M	10^4k_f/s^{-1}
1·44 [a]	0·90	4·2	1·21 [c]
1·61 [a]	0·94	3·5	1·16
1·61 [a]	0·94	3·5	1·17
5·00 [b]	0·80	3·3	1·19
5·00 [b]	0·80	1·8	1·19
9·68 [a]	0·71	3·4	1·39
19·3 [a]	0·42	4·4	1·57

[a] Iron(II) perchlorate. [b] Iron(II) sulphate. [c] Also contained Cu^{2+} (1·48 × 10^{-2}M).

Inhibiting effects were found under two circumstances. First using MgSO$_4$ (0·2M) in HClO$_4$ (0·2M), a low value for $k_{obs} = 6{\cdot}6 \times 10^{-5}$ s^{-1} at 25·0 °C, I = 1·00M, presumably reflects the formation of the ion *trans*-[Co(NH$_3$)$_4$(SO$_3$)(SO$_4$)]$^-$. Secondly at [H$^+$] <0·01M, where the sulphite product is less extensively protonated, the observed rate decreased. For instance at pH 4·35, maintained by 0·05M-acetic acid–0·05M-sodium acetate, I = 1·00M, two runs with [Complex] = 1·47 × 10^{-3} and 5·92 × 10^{-3}M gave $k_{obs} = 7{\cdot}6 \times 10^{-5}$ and $7{\cdot}8 \times 10^{-5}$ s^{-1} at 25·0 °C respectively. The latter run was monitored over the range 650—350 nm and showed a different behaviour from that obtained at [H$^+$] = 0·01—1·00M, consistent with the build-up of the bis(sulphito) complex.

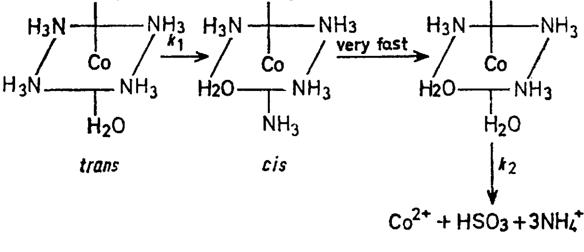
Stoicheiometry.—Estimations of [Co^{2+}] produced showed an exact equivalence with the concentration of cobalt(III) complex, irrespective of whether [Co(NH$_3$)$_5$(SO$_3$)]$_2$SO$_4$,2H$_2$O or *trans*-[Co(NH$_3$)$_4$(H$_2$O)(SO$_3$)]Cl was used. Results are given in the Experimental section.

Several experiments were undertaken in the presence of radical scavengers in order to determine the part (if any) played by the free radical HSO$_3$. Runs under air-free conditions initially containing Fe^{2+} were analysed for Fe^{3+} after completion, by the method described in the Experimental section. Allowance was made for Fe^{3+} impurity in Fe^{2+} stock solutions. Runs corresponding to the last five entries in Table 3 were found to contain (2·96 ± 0·06), (3·18 ± 0·12), (1·70 ± 0·06), (3·28 ± 0·15), and (3·95 ± 0·06) × 10^{-3}M-Fe^{3+} respectively compared with initial complex concentrations of 3·5, 3·3, 1·8, 3·4, and 4·4 × 10^{-3}M. A run having an initial concentration of 8·44 × 10^{-3}M-ammonium iron(III) sulphate and 3·51 × 10^{-3}M-complex was found after complete reaction to contain only (7·04 ± 0·05) × 10^{-3}M-Fe^{3+}.

Quantitative determination of low concentrations of sulphite, sulphate, and dithionate ions is difficult. Our semi-quantitative results showed that sulphite, sulphate, and dithionate ions were products. At [H$^+$] 0·01—1·00M, products associated with reactions of the free radical HSO$_3$ in no way affected the kinetic data (Table 1).

Mechanism.—The fact that neither reaction products nor radical scavengers affected the rate of reaction (Table 1) or the typical shape of plots (Figure 3) leads us to believe that a two-stage mechanism is operating. Consecutive-reaction treatment [13] showed that the observed shape of the plots will be obtained if the first (k_1) and second (k_2) stages are of the same order. Further calculations showed that this type of plot will result irrespective of whether k_1 or k_2 is the slower. However we calculated that the maximum conversion of starting complex to intermediate was 68·4% for $k_1 = 5k_2$ but only 13·4% for $k_2 = 5k_1$. On this basis it is concluded that k_1 is the slower and can be equated to k_{obs} since no marked shifts in the spectrum were observed corresponding to build-up of an intermediate. For instance it was not possible to detect any changes over the range 550—330 nm when a run at 15 °C (Table 1) was scanned for 25 min. Thereafter a drop in intensity over the entire range was observed, consistent with decomposition to Co^{2+}.

We suggest that the initial stage is an isomerisation, in view of the similarity between the activation parameters for k_{obs} (= k_1), $\Delta H^\ddagger = 26{\cdot}5 \pm 0{\cdot}1$ kcal mol^{-1}, $\Delta S^\ddagger = 12{\cdot}5 \pm 0{\cdot}4$ cal K^{-1} mol^{-1}, and published values for isomerisation of cobalt(III) complexes.[14,15] Rapid loss of the *trans*-ammine ligand from the *cis*-aquosulphito-complex [equation (1)] leads to the intermediate which may undergo the redox reaction. The net result of the sequence is substitution of an aquo- for an ammine ligand and hence



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[13] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanisms,' John Wiley, 1953, p. 154.

[14] W. Kruse and H. Taube, *J. Amer. Chem. Soc.*, 1961, **83**, 1281.

[15] S. Batt and P. M. Kwantes, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2407.

an increase in oxidation potential of cobalt(III). Such a mechanism is nicely confirmed by the results in the presence of Fe^{2+}.

DISCUSSION

Redox decomposition of the complex *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]^+$ tells us little about electron transfer and the rate-determining process (k_{obs}), as discussed above, involves substitution (k_1), most probably isomerisation. It is obvious from the typical plot (Figure 3) that accurate values of k_2 and corresponding activation parameters cannot be obtained by consecutive-reaction treatment,[13] but one can estimate $k_2 = ca.\ 6 \times 10^{-4}\ s^{-1}$ at 25·0 °C and $I = 1{\cdot}00$M ($LiClO_4$). Though k_2 has been equated with a redox process [equation (1)] as the simplest mechanism, there is no proof that electron transfer is involved and it may be that k_2 relates to yet another substitution step.

The two effects in the presence of Fe^{2+}, namely an increased rate and loss of the initial curvature, can be interpreted in terms of equations (2) and (3). From the

$$Fe^{2+} + [Co(NH_3)_4(H_2O)(SO_3)]^+ \xrightarrow{k_3} Fe^{3+} + Co^{2+} \quad (2)$$

$$Fe^{2+} + [Co(NH_3)_3(H_2O)_2(SO_3)]^+ \xrightarrow{k_4} Fe^{3+} + Co^{2+} \quad (3)$$

limited data in Table 3, k_f has the form (4) and at 25·0 °C, $I = 1{\cdot}00$M ($LiClO_4$), $k_3 = ca.\ 2{\cdot}4 \times 10^{-4}\ l\ mol^{-1}$

$$k_f = k_{obs} + k_3[Fe^{2+}] \quad (4)$$

s^{-1}. No curvature of plots was observed at $[Fe^{2+}] = ca.\ 0{\cdot}1$M. The combined processes involving loss of intermediate ($k_2 + k_4[Fe^{2+}]$) must be faster therefore than those involving loss of starting complex ($k_1 + k_3[Fe^{2+}]$) by a factor of $\geqslant ca.\ 20$. A rough estimate gives $k_4 \geqslant ca.\ 2 \times 10^{-2}\ l\ mol^{-1}\ s^{-1}$ and the ratio $k_4 : k_3 \geqslant 80$. This is an entirely reasonable result since it represents the increase in rate of reduction brought about by replacement of an ammine by an aquo-ligand [equations (2) and (3)].

One of the surprising aspects to this study was the apparent inactivity of the free radical HSO_3 toward the complex. At low $[Fe^{2+}]$, where reduction of the complex by Fe^{2+} is negligible, almost quantitative conversion to Fe^{3+} was observed consistent with equation (5). As with the previously studied ethylenediamine (en) complex,[2] no effect was observed on the rate. The

$$Fe^{2+} + HSO_3 \rightleftharpoons Fe^{3+} + HSO_3^- \quad (5)$$

introduction of other known radical scavengers (Cu^{2+}, I^-, or Fe^{3+}) similarly had no effect on the rate. The implication is that the radical does not react with a second molecule of complex, but in the absence of scavengers reacts with itself to give dithionate or sulphite and sulphate ions. Since the radical consumes both Fe^{2+} and Fe^{3+}, stoicheiometric determinations do not give quantitative information but are merely intended to show the existence of the free radical.

The observed rate constant in the presence of excess of oxygen is approximately double that under air-free conditions. This suggests that although the free radical HSO_3 does not react with the complex, it does react with oxygen to give a free radical which then reacts with the complex. In this system the presence of oxygen enhances the rate, which is in contrast to the behaviour in redox decomposition of the ion $[Co(C_2O_4)_3]^{3-}$ where inhibition occurs.[16] An obvious difference between the complexes is their lability. It may be that the reactivities of different free radicals towards the ion *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]^+$ reflects their ability to co-ordinate at the labile site.

EXPERIMENTAL

Preparations.—Penta-amminesulphitocobalt(III) *sulphate dihydrate.* $CoCl_2,6H_2O$ (40 g, AnalaR) was dissolved in water (100 cm^3) and added to a mixture of ammonium carbonate (100 g, AnalaR) in water (400 cm^3) and concentrated ammonia (250 cm^3). Air was then drawn through the solution for 12 h. To the solution (500 cm^3) was added $Na_2S_2O_5$ (11 g). This was then set aside in a beaker (500 cm^3) open to the atmosphere. At the first sign of crystallisation (*ca.* 3 days) the solution was filtered and the filtrate transferred to an open dish. After a further 3 days the brown plates of penta-amminesulphitocobalt(III) sulphate dihydrate were filtered off and dried by suction. Allowing evaporation to continue for longer periods led to contamination by a red impurity. Yield 6 g {Found: N, 24·0; H, 6·05; Co, 20·3, 20·5; S, 16·7. $[Co(NH_3)_5(SO_3)]_2SO_4,2H_2O$ requires N, 24·1; H, 5·85; Co, 20·35; S, 16·6%}. Only one water molecule of crystallisation was removed after setting aside the complex for 1 month over P_2O_5; loss in weight 3·2% (calc. 3·1%).

trans-*Tetra-ammineaquosulphitocobalt*(III) *chloride.* Finely ground $[Co(NH_3)_5(SO_3)]_2SO_4,2H_2O$ (0·7 g) was shaken for 4 min with 0·1M-$HClO_4$ (250 cm^3) and then cooled on ice. Whilst cooling, portions of the solution were added to a column of Dowex 50W-X12 cation-exchange resin in the hydrogen-ion form (height 2 cm) kept cold by means of an ice–water jacket. Gas pressure was applied to the column to accelerate the procedure. The complex was then eluted with ice-cold concentrated HCl straight into ice-cold methanol (50 cm^3), and immediately gave a precipitate which was collected and washed with ethanol and ether, the whole preparation being completed within 30 min. The product was dissolved in the minimum volume of 0·1M-HCl (*ca.* 50 ml), filtered, and re-crystallised by adding an equal volume of methanol, and collected as before. Yield 0·3 g {Found: N, 21·6; H, 5·40; Co, 22·0, 22·3; S, 12·0. *trans*-$[Co(NH_3)_4(H_2O)(SO_3)]Cl$ requires N, 21·5; H, 5·35; Co, 22·6; S, 12·3%}. No loss in weight was observed after setting aside the complex over P_2O_5 for 1 week.

Lithium perchlorate was prepared from the carbonate and recrystallised three times. Iron(III) perchlorate was prepared from iron(II) perchlorate, prepared in turn from iron-sponge powder (Johnson Matthey, Specpure). The 0·5M-NH_3–0·5M-NH_4Cl buffer was prepared by making up ammonium chloride (5·3 g, AnalaR) and sodium hydroxide (2·0 g, AnalaR) to 100 cm^3.

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[16] N. S. Rowan, R. M. Milburn, and M. Z. Hoffman, *Inorg. Chem.*, 1972, **11**, 2272.

Kinetic runs and visible spectra were determined on a Unicam SP 500 manual spectrophotometer fitted with a thermostatted cell housing. Repeat spectra were carried out on a Unicam SP 800 spectrophotometer. I.r. spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer. Analyses of N, H, and S were undertaken by Pascher Mikroanalytisches Laboratorium, Bonn. Cobalt was determined spectrophotometrically at 690 nm as $[CoCl_4]^{2-}$–$[CoCl_3H_2O]^-$ by setting aside solutions of complex in 0·1M-$HClO_4$ overnight to form Co^{2+}. Samples (1 cm^3) were made up to 10 cm^3 with concentrated HCl and the method standardised using $CoCl_2,6H_2O$ (AnalaR). Iron(III) was determined spectrophotometrically at 460 nm as $FeNCS^{2+}$. Aliquot portions (0·1 cm^3) were abstracted into 0·01M-NH_4SCN–0·5M-$HClO_4$ (5 cm^3) and the method standardised using ammonium iron(III) sulphate (AnalaR).

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