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Kinetic Data for SO_2 Uptake by Rh(III) and Cr(III) Hydroxo Complexes in Aqueous Solution

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The complexes $Rh(NH_3)_5OH^{2+}$ and $Cr(NH_3)_5OH^{2+}$ react very rapidly with dissolved SO_2 to form the O-bonded sulfito species $Rh(NH_3)_5OSO_2^+$ and $Cr(NH_3)_5OSO_2^+$, respectively. The unstable $M(NH_3)_5OSO_2^+$ species lose SO_2 on acidification to regenerate the $M(NH_3)_5OH_2^{3+}$ species, or undergo subsequent isomerization and/or substitution reactions. The kinetics of the SO_2 uptake reactions were studied over wide pH and [total S] ranges, from which it follows that $k = (1.8 \pm 0.3) \times 10^8$ M^{-1} sec^{-1} for M = Rh(III) and $k = (2.9 \pm 0.6) \times 10^8$ M^{-1} sec^{-1} for M = Cr(III) at 25 °C and an ionic strength of 1.0 M *($NaClO_4$). The results are discussed in reference to other SO_2 and CO_2 uptake data reported in the literature.*

Introduction

The reaction of CO_2 with transition metal hydroxo complexes of the type ML_5OH^{2+} and $ML_4(OH)_2^+$ (M = Co(III), Rh(III) and Ir(III)) to form mono- and bidentate carbonato complexes, has been studied in great detail in recent years [1–4]. More recently [5] it was reported that the complex species $Co(NH_3)_5OH^{2+}$ is capable of reacting with SO_2 to form $Co(NH_3)_5OSO_2^+$, which can undergo a rapid acid-catalyzed decomposition (loss of SO_2) or a slow intramolecular redox reaction during which Co(II) and SO_4^{2-} are produced. The latter study has now been extended to the corresponding complexes of Rh(III) and Cr(III).

Experimental

Materials

$[Rh(NH_3)_5OH_2](ClO_4)_3$ and $[Cr(NH_3)_5OH_2](ClO_4)_3$ were prepared according to standard literature procedures [6–8]. Chemical analyses were in agreement with the theoretical values and the uv–visible spectra (recorded on a Unicam SP 1800 spectrophotometer) were in agreement with those reported elsewhere [9–11] (see Table I). All chemicals used, were of reagent grade, $Na_2S_2O_5$ was used as source of sulfite [5] and deionized distilled water was used in all solutions.

Measurements

The acid dissociation constants of $Rh(NH_3)_5OH_2^{3+}$ and $Cr(NH_3)_5OH_2^{3+}$ were determined at 25 °C and an

TABLE I. UV–Visible Absorption Spectra of Some Rh(III) and Cr(III) Species.

Complex Species	λ_{max} nm	ϵ M^{-1} sec^{-1}	Reference
$Rh(NH_3)_5OH_2^{3+}$	315, 263	105, 94	This work
	316, 264	105, 94	9
	314	112	10
	315, 262	105, 95	16
$Rh(NH_3)_5OSO_2^+$	258	~2100	This work[a]
$Cr(NH_3)_5OH_2^{3+}$	360, 483	31, 38	This work
	358, 480	31, 37	11
$Cr(NH_3)_5OSO_2^+$	264, 373, 510	~3800, 33, 47	This work[b]

[a] pH ~ 6.5. [b] pH ~ 4.5.

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TABLE II. Dependence of k_{obs} on pH and [total S] for SO_2 Uptake by $Rh(NH_3)_5OH^{2+}$.[a]

pH	[total S] *M*	k_{obs}[b] sec^{-1}	k_1[c] $\times 10^{-8}$ M^{-1} sec^{-1}	(k_2/K_4)[d] $\times 10^{-6}$ M^{-1} sec^{-1}
7.13	0.01	0.875	1.67	
7.09	0.01	1.22	2.01	
6.90	0.01	2.26	1.98	
6.60	0.01	4.49	1.70	
6.25	0.01	10.8	2.01	
6.17	0.01	11.7	1.92	
5.93	0.01	20.3	2.50	
6.02	0.02	22.4	1.53	
6.05	0.03	32.0	1.50	
5.99	0.04	44.0	1.45	
5.94	0.05	53.6	1.34	
		Mean:	1.78 ± 0.34	
5.49	0.01	34.1	1.78[e]	4.56
5.11	0.01	59.4	1.78[e]	4.88
4.72	0.01	103	1.78[e]	4.21
4.33	0.01	170	1.78[e]	3.14
4.12	0.01	275	1.78[e]	3.31
3.57	0.01	>800[f]	–	–
			Mean:	4.02 ± 0.76

[a] [Rh(III)] = 5 × 10^{-4} *M*, Temp. = 25 °C, ionic strength = 1.0 *M* ($NaClO_4$), wavelength = 260 nm. [b] Average value of at least five kinetic runs. [c] Calculated from eqn. (2). [d] Calculated from eqn. (3). [e] Mean value of k_1 from data at pH > 5.5 [f] Too fast to measure accurately, within mixing time of stopped flow instrument.

ionic strength of 1.0 *M* ($NaClO_4$) by a conventional pH titration, using a Metrohm E 500 digital pH meter. The pK values were found to be 6.80 ± 0.05 and 5.20 ± 0.05, respectively, which are in good agreement with values reported elsewhere [8–10]. All rate measurements were made at 25 °C and an ionic strength of 1.0 *M* ($NaClO_4$) using a Durrum Model 110 stopped flow spectrophotometer. The 'equilibrium method' [1] was employed to study the SO_2 uptake processes in a similar way as described in detail before [5]. The observed pseudo-first-order rate constants were calculated in the usual way, and the corresponding semi-log plots were linear for at least two to three half-lives of the reaction.

Results and Discussion

Some preliminary experiments were performed to study the overall reaction sequence. When an excess of $Na_2S_2O_5$ is added to, or SO_2 gas is bubbled through, buffered (phosphate–citric acid [12]) solutions of $M(NH_3)_5OH_2^{3+}$ (M = Rh(III) and Cr(III)) at pH ~ 5, the uv–visible spectra of the latter species undergo instantaneous and significant changes. Immediate acidification (pH < 2) of the so-formed species, which are presumably $M(NH_3)_5OSO_2^+$, caused an instantaneous colour change for M = Cr(III) and the resulting spectrum is in exact agreement with that of $Cr(NH_3)_5OH_2^{3+}$. This reverse reaction was more difficult to observe for M = Rh(III) since acidification of sulfite-containing solutions result in the formation of 'H_2SO_3', *i.e.* SO_2, which strongly absorbs at 278 nm (ϵ ~ 240 M^{-1} cm^{-1}) and completely overrules the spectrum of $Rh(NH_3)_5OH_2^{3+}$. However, if blank corrections are made for the absorbance of SO_2, the spectrum of the acidified species is in agreement with that of $Rh(NH_3)_5OH_2^{3+}$. The reversibility of the process, *i.e.* uptake and loss of SO_2 on acidification, is considered as important evidence for the existence of the $M(NH_3)_5OSO_2^+$ species [5]. The maximum build-up of the latter species depends on the pH and sulfite concentration of the solutions (see kinetic data). The spectra of the involved species are summarized in Table I, from which it follows that the sulfito complexes exhibit a very strong absorption band around 260 nm. A similar absorption was reported [5] for the $Co(NH_3)_5OSO_2^+$ species at 330 nm.

It is important to note that the rapid formation processes of O-bonded sulfito complexes are followed by slower, secondary reactions which may include linkage isomerization (O- to S-bonded) and/or sub-

TABLE III. Dependence of k_{obs} on pH and [total S] for SO_2 Uptake by $Cr(NH_3)_5OH^{2+}$.[a]

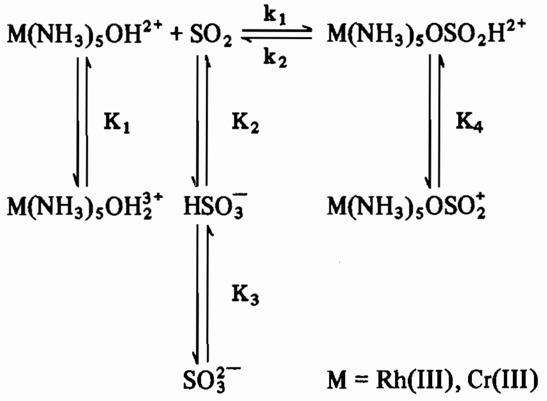
pH	[total S] M	k_{obs}[b] sec^{-1}	k_1[c] × 10^8 M^{-1} sec^{-1}
7.20	0.01	1.96	3.53
7.10	0.01	3.36	3.94
6.89	0.01	8.06	3.93
6.87	0.01	7.54	3.39
6.64	0.01	16.1	2.93
6.24	0.01	49.8	2.23
5.92	0.01	146	2.57
5.51	0.01	358	2.52
6.69	0.02	25.3	2.79
6.57	0.03	55.7	2.59
6.46	0.04	103	2.40
6.39	0.05	149	2.19
		Mean:	2.92 ± 0.63

[a] [Cr(III)] = 5 × 10^{-4} M, Temp. = 25 °C, ionic strength = 1.0 M ($NaClO_4$), wavelength = 260 nm. [b] Average value of at least five kinetic runs. [c] Calculated from eqn. (2).

sequent substitution processes to yield such species as $M(NH_3)_5SO_3^+$, *trans*-$M(NH_3)_4(OH_2)(OSO_2)^+$, *trans*-$M(NH_3)_4(OH_2)(SO_3)^+$ and *trans*-$M(NH_3)_4(SO_3)_2^-$ [5, 13–15]. These secondary reactions made it impossible to isolate the 'intermediate' $M(NH_3)_5OSO_2^+$ species.

We now turn to a discussion of the kinetic data. SO_2 uptake by $Rh(NH_3)_5OH^{2+}$ was studied over the ranges $3.5 < pH < 7.2$ and $0.01 \leqslant [\text{total S}] \leqslant 0.06\ M$ for which the results are summarized in Table II. It was observed that the overall absorbance increase during SO_2 uptake remained constant at pH > 5.5, but decreased significantly with decreasing pH at pH < 5.5. However, the value of k_{obs} increases significantly at lower pH, indicating that the reverse step (acid-catalyzed SO_2 elimination) becomes significant at pH < 5.5 [5] and contributes to the value of k_{obs}. A mechanism for the SO_2 uptake/elimination process [1, 5] is outlined in Scheme I. Participating hydrogen ions are omitted from the scheme for simplicity reasons and all K s are defined as *acid dissociation* constants. The rate law for the formation and decomposition of $M(NH_3)_5OSO_2^+$ is [5]

$$k_{obs} = k_1 \left\{\frac{K_1}{K_1 + [H^+]}\right\}\left\{\frac{[H^+]^2}{[H^+]^2 + K_2[H^+] + K_2K_3}\right\}[\text{total S}] + k_2\left\{\frac{[H^+]}{[H^+] + K_4}\right\} \ldots\ldots \quad (1)$$



Scheme I

At low $[H^+]$, *i.e.* at pH > 5.5 where no SO_2 elimination reaction occurs, eqn. (1) reduces to

$$k_{obs} = k_1 \left\{\frac{K_1}{K_1 + [H^+]}\right\}\left\{\frac{[H^+]^2}{[H^+]^2 + K_2[H^+] + K_2K_3}\right\}[\text{total S}] \ldots\ldots \quad (2)$$

Since pK_2 = 1.9, pK_3 = 6.3 [6] and pK_1 = 6.8 (for M = Rh(III) – see Experimental Section) at 25 °C and an ionic strength of 1.0 M ($NaClO_4$), k_1 was calculated using eqn. (2) for all the values of k_{obs} at pH > 5.5 in Table II. It follows that a fairly constant value for k_1 is obtained over the pH and [total S] ranges concerned, with an average value of (1.8 ± 0.3) × 10^8 M^{-1} sec^{-1} at 25 °C.

At higher $[H^+]$, *i.e.* at pH < 5.5, uptake and elimination of SO_2 occur, with the result that eqn. (1) is applicable and can be rewritten in the form

$$k_{obs} - k_1 \left\{\frac{K_1}{K_1 + [H^+]}\right\}[SO_2] = k_2' =$$

$$= k_2 \left\{\frac{[H^+]}{[H^+] + K_4}\right\}$$

Calculations indicated that k_2' depends, within experimental error limits, linearly on $[H^+]$ such that $K_4 >> [H^+]$ and the above equation simplifies to [5]

$$k_2/K_4 = k_{obs} - k_1 \left\{\frac{K_1}{K_1 + [H^+]}\right\} \times [SO_2]\ /[H^+] \ldots\ldots \quad (3)$$

The value of k_2/K_4 in Table II is once again fairly constant over the pH range concerned and has an average value of (4.0 ± 0.8) × 10^6 M^{-1} sec^{-1} at 25 °C, which is very close to that reported for the Co(III) analogue [5].

Similar rate data for the uptake of SO_2 by $Cr(NH_3)_5OH^{2+}$ are summarized in Table III. For this species the pH range was limited to pH > 5.5 since the SO_2 uptake and possible SO_2 elimination processes occurred too fast [8] for accurate measurements at pH < 5.5. No evidence for the occurrence of the reverse process was observed at pH > 5.5, such that eqn. (2) can be used to calculate the value of k_1. According to the data in Table III, k_1 is fairly constant over the pH and [total S] ranges concerned, with an average value of (2.9 ± 0.6) × 10^8 M^{-1} sec^{-1} at 25 °C.

k_1 for SO_2 uptake by $Co(NH_3)_5OH^{2+}$ was reported [5] to be (4.7 ± 0.3) × 10^8 M^{-1} sec^{-1} at 25 °C, which is slightly larger than those reported above for SO_2 uptake by $Rh(NH_3)_5OH^{2+}$, *viz.* (1.8 ± 0.3) × 10^8 M^{-1} sec^{-1}, and $Cr(NH_3)_5OH^{2+}$, *viz.* (2.9 ± 0.6) × 10^8 M^{-1} sec^{-1}. However, if the order of magnitude of these values is taken into account, it follows that k_1 is almost constant for the three metal centres with an average value of (3.1 ± 1.5) × 10^8 M^{-1} sec^{-1} at 25 °C. It has previously been emphasized that log k_1 for CO_2 uptake by various metal hydroxo complexes [17, 18], depends linearly on the pK value of the corresponding aquo form of the complex species. This relation does not seem to hold for SO_2 uptake reactions over the limited range of k_1 and pK_1 values concerned.

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