

**Figure 1.** Plot of  $\log(k_{12}/M^{-1} s^{-1})$  against  $\log K_{12}$ , for reactions  $A^+ + Rh_2(OAc)_4 \rightarrow A + Rh_2(OAc)_4^+$ , where  $A^+$  denotes the oxidants shown. The straight line is drawn with slope 0.5.

$k_{22}$  is the self-exchange rate constant for the couple  $Rh_2(OAc)_4^+/Rh_2(OAc)_4$ , and  $Z$  is the collision rate constant for uncharged reactants. Thus, for a series of reactions with the same or similar mechanisms,<sup>16</sup> with similar values of  $\log k_{11}$ , and with small values of  $\log f_{12}$ , the plot of  $\log k_{12}$  against  $\log K_{12}$  is expected to be a straight line of slope 0.5, and the intercept at  $\log K_{12} = 0$  is  $1/2(\langle \log k_{11} \rangle + \log k_{22})$ , where  $\langle \log k_{11} \rangle$  is the mean of  $\log k_{11}$  for the reactions in question.

For reactions 4-6, such a plot is obtained, as shown in Figure 1, with  $1/2(\langle \log k_{11} \rangle + \log k_{22}) = 1.4 \pm 0.5$ .

Of the three self-exchange values,  $k_{11}(Fe^{III/II})$  is the best established (Table II). For the cerium couple, the estimate  $\log k_{11}(Ce^{IV/III}) \sim 0.5$  involves an extrapolation from 6 M  $HClO_4$  to the present medium (Table II, footnote *f*). As regards the  $V^{V/IV}$  couple, Rosseinsky<sup>16</sup> found a correlation of rates of reactions of  $V^{IV}$  and  $Fe^{II}$  with a wide range of oxidants, and after excluding noncationic oxidants, which could bind strongly to the reductants, he deduced  $\log k_{11}(V^{V/IV}) = 1.0$  in 1.0 M  $HClO_4$ . Thus the assumption of similar  $k_{11}$  values in our three reactions seems justified, and taking  $\langle \log k_{11} \rangle = 0.8$ , we propose  $\log k_{22} = 1.2 \pm 1.0$ , for the couple  $Rh_2(OAc)_4^+/Rh_2(OAc)_4$ , at 25 °C in 1.0 M  $HClO_4$ . The  $\log f_{12}$  terms (Table II) are small enough not to disturb this result. The value of  $k_{22}$  is in the range expected for a redox couple that requires appreciable relaxation of bonds in the inner coordination sphere.<sup>21</sup> On going from  $[Rh_2(OAc)_4(OH_2)_2]^+$  to  $[Rh_2(OAc)_4(OH_2)_2]$ , the M-M distance increases by 3.0%, the M-OH<sub>2</sub> distance by 4.0%, and the mean M-O(carboxyl) distance by 1.2%.<sup>4,5</sup> (Compare the increase of 7.0% in the Fe-O distance between  $Fe(OH_2)_6^{3+}$  and  $Fe(OH_2)_6^{2+}$ .)

The reaction  $Ce^{IV} + Rh_2(OAc)_4$  is slower in 0.5 M  $H_2SO_4$  than in 1 M  $HClO_4$  by a factor of only about 3. The non-bridging ligand effect<sup>23</sup> of sulfate ion would lead to a factor of about 250 (based on eq 7 and the equilibrium constants shown in Table II). The predominant form of  $Ce^{IV}$  in the sulfate medium is  $Ce(SO_4)_3^{2-}$ ,<sup>24</sup> and the effective 80-fold enhancement in rate is presumably due to bridging by sulfate ion, from Ce to the axial site of the  $Rh_2(OAc)_4^+$  ion. In the reaction  $Ce^{IV} + Fe^{II}(aq)$ , where bridging is also possible, the effective enhancement is greater still, the rate in 0.5 M  $H_2SO_4$

being higher than that in 1 M  $HClO_4$ .<sup>25</sup>

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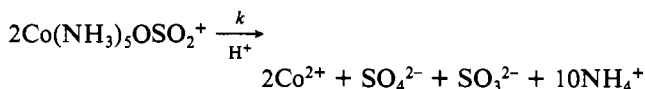
### Mechanistic Information from the Effect of Pressure on the Intramolecular Electron-Transfer Reaction of O-Bonded (Sulfito)pentaamminecobalt(III) in Aqueous Solution

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Recent studies from this laboratory<sup>1-3</sup> have reported significant effects of pressure on some typical electron-transfer reactions involving Co(III) complexes in a nonaqueous medium. Similar results have been reported elsewhere<sup>4,5</sup> for these and closely related reactions in an aqueous medium. These results exhibit interesting tendencies that could form a good basis for discriminating between various possible electron-transfer mechanisms. A detailed understanding of the effects is rather difficult at present due to lack of data on a sufficient number of representative systems. The recent addition of a high-pressure stopped-flow unit<sup>6</sup> to our instrumentation has significantly expanded the range of systems that can now be studied.

In some earlier work,<sup>7</sup> the kinetics and mechanism of the formation and acid-catalyzed decomposition reactions of O-bonded (sulfito)pentaamminecobalt(III) were studied in great detail. These reactions involve fast uptake and loss of  $SO_2$ , respectively, during which no Co-O bond breakage occurs.<sup>8</sup> The  $Co(NH_3)_5OSO_2^+$  species undergoes a subsequent fairly rapid intramolecular redox reaction<sup>7</sup> according to the overall process



for which  $k = (1.4 \pm 0.3) \times 10^{-2} s^{-1}$  at 25 °C. We have now studied the pressure dependence of this reaction and found an extraordinary high positive volume of activation.

### Experimental Section

$Co(NH_3)_5OSO_2^+$  was prepared in solution by treating a solution of  $[Co(NH_3)_5OH_2](ClO_4)_3^{7,9}$  with  $Na_2S_2O_5$  at pH  $\sim 6$ , maintained by using a McIlvaine citric acid-phosphate buffer system.<sup>10</sup> This

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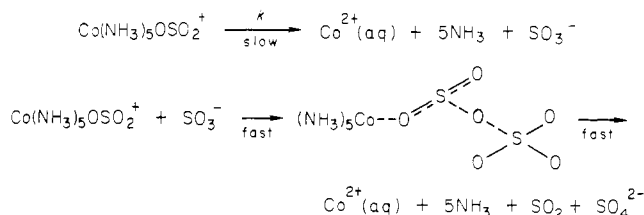
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Table I.  $k_{\text{obsd}}$  as a Function of Pressure for the Intramolecular Electron-Transfer Reaction of  $\text{Co}(\text{NH}_3)_5\text{OSO}_2^+$ <sup>a</sup>

pressure, bar	stopped-flow method $10^3 k_{\text{obsd}}^b, \text{s}^{-1}$	conventional method $10^3 k_{\text{obsd}}^c, \text{s}^{-1}$
10	$1.51 \pm 0.05$	$1.65 \pm 0.03$
250	$1.17 \pm 0.11$	$1.12 \pm 0.04$
500	$0.86 \pm 0.09$	$0.78 \pm 0.02$
750	$0.49 \pm 0.03$	$0.52 \pm 0.03$
1000	$0.41 \pm 0.01$	$0.37 \pm 0.02$
$\Delta V^\ddagger, \text{cm}^3 \text{mol}^{-1}$	$+34.4 \pm 2.9$	$+34.6 \pm 0.5$

<sup>a</sup> Conditions:  $[\text{Co}(\text{III})] = 5 \times 10^{-4} \text{ M}$ ,  $[\text{S}]_{\text{total}} = 0.04 \text{ M}$ , pH 6.2, ionic strength 1 M. <sup>b</sup> Temperature 25.0 °C, mean value of between 6 and 12 kinetic runs. <sup>c</sup> Temperature 14.4 °C, mean value of 3 kinetic runs.

#### Scheme I



was performed in a high-pressure stopped-flow instrument<sup>6</sup> at 25 °C such that the subsequent redox reaction could be followed immediately. A series of experiments were also performed at 15 °C on a conventional Zeiss PMQ II spectrophotometer equipped with a thermostated ( $\pm 0.1$  °C) high-pressure cell.<sup>11</sup> During these measurements the Co(III) complex was added to a precooled buffer solution containing  $\text{Na}_2\text{S}_2\text{O}_3$  and then rapidly transferred to a "pillbox" optical cell.<sup>12</sup> The ionic strength of the solutions was adjusted with  $\text{NaClO}_4$ , and chemicals of analytical reagent grade and doubly distilled water were used throughout this study.

The redox reaction was followed at 330 nm, where the  $\text{Co}(\text{NH}_3)_5\text{OSO}_2^+$  species has an absorbance of  $2300 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>1,13</sup> The observed first-order rate constants,  $k_{\text{obsd}}$ , were calculated from plots of  $\ln(A_t - A_\infty)$  vs.  $t$ , where  $A_t$  and  $A_\infty$  are the absorbances at time  $t$  and infinity, respectively. Such plots were linear for at least 3 half-lives of the reaction.

#### Results and Discussion

The values of  $k_{\text{obsd}}$  as a function of pressure are summarized in Table I. Plots of  $\ln k_{\text{obsd}}$  vs. pressure are linear within the experimental errors involved and result in volumes of activation of  $+34.4 \pm 2.9$  and  $+34.6 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$  at 25.0 and 14.4 °C, respectively. The values of  $k_{\text{obsd}}$  at 10 bar are in good agreement with those reported before<sup>7</sup> for similar conditions but at ambient pressure. These volumes of activation are indeed very large and among the highest ever reported for the reactions of Co(III) complexes.<sup>13</sup> Very recently, Saito and co-workers<sup>14</sup> reported an overall volume of activation of  $+36 \text{ cm}^3 \text{ mol}^{-1}$  for the outer-sphere electron-transfer process within a molybdate(V)-cobalt(III) ion pair, of which  $24 \text{ cm}^3 \text{ mol}^{-1}$  was ascribed to the change in volume during the formation of the ion pair and  $12 \text{ cm}^3 \text{ mol}^{-1}$  to the volume of activation for the electron-transfer process. The magnitude of  $\Delta V^\ddagger$  for the intramolecular redox reaction of  $\text{Co}(\text{NH}_3)_5\text{OSO}_2^+$  is such that it calls for a detailed discussion.

Various pieces of indirect evidence in favor of an intramolecular redox reaction were reported in our earlier study,<sup>7</sup> and the suggested redox mechanism is outlined in Scheme I. The first electron-transfer step is assumed to be rate determining

and produces  $\text{Co}^{2+}$  and a  $\text{SO}_3^-$  radical, which is scavenged effectively in the subsequent non-rate-determining steps. Some experiments were recently performed on a conventional stopped-flow instrument coupled to an OMA Type II (Princeton Applied Research) rapid-scanning spectrophotometer. The spectra, recorded at intervals of 5 s at 25 °C from 250 to 500 nm, exhibited gradual decreases in absorbance during the redox reaction and showed no evidence for the formation of any stable intermediates. Under the present experimental conditions (see Table I) the  $\text{SO}_2$  uptake reaction for the formation of  $\text{Co}(\text{NH}_3)_5\text{OSO}_2^+$  is very fast ( $k = 170 \text{ s}^{-1}$  at 25 °C<sup>7</sup>) and does not interfere with the subsequent redox process. Furthermore, the redox reaction is fairly pH independent under the present conditions,<sup>7</sup> such that small fluctuations in pH, due to a possible pressure dependence of the buffer system, will not have any major influence on the value of  $k_{\text{obsd}}$ .

As a first possibility, linkage isomerization from an O- to a S-bonded sulfito complex may partially account for an increase in volume during the redox process. However, it is known<sup>15,16</sup> that the S-bonded species undergoes a much slower redox reaction than the O-bonded species, which rules out this possibility. In addition, such an isomerization process should have been observed during the rapid-scan experiments since the O- and S-bonded species show significantly different spectra.<sup>11,17,18</sup>

A more likely explanation is that the volume increase results from an intrinsic contribution due to bond breakage during the electron-transfer process and from a solvational contribution due to charge neutralization during this reaction. A similarly large positive  $\Delta V^\ddagger$  value was recently<sup>19</sup> found for the electron-transfer step in the outer-sphere redox reaction between  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$  and  $\text{Fe}(\text{CN})_6^{4-}$ , which could only be ascribed to a significant change in solvation due to partial charge neutralization. The suggested rate-determining electron-transfer step in Scheme I involves significant bond breakage and charge neutralization components to partially account for the observed volume of activation. In addition, the present observations do not rule out a redox mechanism that involves the dissociative release of one or more  $\text{NH}_3$  ligands under the trans-effect influence of the O-bonded sulfito ligand.<sup>16</sup> In such a case *trans*- $\text{Co}(\text{NH}_3)_4(\text{OH}_2)\text{OSO}_2^+$  could be formed, which may undergo a significantly faster redox reaction than the pentaammine species.<sup>15</sup> During the dissociative release of an  $\text{NH}_3$  ligand a maximum intrinsic volume increase of  $24.8 \text{ cm}^3 \text{ mol}^{-1}$ , i.e., the partial molar volume of  $\text{NH}_3$ ,<sup>20</sup> can be expected. Arguments in favor of the latter interpretation are as follows: the rate constant for the redox reaction of  $\text{Co}(\text{NH}_3)_5\text{OSO}_2^+$  is almost identical with the rate constant for the release of  $\text{NH}_3$  during the formation of  $\text{Co}(\text{NH}_3)_4\text{SO}_3^+$  from  $\text{Co}(\text{NH}_3)_5\text{SO}_3^+$ ;<sup>16</sup> the complexes  $\text{Co}(\text{tetren})\text{OSO}_2^+$  and *trans*- $\text{Co}(\text{NH}_3)_4(\text{CN})\text{OSO}_2$  do not undergo a significant redox reaction<sup>17,21</sup> and only exhibit O- to S-bonded linkage isomerization as a subsequent reaction following the  $\text{SO}_2$  uptake process, which is probably due to the absence of a labile  $\text{NH}_3$  group trans to the sulfito ligand.

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**Registry No.**  $\text{Co}(\text{NH}_3)_5\text{OSO}_2^+$ , 19394-96-8.

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