

Kinetics and mechanism of the reactions of hexaaqua rhodium (III) with sulphur (IV) in aqueous medium

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Abstract. An O-bonded sulphito complex, $\text{Rh}(\text{OH}_2)_5(\text{OSO}_2\text{H})^{2+}$, is reversibly formed in the stopped-flow time scale when $\text{Rh}(\text{OH}_2)_6^{3+}$ and $\text{SO}_2/\text{HSO}_3^-$ buffer ($1 < \text{pH} < 3$) are allowed to react. For $\text{Rh}(\text{OH}_2)_5\text{OH}^{2+} + \text{SO}_2 \rightleftharpoons \text{Rh}(\text{OH}_2)_5(\text{OSO}_2\text{H})^{2+}$ (k_1/k_{-1}), $k_1 = (2.2 \pm 0.2) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_{-1} = 0.58 \pm 0.16 \text{ s}^{-1}$ (25°C , $I = 0.5 \text{ mol dm}^{-3}$). The protonated O-sulphito complex is a moderate acid ($K_a = 3 \times 10^{-4} \text{ mol dm}^{-3}$, 25°C , $I = 0.5 \text{ mol dm}^{-3}$). This complex undergoes (O, O) chelation by the bound bisulphite with $k = 1.4 \times 10^{-3} \text{ s}^{-1}$ (31°C) to $\text{Rh}(\text{OH}_2)_4(\text{O}_2\text{SO})^+$ and the chelated sulphito complex takes up another HSO_3^- in a fast equilibrium step to yield $\text{Rh}(\text{OH}_2)_3(\text{O}_2\text{SO})(\text{OSO}_2\text{H})$ which further undergoes intramolecular ligand isomerisation to the S-bonded sulphito complex: $\text{Rh}(\text{OH}_2)_3(\text{O}_2\text{SO})(\text{OSO}_2\text{H}) \rightarrow \text{Rh}(\text{OH}_2)_3(\text{O}_2\text{SO})(\text{SO}_3^-)$ ($k_{\text{iso}} = 3 \times 10^{-4} \text{ s}^{-1}$, 31°C). A dinuclear (*m*-O, O) sulphite-bridged complex, $\text{Na}_4[\text{Rh}_2(\text{m-OH})_2(\text{OH})_2(\text{m-OS}(\text{O})\text{O})(\text{O}_2\text{SO})(\text{SO}_3)(\text{OH}_2)]5\text{H}_2\text{O}$ with (O, O) chelated and S-bonded sulphites has been isolated and characterized. This complex is sparingly soluble in water and most organic solvents and very stable to acid-catalysed decomposition.

Keywords. Rhodium–sulphur complexes; intramolecular ligand isomerisation; sulphite-bridged complexes.

1. Introduction

Rhodium forms a variety of complexes in various oxidation states ranging from +1 to +6. Interest on the coordination chemistry of rhodium continues to be in accelerating pace due to interesting chemical reactivity, anti tumour activity, electronic structure, and catalytic functions of its complexes with potential industrial applications.¹

$\text{Rh}^{\text{II}}(\text{bipy})_2/\text{Rh}^{\text{III}}(\text{bipy})_3$ are believed to be involved in the photo reduction of water.² In recent years, kinetic studies of labile rhodium (II) ($4d^7$) complexes³ and the relatively more stable rhodium(IV) complexes⁴ have been reported. The most extensive kinetic and structural investigations, however, have centred around low-spin rhodium (III) complexes,^{1,5(a-k)} of which the hexa-aquarhodium (III), $\text{Rh}(\text{OH}_2)_6^{3+}$, is important. Harris *et al.*^{5b} observed that the rate constants of anation of $\text{Rh}(\text{OH}_2)_6^{3+}$ by Cl^- and Br^- were virtually independent of the anating ligand and compared well with the water exchange rate constant of the aqua cation. On this basis, they proposed a

dissociative interchange mechanism for the aqua ligand substitution of $\text{Rh}(\text{OH}_2)_6^{3+}$. Recent theoretical studies⁶ and experimental investigations⁷ (i.e. activation volume measurements) of the bromide anation of $\text{Rh}(\text{OH}_2)_6^{3+}/\text{Rh}(\text{OH}_2)_5\text{OH}^{2+}$ have pointed out that the aqua ligand substitution of $\text{Rh}(\text{OH}_2)_6^{3+}$ involves associative interchange mechanism (I_a) while the same for the hydroxopentaaquarhodium (III), $\text{Rh}(\text{OH}_2)_5\text{OH}^{2+}$ is essentially dissociative interchange (I_d). However, the possibility of ion-pairing of $\text{Rh}(\text{OH}_2)_6^{3+}$ and $\text{Rh}(\text{OH}_2)_5\text{OH}^{2+}$ with anionic nucleophiles cannot be overlooked as pointed out by Richens *et al.*⁷ A further point of interest on the ligand substitution reactions of $\text{Rh}(\text{OH}_2)_5\text{X}^{2+}$ ($\text{X} = \text{Cl}^-$, Br^- , I^- and OH^-) is the *trans* effect of the ligand X^- which facilitates the substitution of the aqua ligand *trans* to X .^{5b,7}

It is known that sulphite exerts very strong kinetic and structural *trans* effects in several (sulphito) aminocobalt (III) complexes in which it is S-bonded to the metal centre.⁸ Such studies on rhodium (III) are rare. There is, however, a report on the formation of the O-bonded sulphito complex, $\text{Rh}(\text{NH}_3)_5(\text{OSO}_2)^+$ ⁹ which is reversibly formed in solution. Ford *et al.*¹⁰

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have investigated the photochemical reactions of *trans*-(NH₃)₄Rh(NCS)(SO₃) and *trans*-Rh(NH₃)₄(SO₃)₂⁻ (both S-bonded sulphito complexes). The *tris* sulphito rhodium (III) complexes, K₃[Rh(SO₃)₃]2H₂O and K₃[Rh(SO₃)₃(NH₃)₃] 3·5 H₂O have been reported.¹¹ However, the details of *cis/trans*-labilising action of O/S-bonded sulphito complexes of Rh^{III} have not been investigated in detail although S-bonded sulphite in *trans*-(NH₃)₄Rh(Cl)SO₃ has been reported¹⁰ to exert trans effect.

Our current interest on the reactions of S^{IV} with transition metal complexes^{8,12-14} prompted us to investigate the aqua ligand substitution of Rh(OH₂)₆³⁺ by S^{IV} with the intention of examining (i) the mechanism of reaction of SO₂/HSO₃⁻/SO₃²⁻ with rhodium (III), and (ii) the *cis/trans*-labilising effect of sulphite if any in the corresponding sulphito complexes. It is pertinent to mention here that SO₂ has proved to be a versatile ligand capable of direct coordination to metal centres, especially Ru^{II}, with several bonding modes,¹⁵ and HSO₃⁻/SO₃²⁻ are excellent nucleophiles.

It would be of great interest to examine the possibilities of direct SO₂ interaction with Rh(OH₂)₆³⁺/Rh(OH₂)₅(OH)²⁺ replacing the aqua ligand, and insertion of SO₂ in Rh^{III}-OH, besides substitution of the aqua ligands by HSO₃⁻/SO₃²⁻.

2. Experimental

Solutions of Rh(OH₂)₆³⁺ in dilute perchloric acid were prepared by digesting RhCl₃·3H₂O (Johnson–Mathey) with 70% perchloric acid till free from chloride and diluting to desired volume. The stock solution of Rh³⁺(aq.) was diluted appropriately and the [H⁺] was estimated by pH measurements. A standard calibration curve using HClO₄ solution of known concentration was used to convert pH data to p[H⁺] = (-log [H⁺]).^{12b} The concentration of Rh³⁺ in the stock solution was checked spectrophotometrically {*e* = 67·4 and 62 dm³ mol⁻¹ cm⁻¹ at 311 and 396 nm for Rh(OH₂)₆³⁺ respectively}.⁷ Analytical grade reagents were used. Sodium meta bisulphite (Na₂S₂O₅) (GRE Merck) was the source of S^{IV} which in aqueous solution is rapidly hydrolysed to an equilibrium mixture of SO₂/HSO₃⁻/SO₃²⁻. Fresh solution of S^{IV} was prepared every time before starting the kinetics and equilibrium measurements. Sodium perchlorate was prepared by mixing standard solutions of NaOH and HClO₄. The pH of the stock NaClO₄ solution was adjusted to 6. Freshly prepared

doubly distilled water (the second distillation was made from alkaline KMnO₄) received from a glass distillation apparatus was used for solution preparation.

The pH measurements were made on a Systronics digital pH meter model 335 equipped with a combined electrode, CL 51 (0 < pH < 14). The reference electrode was filled with 3 mol dm⁻³ NaCl saturated with AgCl. NBS buffers of pH 4·01, 6·86 and 9·2 were used to calibrate the instrument. The spectral measurements and kinetic runs were made using a PC-operated Systronics UV-Visible spectrophotometer model 119; 1 cm matched quartz cells were used. Na was estimated flame photometrically using a Systronics digital flame photometer model 125 and by AAS using a Varian atomic absorption spectrometer Spectro AA 20+. IR spectra (KBr disc) were recorded on Shimadzu 8300 and a Nicolet FTIR spectrometers. Sulphur and hydrogen were analysed on a Perkin–Elmer 240C CHNS analyser.

Na₄[Rh₂(OH)₄(SO₃)₃]·6H₂O was prepared as follows. A mixture of 0·5 g (0·0019 mole) of RhCl₃·3H₂O and 0·4 g (0·0021 mole) of Na₂S₂O₅ in 50 cm³ of water was refluxed on a water bath. A white solid formed immediately. Heating was continued for 24 h after which the solid was collected on a sintered glass funnel (G2), washed with cold water followed by ethanol and ether, and stored over silica gel in a dessicator. Qualitative tests for Cl⁻ using K₂Cr₂O₇ and H₂SO₄ (chromyl chloride test) was negative while there was reduction of dichromate to Cr³⁺ thus indicating the presence of sulphite. Analysis: S, 12·5; Rh, 28·5, Na, 12·1, H, 1·91, C, 0·14%. Calcd. for Na₄Rh₂S₃O₁₉H₁₆ (formula wt. = 713·8): S, 13·4; Rh, 28·8; Na, 12·8, H, 2·2%.

Rh^{III} content was analysed by two methods. The complex was decomposed with 70% HClO₄ at sand bath temperature and suitably diluted in distilled water. The absorbance for Rh(OH₂)₆³⁺ was measured at 396 nm as mentioned. In a second method,¹⁶ a known volume of the decomposed complex solution was treated with freshly prepared stannous bromide (using Sn and 48% HBr) and 70% HClO₄ to develop yellow colour and then diluted to 50 cm³ ([Rh]_T = 3 mg/cm³). Absorbance was measured after 25 min at 427 nm (*e* = 2·9 × 10⁴ dm³ mol⁻¹ cm⁻¹). A blank correction was also applied. Rh% calculated by these two methods agreed to ± 2%.^{5b}

The fast reactions were studied by a stopped flow spectrophotometer SF 51 (M/s Hitech, UK). The details of the experimental procedure were essentially

the same as described in our earlier work.¹² Reaction was studied under pseudo-first order condition with respect to $[S^{IV}]_T$. The working wavelength was 290 nm at which the mixtures of $Rh^{3+}(aq)$ and S^{IV} (pH = 1.4–3.0) displayed an exponential increase in absorbance with time characteristics of a first-order reaction. At least seven replicate runs were taken for each composition and k_{obs} data are collected in table 1. Replicate runs using different sets of freshly prepared solutions of a given composition reproduced k_{obs} within the error limits ($s(k_{obs})$).

The slow reactions were monitored by conventional spectrophotometry. The reaction was initiated by mixing the reactants in a volumetric flask (50, 25 or 10 cm³) diluting to the appropriate volume and then transferring the mixture to the spectrophotometric cell. The time delay was noted (~30 s) and the progress of the reaction was monitored at a suitable wavelength (see table 2). Some runs (at >30°C, $k_{obs} < 10^{-4} s^{-1}$) were also made by batch sampling method which involved thermostating the reaction mixture in a water thermostat and then drawing samples at known time intervals for absorbance measurements.

All calculations were made on a PC.

3. Results and discussion

The UV-Visible spectra of $Rh(OH_2)_6^{3+}$, $[S^{IV}]$ and a mixture of the two at pH = 3.2 clearly display an interaction between the two (see figure 1). On mixing the two reactants an absorption maximum appears at 280 nm instantaneously. The aqua ligand substitution reactions of $Rh(OH_2)_6^{3+}$ and its aqua-hydroxo analogue are extremely slow.^{5(b-h),7} For example, the water exchange rate constants (k_{ex}) of $Rh(OH_2)_6^{3+}$ and its aqua-hydroxo analogue, $Rh(OH_2)_5OH^{2+}$, are 2.3×10^{-6} and $4.2 \times 10^{-3} s^{-1}$ at 70°C respectively.¹⁷ It is, therefore, not likely that the direct replacement of the aqua ligand by any of the S^{IV} species (SO_2 , HSO_3^- or SO_3^{2-}) will be too fast to account for the observed spectral changes. The behaviour of $Rh(OH_2)_6^{3+} + S^{IV}$ is very similar to that of $(NH_3)_5RhOH^{2+} + S^{IV}$ for which fast formation of the O-bonded sulphito complex was observed.⁹ Several (aqua)(amine)cobalt (III) ions have been shown to undergo fast and reversible formation of the O-bonded sulphito complexes in the presence of SO_2 in mild acidic media.⁸

On immediate acidification of the reaction mixture of $Rh(OH_2)_6^{3+} + S^{IV}$ to pH 1, the characteristic

absorption band at 280 nm, however, intensified. This is due to the strong absorption of $SO_2(aq.)$ ($\epsilon(280\text{ nm}) = (2.28 \pm 0.09) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, this work; $\epsilon \sim 240 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 278 nm reported by van Eldik⁹). After correcting for the absorption of $SO_2(aq.)$ it turned out that the instantaneously formed Rh^{III} -sulphito complex also decayed very rapidly on acidification. Since O-bonded sulphito complexes undergo very rapid acid-catalysed elimination of SO_2 ,^{5g,8} it is concluded that the rapid spectral changes observed are due to the reversible formation of the O-bonded sulphito complex, $Rh(OH_2)_5(OSO_2)^+$ {I max, nm ($\epsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 280 (2700)} whose spectral parameters agree well with those for $(NH_3)_5Rh(OSO_2)^+$ {I max, nm ($\epsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 258 (~2100)}.⁹

The repetitive spectral scans of the reaction mixture on extended time scale displayed profound changes (figure 2) due to the slow secondary reactions of the O-bonded sulphito complex (see later).

SO_2 in aqueous medium retains its identity with equilibria as shown below.

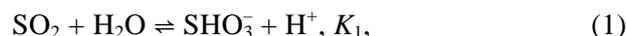


Table 1. Rate constants (k_{obs}) for the reversible formation of $[Rh(OH_2)_5(OSO_2H)]^{2+}$.^a

$[S^{IV}]_T$ (mol dm ⁻³)	pH	k_{obs} (s ⁻¹)	k_{cal} (s ⁻¹)
0.020	2.90	1.5 ± 0.2	1.2
0.040	2.96	1.7 ± 0.2	1.9
0.050	2.92	2.3 ± 0.2	2.3
0.060	3.00	2.6 ± 0.2	2.6
0.080	3.06	3.3 ± 0.4	3.2
0.100	3.01	4.6 ± 0.7	4.0
0.020	1.47	1.1 ± 0.2	0.86
0.020	2.35	1.3 ± 0.2	1.3
0.020	2.92	0.90 ± 0.2	1.1
0.020	2.24	1.2 ± 0.2	1.2
0.040	1.52	1.2 ± 0.1	1.2
0.040	1.49	1.2 ± 0.2	1.2
0.040	1.54	1.4 ± 0.2	1.3
0.040	1.56	1.3 ± 0.2	1.3
0.040	1.60	1.2 ± 0.2	1.3

k_1 (dm³ mol⁻¹ s⁻¹); $(2.1 \pm 0.2) \times 10^3$; K_d (mol dm⁻³); 3.8×10^{-4} ; k_{-1} (s⁻¹); 0.58 ± 0.16 ; k_2 (dm³ mol⁻¹ s⁻¹); 0.002 ± 5.3 ; F^b 9.4

^a25.0 ± 0.1°C; $[Rh^{III}]_T = 5.0 \times 10^{-4}$, $I = 0.5 \text{ mol dm}^{-3}$; $I = 290 \text{ nm}$

^b $F = \sigma[(k_{cal} - k_{obs})/s(k_{obs})]^2$

Table 2. Rate constants for the (O, O) chelation by O-bonded sulphito complex and formation of the disulphito complex.^a

$[S^{IV}]_T$ (mol dm ⁻³)	pH	$10^3 f_{\text{obs}}$ (s ⁻¹)	$10^4 s_{\text{obs}}$ (s ⁻¹)	$10^4 k_{\text{cal}}^s$ (s ⁻¹)	$10^4 k_{\text{cal}}^c$ (s ⁻¹)
0.0025	3.66	1.78 ± 0.56	0.99 ± 0.07	0.68	1.16
0.005	3.65	1.40 ± 0.64	1.71 ± 0.22	0.75	1.15
0.010	2.73	1.60 ± 0.19	0.33 ± 0.05	0.65	0.44
0.010	3.11	1.35 ± 0.15	0.75 ± 0.09	0.69	0.59
0.010	3.46	1.51 ± 0.16	0.84 ± 0.05	0.78	0.88
0.010	3.88	1.30 ± 0.23	1.84 ± 0.08	1.04	1.60
0.010	4.18	1.54 ± 0.78	3.14 ± 0.35	1.45	2.41
0.010	4.88	2.58 ± 1.36	4.70 ± 0.24	4.76	4.60
0.015	3.58	1.60 ± 0.26	1.09 ± 0.08	0.93	1.04
0.020	4.05	1.08 ± 0.21	1.92 ± 0.03	1.84	2.03
0.030	3.30	1.52 ± 0.20	0.77 ± 0.03	0.94	0.73
0.030	3.85	2.56 ± 1.49	1.83 ± 0.09	1.77	1.53
0.040	4.11	1.76 ± 0.37	2.90 ± 0.11	3.42	2.20

$$k_1(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})^b = (0.00014 \pm 99) \times 10^{-4}; A(\text{s}^{-1})^c = (3.28 \pm 1.12) \times 10^{-4}$$

$$k_2 K_h (\text{s}^{-1})^b = (5.4 \pm 0.8) \times 10^{-7}; B(\text{s}^{-1} \text{mol dm}^{-3})^c = (2.27 \pm 0.45) \times 10^{-8}$$

$$k_{-2} (\text{s}^{-1})^b = 0.62 \pm 0.19; C (\text{mol dm}^{-3})^c = (3.7 \pm 1.7) \times 10^{-5}$$

$$K_h (\text{mol dm}^{-3})^b = 1.0 \times 10^{-6}; F^d = 274; F^d = 102$$

$$^a 31.8 \pm 0.2^\circ\text{C}, I = 0.5, 10^4 [\text{Rh}^{III}]_T = 1.17 \text{ or } 2.4 \text{ mol dm}^{-3}; I = 250 \text{ nm}$$

^bCalculated values are based on (6) (see text) using the best fit values of k_1 , $k_2 K_h$, k_{-2} and K_h

^cCalculated values are based on (7)

$$^d F = \bar{O} [10^4 (k_{\text{cal}}^s - k_{\text{obs}}^s / S (k_{\text{obs}}^s))]^2$$

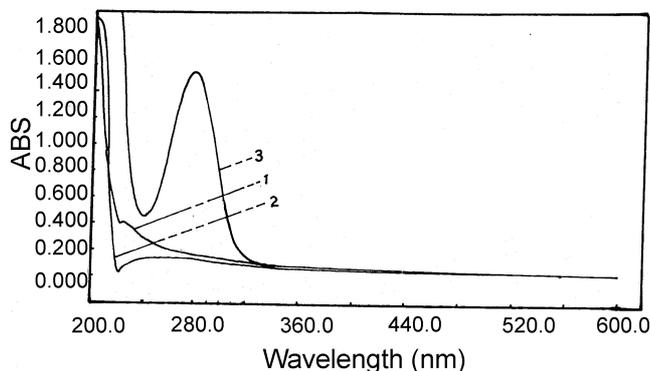


Figure 1. Absorption spectra of $\text{Rh}(\text{OH}_2)_6^{3+} + \text{S}^{\text{IV}}$ mixtures. $[\text{Rh}(\text{OH}_2)_6^{3+}]_T = 5.8 \times 10^{-4}$, $[\text{S}^{\text{IV}}]_T = 5.8 \times 10^{-3}$ mol dm⁻³, pH = 3.2 (25°C); (1) $\text{Rh}(\text{OH}_2)_6^{3+}$, (2) S^{IV} , (3) $[\text{Rh}(\text{OH}_2)_6^{3+} + \text{S}^{\text{IV}}]$.

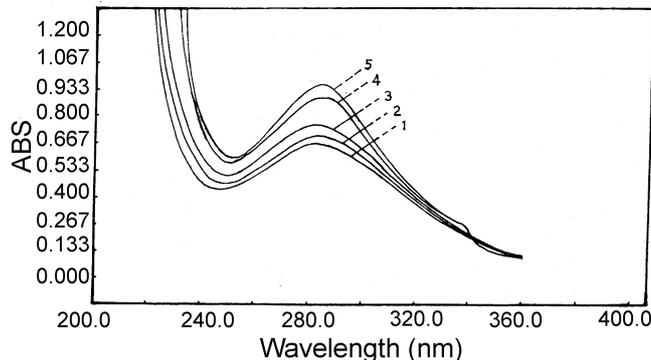


Figure 2. Repetitive spectral scans of $\text{Rh}(\text{OH}_2)_6^{3+} + \text{S}^{\text{IV}}$ at 25°C. $[\text{Rh}^{3+}]_T = 2.4 \times 10^{-4}$, $[\text{HSO}_3^-]_T = 0.01$, $I = 0.5$ mol dm⁻³, pH = 3.60; Curves generated after 1 min (1), 15 min (2), 40 min (3), 80 min (4) and 110 min (5) of mixing.

where SHO_3^- denotes $[\text{bisulphite}]_T$ as equilibrium mixture of H-SO_3^- and H-O-SO_2^- , the latter species predominating to > 75%.¹⁸ All experiments were restricted to $[\text{S}^{\text{IV}}]_T \leq 0.1$ mol dm⁻³ ($K_D = 0.082$ dm³ mol⁻¹ at 25°C, $I = 1.0$ mol dm⁻³)¹⁹ to minimize complications due to dimerisation of bisulphite.

The observed pseudo-first order rate constants for the initial fast reaction of S^{IV} with $\text{Rh}(\text{OH}_2)_6^{3+}$ are collected in table 1. The k_{obs} values are interpreted in terms (see scheme 1) of a fast reaction between $\text{SO}_2(\text{aq.})$ and $\text{Rh}(\text{OH}_2)_5\text{OH}^{2+}/\text{Rh}(\text{OH}_2)_6^{3+}$.

In accord with scheme 1, k_{obs} is given by,

$$k_{\text{obs}} = \{k_1 f_3 + k_2 (1 - f_3)\} f_1 [\text{S}^{\text{IV}}]_T + k_r, \quad (4)$$

$$k_r = k_{-1} + k_{-2} [\text{H}^+] / (1 + K_d / [\text{H}^+]),$$

where $f_1 = [\text{H}^+] / ([\text{H}^+] + K_1)$ (denoting fraction of $[\text{S}^{\text{IV}}]_T$ as SO_2), K_1 is the acid ionisation constant of SO_2 , $f_3 = K_3 / ([\text{H}^+] + K_3)$ (i.e. the fraction of $\text{Rh}(\text{OH}_2)_6^{3+}$ as $\text{Rh}(\text{OH}_2)_5\text{OH}^{2+}$), and K_3 is the acid dissociation constant of $\text{Rh}(\text{OH}_2)_6^{3+}$. The ionisation of HSO_3^- to

SO_3^{2-} ($\text{p}K = 6.6$ at 25°C , $I = 0.5 \text{ mol dm}^{-3}$)²⁰ was neglected. When data were fitted to (4) using $\text{p}K_1 = 1.8$ ($I = 0.5 \text{ mol dm}^{-3}$, 25.0°C)²⁰ and initially guessed value of $\text{p}K_3 = 3.3$,²¹ the $k_{-2}[\text{H}^+]$ term turned out statistically insignificant. Setting $k_{-1} + k_{-2}[\text{H}^+]$ as k_{-1} the data were refitted to (4). The best fit value of $\text{p}K_3$ turned out to be 3.4 and the calculated parameters are presented in table 1.

It is interesting to note that the SO_2 uptake rate constant (k_1) for $\text{Rh}(\text{OH}_2)_5\text{OH}^{2+}$ is 10^5 times smaller than the same for $\text{Rh}(\text{NH}_3)_5\text{OH}^{2+}$ ($k_1 = 1.8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C , $I = 1.0 \text{ mol dm}^{-3}$)⁹ but comparable to that of $\text{Cr}(\text{OH}_2)_5\text{OH}^{2+}$ ($k_1 = 4.4 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C , $I = 1.0 \text{ mol dm}^{-3}$)²². The k_1 values parallel the basicity of the M-OH^{2+} species as adjudged by the $\text{p}K$ of the corresponding aqua cations ($\text{p}K_3 = 6.8$ and 3.88 for $(\text{NH}_3)_5\text{RhOH}_2^{3+}$ and $\text{Cr}(\text{OH}_2)_6^{3+}$ respectively at 25°C and $I = 1.0 \text{ mol dm}^{-3}$)^{9,22}.

This is in conformity with Bronstead catalysis law which has been found to be valid for SO_2 uptake reactions of metal-hydroxo species.^{12c} This work further shows that the reaction of $\text{Rh}(\text{OH}_2)_6^{3+}$ with SO_2 is statistically insignificant ($k_2 = 0.002 \pm 5.3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C , see table 1).

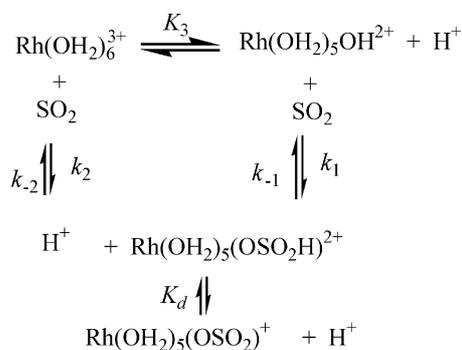
The SO_2 elimination rate constant of $\text{Rh}(\text{OH}_2)_5(\text{OSO}_2\text{H})^{2+}$ ($k_{-1} = 0.58 \text{ s}^{-1}$ at 25°C) is significantly small as compared to that of (tetren) $\text{Co}(\text{OSO}_2\text{H})^{2+}$ ($k_{-1} = 1 \times 10^3 \text{ s}^{-1}$, 25°C)²³. The relevant data for other protonated O-sulphito complexes are not available for comparison. Moritzen *et al*²² did not observe significant protonation of $\text{Cr}(\text{OH}_2)_5(\text{OSO}_2)^+$ ($0.15 < [\text{H}^+] < 1.0 \text{ mol dm}^{-3}$) and reported the second order rate constant for SO_2 elimination as $1.58 \pm 0.04 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (25°C , $I = 1.0 \text{ mol dm}^{-3}$).

The SO_2 elimination reaction of $\text{Rh}(\text{NH}_3)_5(\text{OSO}_2)^+$ was studied by van Eldik⁹ under second order conditions. With a value of $K_d = 1.0 \times 10^{-4}$ the second

order rate constant $4.0 \pm 0.8 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (25°C , $I = 1.0 \text{ mol dm}^{-3}$) translates to $k_{-1} = 4 \times 10^2 \text{ s}^{-1}$.

This remarkable rate difference for the two rhodium complexes must be due to two factors: (i) ease of intra molecular proton transfer from the coordinated bisulphite to the Rh–O bond, and (ii) thermodynamic stability of the hydrogen bonded structure of the bisulphite complex (see figure 3). While the proton transfer will depend upon the basicity of the $\text{Rh}^{\text{III}}\text{–O}$ bond which is expected for $(\text{NH}_3)_5\text{Rh}^{\text{III}}\text{–O}$ to be higher than for $(\text{OH}_2)_5\text{Rh}^{\text{III}}\text{–O}$, the thermodynamic stability due to hydrogen bonding will be accentuated by the presence of the vicinal aqua ligand. Thus both these effects favour overall stabilization of $\text{Rh}(\text{OH}_2)_5(\text{OSO}_2\text{H})^{2+}$ towards SO_2 elimination in comparison to the same for the corresponding ammine complex. It is pertinent to mention here that the stabilizing influence of intra molecular hydrogen bonding in the SO_2 elimination of *cis* $[\text{Co}(1,3 \text{ diaminopropane})_2(\text{OH}_2)(\text{OSO}_2)]^+$ was observed by us earlier.²⁴

A relatively slow reaction was observed when the initially formed O-bonded sulphito complex was allowed to react in excess of HSO_3^- . The time dependence of the spectral scans of the reaction mixture (see figure 2) showed the gradual build up of the product. This reaction was monitored at 250 nm (at which the absorbance due S^{IV} is relatively low) and the absorbance time data under pseudo first order conditions of $[\text{S}^{\text{IV}}]_T$ fitted well to a double exponential equation ($A_{\text{obs}} = C_1 \exp(-k_{\text{obs}}^f t) + C_2 \exp(-k_{\text{obs}}^s t) + A_w$) characteristic of consecutive reactions: $\text{R} \rightarrow \text{INT} \rightarrow \text{P}$ where R, INT and P denote the reactant, intermediate and the final product respectively. The rate constants, k_{obs}^f and k_{obs}^s are collected in table 2. It is worth noting that k_{obs}^f is virtually independent of pH and $[\text{S}^{\text{IV}}]_T$ while k_{obs}^s exhibits virtually little $[\text{S}^{\text{IV}}]_T$ but significant pH dependence. The k_{obs}^s tends to increase with the increase of pH. These results indicate that under the conditions of $[\text{S}^{\text{IV}}]_T$ and pH, rhodium (III) is fully and instantaneously converted



Scheme 1.

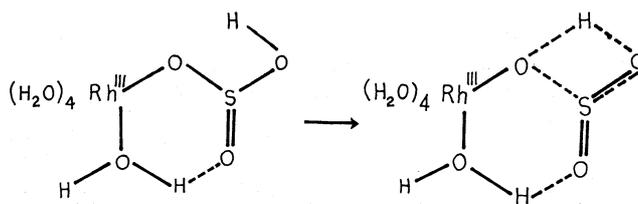


Figure 3. Hydrogen-bonded structure of the rhodium bisulphite complex.

to the O-bonded sulphito species which then undergoes slow transformation to an intermediate, (5) below. The lack of pH dependence of k_{obs}^f ($3.11 \square \text{pH} \square 4.88$) is also consistent with the fact that the O-sulphito complex is not appreciably protonated and also there is little specific H^+ catalysis in its transformation to the intermediate (INT). The average value of k_{obs}^f (weighted mean) is $1.45 (\pm 0.02) \times 10^{-3} \text{ s}^{-1}$ (31.0°C , $I = 0.5 \text{ mol dm}^{-3}$).



The two distinct possibilities of reaction (5) are: (i) slow O, O chelation of the mono dentate sulphito complex, and (ii) intra molecular O to S-ligand isomerisation, $\text{Rh}^{\text{III}}(\text{OH}_2)_5(\text{OSO}_2(\text{H})) \rightarrow \text{Rh}^{\text{III}}(\text{OH}_2)_5(\text{SO}_3)$, the S, O chelation of sulphite being discounted due to the strained 3-membered ring formation. The O- to S-bonded ligand isomerisation has been studied for several cobalt(III)-amine-sulphito complexes for which k_{iso} is essentially 10^{-4} s^{-1} (25°C).^{8,23,25} The $[\text{Pt}(\text{NH}_3)_4(\text{OH}_2)(\text{OSO}_2)]^{2+}$ is reported to isomerise to its S-bonded analogue with $k_{\text{iso}} = 4.0 \times 10^{-5} \text{ s}^{-1}$ (25°C).²⁶ Moritzen *et al*²² reported a value of $2 \times 10^{-4} \text{ s}^{-1}$ (25°C) for $\text{Cr}(\text{OH}_2)_5(\text{OSO}_2)^+$. Since S-sulphite is a soft ligand and $\text{Cr}(\text{OH}_2)_6^{3+}$ is a hard metal ion, the ligand isomerisation in this system is less likely. On the other hand this could be due to the O, O chelation by sulphite. Since the reactions of Rh^{III} complexes are slower than those of Cr^{III} and Co^{III} ,^{5b,c,f,h} we are led to believe that the reaction (5) is not likely the ligand isomerisation but O, O chelation by sulphite. This being an intra molecular process, is likely favoured by the *cis*-labilising effect of the O-bonded sulphite (mono dentate) and accentuated by the presence of the displaceable aqua ligand. It is worth noting that the *cis* and *trans*-activation of the O-bonded sulphite has been observed in the $\text{SO}_3^{2-}/\text{HSO}_3^-$ catalysed aquation of $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{2+}$ ($\text{X} = \text{Cl}^-, \text{NCS}^-$)^{27,28} and in the aqua ligand substitution of *trans*- $[\text{Cr}(\text{salen})(\text{OH}_2)(\text{OSO}_2)]^-$ (*salen* = N,N'-ethylene bis salicylidinimine).²⁹ This is the first report on the *cis*-activating influence of O-bonded sulphite in a Rh^{III} -O-sulphito complex.

The chelation reaction (5) is further succeeded by sulphite substitution for the aqua-sulphito complex with which k_{obs}^s is associated. Earlier reports on the halide anation of the $\text{Rh}(\text{OH}_2)_6^{3+}/\text{Rh}(\text{OH}_2)_5\text{OH}^{2+}$ also demonstrated the formation of the dihalogeno species, $\text{Rh}(\text{OH}_2)_4(\text{X})_2^+$ ($\text{X} = \text{Br}^-, \text{Cl}^-$), the entry of the second halide being much faster than the first

one.^{5b,7} Scheme 2 and the relevant rate (6) were considered for interpreting the rate data (k_{obs}^s). The $[\text{HSO}_3^-]$ values were taken to be $(1-f_1)[\text{S}^{\text{IV}}]_{\text{T}}$ (f_1 as defined above) and k_{obs}^s data were fitted to (6). It turned out that $k_{-1}[\text{H}^+]$ term is insignificant and K_h (the acid dissociation constant of $[\text{Rh}(\text{OH}_2)_5(\text{O}_2\text{SO})]^+$ is $1.0 \times 10^{-6} \text{ mol dm}^{-3}$). Hence the value of K_h was held fixed at 1.0×10^{-6} , $k_{-1}[\text{H}^+]$ term was neglected and the rate constants were refitted to the modified form of (6). The value of k_1 turned out statistically insignificant and data fitting was also poor (see table 2).

$$k_{\text{obs}}^s = (k_1 + k_2 K_h / [\text{H}^+]) [\text{HSO}_3^-] / (1 + K_h / [\text{H}^+] + k_{-1} [\text{H}^+] + k_{-2}). \quad (6)$$

Interestingly when k_{obs}^s data were fitted to the empirical (7), the fit improved very significantly (see table 2).

$$k_{\text{obs}}^s = (A + B / [\text{H}^+]) / (1 + C / [\text{H}^+]). \quad (7)$$

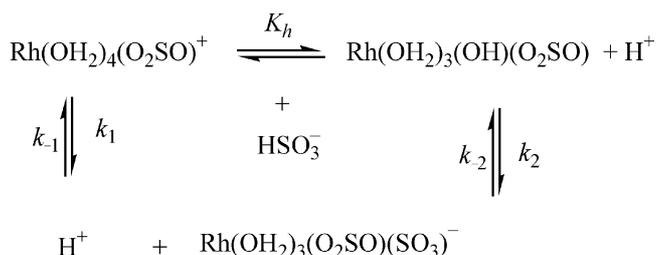
The values of A , B , and C are collected in table 2. These parameters are interpreted in the frame work of a mechanism for the formation of the disulphito complexes (O- and S-bonded isomers) as depicted in scheme 3 for which k_{obs}^s is given by (8).

$$k_{\text{obs}}^s = \{ (k_{2\text{iso}} + k_d / Q) + k_{3\text{iso}} K_d / [\text{H}^+] \} Q [\text{HSO}_3^-] / D_1 + k_{-4} [\text{H}^+], \quad (8)$$

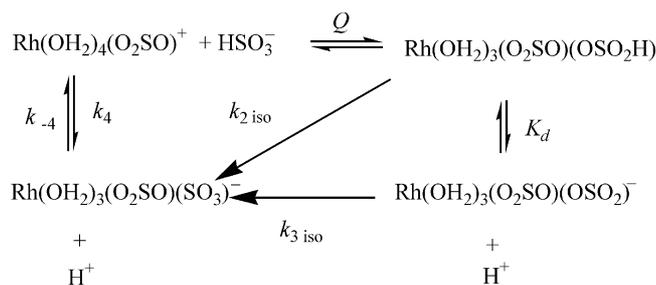
where

$$D_1 = 1 + Q [\text{HSO}_3^-] (1 + K_d / [\text{H}^+]). \quad (9)$$

Q is the equilibrium quotient for the formation of the disulphito complex, $[\text{Rh}(\text{OH}_2)_3(\text{O}_2\text{SO})(\text{OSO}_2\text{H})]$ and K_d is its acid dissociation constant. It is further assumed that the reaction of HSO_3^- with the (aqua)(sulphito) complex to yield, $\text{Rh}(\text{OH}_2)_3(\text{O}_2\text{SO})$



Scheme 2.



Scheme 3.

(OSO₂H) is fast and equilibrium controlled as this is kinetically equivalent to the reaction of the hydroxosulphito complex with SO₂ and to that of the fast SO₂ addition reaction of Rh(OH₂)₅OH²⁺. Assuming that $Q[\text{HSO}_3^-](1 + K_d/[\text{H}^+]) \gg 1$, (8) and (9) yield (10) which is essentially equivalent to (7) but for the reverse reaction of the disulphito complex, [Rh(OH₂)₃(O₂SO)(SO₃)⁻]. Data fitted to (10) showed that $k_{-4}[\text{H}^+]$ is indeed insignificant and hence A , B , C of (7) are reconciled with $(k_{2\text{iso}} + k_4/Q)$, $(k_{3\text{iso}}K_d)$ and K_d of (10) respectively,

$$k_{\text{obs}}^s = \{(k_{2\text{iso}} + k_4/Q) + k_{3\text{iso}}K_d/[\text{H}^+]\} / (1 + K_d/[\text{H}^+] + k_{-4}[\text{H}^+]) \quad (10)$$

The value of $k_{3\text{iso}}$ ($= B/C$) is $(6.1 \pm 3.0) \times 10^{-4} \text{ s}^{-1}$ (31°C) which reflects the (O, O chelated) sulphite induced O- to S-bonded isomerisation of coordinated (monodentate) sulphite (see scheme 3) in [Rh(OH₂)₃(O₂SO)(O-SO₂)⁻]. Assuming that $k_{2\text{iso}} \gg k_4/Q$, the optimised value of $k_{2\text{iso}}$ ($= A$) is $(3 \pm 1) \times 10^{-4} \text{ s}^{-1}$ which is also comparable to the value of $k_{3\text{iso}}$.

4. Equilibrium study for the formation of Rh(OH₂)₅(OSO₂H)²⁺

An attempt was made to study the initial rapid equilibrium formation of the sulphito complex. The absorbances of the mixtures of Rh(OH₂)₆³⁺ and S^{IV} ($I = 0.5 \text{ mol dm}^{-3}$) were measured immediately (within 2 min of mixing) at 280 nm. Data are collected in table 3. Assuming scheme 1 for the rapid and reversible formation of the O-sulphito complex the absorbance data at a fixed total [Rh³⁺]_T and varying [S^{IV}]_T and pH after correcting for the absorbance of [S^{IV}]_T is given by (11)

$$\ddot{A}_{\text{obs}} = \{A'(1 + [\text{H}^+]/K_3) + A''K_{\text{eq}}f_1[\text{S}^{\text{IV}}]_T\} / \{1 + [\text{H}^+]/K_3 + K_{\text{eq}}f_1[\text{S}^{\text{IV}}]_T\}, \quad (11)$$

Table 3. Initial rapid equilibrium formation of Rh(OH₂)₅(OSO₂H)²⁺.^a

[S ^{IV}] _T (mol dm ⁻³)	pH	A _{obs} ^b	A' _{obs} ^b	ÄA _{aobs} ^b
0.001	2.51	0.176	0.039	0.137
0.002	2.53	0.278	0.075	0.203
0.003	2.56	0.388	0.105	0.283
0.004	2.50	0.510	0.158	0.352
0.005	2.63	0.496	0.153	0.343
0.006	2.68	0.562	0.167	0.396
0.008	2.69	0.653	0.217	0.436
0.010	2.59	0.781	0.333	0.448

$A''_{\text{obs}}K_{\text{eq}} = (7.87 \pm 0.75) \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$; $K_{\text{eq}} = (1.20 \pm 0.19) \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$; $F^c = 0.176$

^a[Rh^{III}]_T = 2.4×10^{-4} , $I = 0.5 \text{ mol dm}^{-3}$, 30.0°C, $l = 280 \text{ nm}$, cell path = 1 cm

^bA_{obs} and A'_{obs} denote absorbances of the mixture of Rh^{III} and S^{IV} and in absence of Rh^{III} respectively; ÄA_{obs} = A_{obs} - A'_{obs}. A_{obs} = 0.028 for [Rh^{III}]_T = $2.4 \times 10^{-4} \text{ mol dm}^{-3}$ at pH = 2.55 ± 0.02 , [S^{IV}]_T = 0 and $I = 0.5 \text{ mol dm}^{-3}$

^cF = Ö[10(ÄA_{obs} - ÄA_{cal})]²

Table 4. Equilibrium data for the formation of the disulphito complex, Rh(OH₂)₄(SO₃)₂⁻.^a

[S ^{IV}] _T (mol dm ⁻³)	pH	A _{obs} (280 nm)	A(S ^{IV}) ^b (280 nm)
0.005	3.16	0.610	0.071
0.010	3.49	0.747	0.094
0.015	3.49	0.875	0.141
0.020	3.46	0.923	0.195
0.030	3.46	1.142	0.292
0.040	3.44	1.321	0.398
0.050	3.41	1.447	0.515
0.030	3.14	1.247	0.441
0.030	3.20	1.255	0.405
0.030	3.40	1.122	0.312

$(A'' - A')^{-1}$; 1.87 ± 0.18 ; $[(A'' - A')K_{2\text{eq}}]^{-1}$; 41.7 ± 3.8 ; A' ; 0.41 ; $K_{2\text{eq}} (4.5 \pm 0.6) \times 10^{-2}$; CRC^c ; 0.967

^a31.0°C, $I = 0.5 \text{ mol dm}^{-3}$

^bA(S^{IV}) (280 nm) = $e_1 f_1[\text{S}^{\text{IV}}]_T + e_2 (1 - f_1)[\text{S}^{\text{IV}}]_T$; $e_1 = (2.28 \pm 0.09) \times 10^2$, $e_2 = 4.95 \pm 0.43 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

^cCorr. coeff. of the double reciprocal plot

where A' and A'' denote A_{obs} at [S^{IV}]_T = 0 (i.e. for Rh^{III} alone at the same pH and ionic strength) and for the complete transformation of [Rh³⁺]_T to its O-sulphito complex, Rh-OSO₂H²⁺ respectively, K₁, K₃ are as defined earlier, and K_{eq}(= k_1/k_{-1}): is the equilibrium constant. Data were fitted to (11) using pK₃ = 3.4 (see above) and pK₁ = 1.8 and we obtained K_{eq} = $1.2 (\pm 0.2) \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$, A''K_{eq} = $(7.87 \pm 0.75) \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ (31.0°C, $I = 0.5 \text{ mol dm}^{-3}$), and e (80 nm) = $2,728 \pm 500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (e = A''/

Table 5. Infrared data of some sulphito complexes.

Complex	Frequency (cm ⁻¹)			
K ₆ [Pt(SO ₃) ₄]2H ₂ O ^a	1082, 1057	964	660	540
<i>Cis</i> -K ₂ [Pd(SO ₃) ₂ (NH ₃) ₂] ^a	1093, 1056	995, 977, 958, 831, 792, 771	655, 622	569, 522, 505
<i>Trans</i> -K ₂ [Pd(SO ₃) ₂ (NH ₃) ₂] ^a	1074	986, 958, 837, 812	646	525, 511
K ₃ [Rh(SO ₃) ₃ (NH ₃) ₃]3·5H ₂ O ^a	1107, 1056, 1017	954, 800	638	524
K ₃ [Rh(SO ₃) ₃]2H ₂ O ^a	1157, 1113, 1058	939	690, 647	527
K ₂ [Pd(SO ₃) ₂] ^a	1157, 1099, 1056	933, 904	664, 637	563, 516, 497
K ₂ [Pt(SO ₃) ₂]2H ₂ O ^a	1166, 1092, 1036	977		
[Co(NH ₃) ₅ (SO ₃)]Cl ^a	1110	985	633	519
[Co(NH ₃) ₅ (SO ₃)]Cl, H ₂ O ^b	1105	994, 985	640	525
[N ₃ Cr(<i>m</i> OH) ₂ (<i>m</i> OS(O)O)CrN ₃](ClO ₄) ₂ , 3H ₂ O ^c		974, 940, 912, 832, 866	640	
Na ₄ [(HO)(SO ₃)-Rh(<i>m</i> OH) ₂ (<i>m</i> OS(O)O) Rh(OH)(SO ₃)] ₂ , 6H ₂ O ^d	1175, 1121, 1067	957	689, 642	552, 523
Cu ₃ (<i>m</i> O-S(OH)O) ₂ (salpd) ₂ (OH ₂) ₂ ^e	1057, 1038	853	617	585

^aRef 11(b); ^bRef (33); ^cRef (31); ^dThis work; ^eRef (30)

[Rh³⁺]_T) for the O-sulphito complex. From kinetic data we obtained K_{eq} ($= k_1/k_{-1}$) as $(4 \pm 1) \times 10^3$ dm³ mol⁻¹. The agreement between the two sets of values is good considering the competing secondary reactions.

The equilibrium for the formation of the disulphito complex, Rh(OH₂)₃(O₂SO)(SO₃)⁻ (see scheme 3) was also studied at constant [Rh^{III}]_T and varying [S^{IV}]_T. The mixed solutions of appropriate compositions were equilibrated for ca. 10*t*_{1/2} as judged by the values of k_{obs}^s . The absorbance data (280 nm) of the equilibrium mixtures ($[S^{IV}]_T \gg \{[Rh^{III}]_T, I = 0.5 \text{ mol dm}^{-3}\}$) after correcting for the absorbance of S^{IV} (\ddot{A}_{obs}) were fitted to (12b), the linearized form of (12a) where K_{2eq} ($= k_4/k_{-4}$) is the equilibrium constant for the formation of the disulphito complex: Rh(OH₂)₄(O₂SO)⁺ + HSO₃⁻ ⇌ Rh(OH₂)₃(O₂SO)(SO₃)⁻ + H⁺ (K_{2eq}), A' and A'' denote the absorbances of Rh(OH₂)₄(O₂SO)⁺ and Rh(OH₂)₃(O₂SO)(SO₃)⁻ respectively for the same [Rh^{III}]_T.

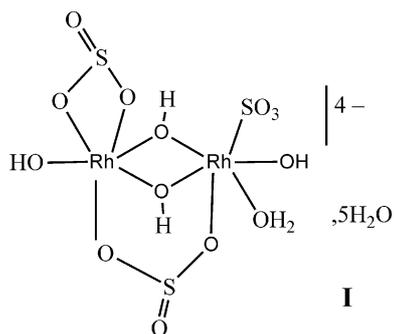
$$\ddot{A}_{obs} = \frac{(A' + A''K_{2eq}[\text{HSO}_3^-]/[\text{H}^+])}{(1 + K_{2eq}[\text{HSO}_3^-]/[\text{H}^+])}, \quad (12a)$$

$$(\ddot{A}_{obs} - A')^{-1} = (A'' - A')^{-1} + [(A'' - A')K_{2eq}]^{-1} X[\text{H}^+]/[\text{HSO}_3^-]. \quad (12b)$$

The relevant data are collected in table 4. The direct sulphite substitution rate constant (k_4) may be 10⁻⁵ dm³ mol⁻¹ s⁻¹ (31°C) based on which k_{-4} ($= k_4/K_{2eq}$) is ca. $\sim 2 \times 10^{-4}$ dm³ mol⁻¹ s⁻¹ supporting the validity of (7) under the experimental conditions (i.e. insignificant $k_{-4}[\text{H}^+]$ term, see scheme 3).

5. Nature of the sulphito complex, Na₄[Rh₂(OH)₄(SO₃)₃] 6H₂O and its reactions

This sulphito complex was isolated as an amorphous white solid, very slightly soluble in water and most organic and aquo-organic solvents. The IR spectrum of the complex is compared with those of several other sulphito complexes in table 5. The presence of water is indicated by strong bands at 3448 and 1637. Multiple bands at 1067–1175 (see table 5) are assigned to the asymmetric S=O stretching of the coordinated sulphite which is split due to the reduction of the local symmetry of the coordinated sulphite from C_{3v} (M-SO₃) to C_s (M-OSO₂ or M-O₂SO).^{11b} The IR spectrum of the complex shows some similarity with that of Na₃Rh(SO₃)₃,^{11b} [Cu₃(*m*OS(OH)-O)₂(salpd)₂(OH₂)₂]³⁰ and [N₃Cr(*m*OH)₂(*m*OS(O)OCrN₃)] (N₃ – a tridentate N-donor ligand)³¹ (see table 5); in the *tris*-sulphito rhodium complex (O, O) chelation by sulphite has been suggested while SO₃²⁻ and HSO₃⁻ act as (O, O) bridges between the metal centres in the latter two complexes. It is also worth noting that the IR spectrum of K₃[Rh(SO₃)₃(NH₃)₃] 3·5 H₂O (see table 5) which has S-bonded sulphite shows multiplets at 1017–1107 while that of *trans*-K₂[Pd(SO₃)₂(NH₃)₂] shows one band at 1074 cm⁻¹. The disodium *trans*-disulphitodiamminepalladate (II) hexahydrate has been structurally characterised³² to have Pd-S coordination and Co-S bond exists in (NH₃)₅CoSO₃⁺ (ref 33). We are led to believe that the rhodium (III)-sulphite complex which we report has both mono dentate S- and (O, O) chelated sulphite and a bridging (*m*OS(O)O) sulphite (tentative struc-



ture **I**). The kinetic results discussed earlier are in favour of the proposed bonding modes of sulphite (O, O chelation and S-coordination).

The *m*O, O sulphite bridge for the Cr(III) complex reported by Maragh *et al.*³¹ has exceptional stability towards acid catalysed aquation in preference to the hydroxo-bridge cleavage. Our complex was also very stable to decomposition in strongly acidic medium. A preliminary spectrophotometric measurements (280 nm, initial rate method) of the acid induced decomposition of this complex in 1 mol dm⁻³ HClO₄ yielded $k = 5 \times 10^{-6} \text{ s}^{-1}$ at 50°C.

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