

## Kinetics of Substitution and Redox Reactions of the $\text{Rh}_2(\text{OOCCH}_3)_4^+$ Complex with Chloride and Bromide Ions<sup>1</sup>

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The title reactions were studied by the stopped-flow method. Rate constants  $k_1^X$  and  $k_{-1}^X$  for forward and reverse reactions  $\text{Rh}_2(\text{OAc})_4^+ + \text{X}^- \rightleftharpoons \text{Rh}_2(\text{OAc})_4\text{X}$  at 5 and 25 °C,  $I = 1.0 \text{ M}$  ( $\text{HClO}_4$ ), are  $k_1^{\text{Cl}^-} = (2.3 \pm 0.6) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  and  $(4.7 \pm 1.6) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{-1}^{\text{Cl}^-} = 14 \pm 6 \text{ s}^{-1}$  and  $60 \pm 14 \text{ s}^{-1}$ ,  $k_1^{\text{Br}^-} = (6.8 \pm 0.8) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  and  $(16.4 \pm 0.5) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , and  $k_{-1}^{\text{Br}^-} = 6 \pm 2 \text{ s}^{-1}$  and  $18 \pm 3 \text{ s}^{-1}$ . Reduction of  $\text{Rh}_2(\text{OAc})_4^+$  by  $\text{Br}^-$  involves the equilibrium  $\text{Rh}_2(\text{OAc})_4\text{Br} + \text{Br}^- \rightleftharpoons \text{Rh}_2(\text{OAc})_4\text{Br}_2^-$  with  $K_2^{\text{Br}^-} = 150 \text{ M}^{-1}$  (25 °C). For the reaction  $\text{Rh}_2(\text{OAc})_4\text{Br}_2^- \rightarrow \text{Rh}_2(\text{OAc})_4 + \frac{1}{2} \text{Br}_2 + \text{Br}^-$ ,  $k = 600 \text{ s}^{-1}$  (25 °C). For the oxidation of  $\text{Rh}_2(\text{OAc})_4$  by  $\text{Cl}_2$ , the rate expression is  $k[\text{Rh}_2(\text{OAc})_4][\text{Cl}_2]$ , with  $k = 120 \text{ M}^{-1} \text{ s}^{-1}$  (25 °C). The intermediate  $\text{Rh}_2(\text{OAc})_4\text{Br}$  was detected by means of a rapid-scanning stopped-flow spectrophotometer.

### Introduction

The binuclear, metal-metal-bonded<sup>2</sup> complex  $\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2$  may be oxidized easily and reversibly in solution to give the ion  $\text{Rh}_2(\text{OAc})_4^+(\text{aq})$ .<sup>3-5</sup> Solid compounds have been isolated,<sup>3,4</sup> and infrared spectroscopic evidence indicates that the tetrakis( $\mu$ -acetato) framework and the metal-metal bond remain intact. The valencies of the rhodium atoms, of average oxidation state 2.5, are indistinguishable on the time scale of metal-ligand vibrations;<sup>4</sup> hence the oxidized complex belongs to class III in the Robin and Day terminology for mixed-valence compounds.<sup>6</sup>

Both the dirhodium(II) and the mixed-valence complexes form adducts with Lewis bases. The donor groups are axially coordinated to the Rh atoms as shown, in the case of the dihydrates, by X-ray crystallography,<sup>2,7,8</sup> and in the case of other donors, by the variation of the lowest energy d-d transition according to the spectrochemical series.<sup>4,9</sup> The uncomplexed ion in aqueous solution is therefore presumably the adduct  $\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2^+$ .

In this paper we report the kinetics of reactions of  $\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2^+$  with halide ions, including rates of anation and of redox reactions, and of the oxidation of  $\text{Rh}_2(\text{OAc})_4$  by  $\text{Cl}_2$ . The experiments include detection of the short-lived mixed-valence bromide adducts by means of a rapid-scanning stopped-flow spectrophotometer.

### Experimental Section

**Equipment.** Kinetic measurements at single wavelengths were made with an Aminco-Morrow stopped-flow spectrometer, with improved thermostating arrangements as described previously.<sup>10</sup> Rapid-scanning measurements were made with the Multiplex stopped-flow spectrophotometer (Applied Photophysics, London). This consists of a

conventional stopped-flow apparatus, with modified optics and signal output. White light from a 100-W quartz-iodine lamp is passed through slits and then through the mixing chamber to a diffraction grating, (f4, blazed at 500 nm), and the dispersed light is received by a linear array of 30 photodiodes. With appropriate scanning circuitry, the signal is taken from each diode in turn and displayed on a storage oscilloscope, thus showing a spectrum consisting of 30 horizontal steps, at 10-nm intervals. By rotation of the grating, any 300-nm range, within the limits 400-1000 nm, can be covered. The total time for observation of the spectrum is  $10^{-4}$  s, and scans can be repeated at any preset time interval from 0.5 ms to 5 s. Photometric accuracy is estimated to be  $\pm 2\%$ .

**Tetrakis( $\mu$ -acetato)-dirhodium(II).** The dimethanol adduct was prepared by the method of Legzdins et al.<sup>11</sup> and heated in a vacuum oven at 55 °C for 20 h to remove all methanol. Anal. Calcd for  $\text{C}_8\text{H}_{12}\text{O}_8\text{Rh}_2$ : C, 21.72; H, 2.71. Found: C, 21.14; H, 2.87 (average of 4 samples).

**Tetrakis( $\mu$ -acetato)-dirhodium(1+) Ion.** A suspension of tetrakis( $\mu$ -acetato)dirhodium(II) (0.21 g) in 1 M perchloric acid (95 mL) was oxidized at a platinum gauze anode, with vigorous stirring and ice cooling. The solution was stored frozen until required.

Alternatively, tetrakis( $\mu$ -acetato)-dirhodium(II) (0.044 g) was dissolved in water (20 mL), and chlorine gas was bubbled through for about 15 min. Excess chlorine was removed by bubbling nitrogen. The brown solution was passed down a column of Amberlite IRA-400 (analytical grade, 14-52 mesh,  $\text{ClO}_4^-$  form (prepared from the  $\text{Cl}^-$  form by using 1 M  $\text{HClO}_4$ )). The flesh pink solution so obtained was passed through a Dowex 50W-X8 ( $\text{H}^+$  form, standard grade, 18-52 mesh). Residual green  $\text{Rh}_2(\text{OAc})_4$  was eluted with water, and then flesh pink  $\text{Rh}_2(\text{OAc})_4^+$  ion was eluted with 1 M perchloric acid.

The spectra of solutions obtained in this way were identical with each other and with that of the product of oxidation of  $\text{Rh}_2(\text{OAc})_4$  with cerium(IV). Solutions slowly decomposed on standing (more rapidly if any attempt was made to reduce the acidity), regenerating the green rhodium(II) complex, but they could be stored indefinitely when frozen. For most work, electrolytically prepared solutions were used. Stock solutions of chlorine were prepared by bubbling gaseous chlorine gas into 1.0 M  $\text{HClO}_4$  and analyzed iodimetrically.

### Results

**Anation Reaction  $\text{Rh}_2(\text{OAc})_4^+ + \text{Cl}^-$ .** On mixing of solutions of  $\text{Rh}_2(\text{OAc})_4^+$  and chloride ion the color changes immediately from flesh pink to brown. Spectrophotometric measurements show evidence of at least two successive equilibria. In the range  $[\text{Cl}^-] = 0-0.03 \text{ M}$ , the point of maximum absorbance change is at  $\lambda \approx 425 \text{ nm}$ , but from  $[\text{Cl}^-] = 0.03$  to 1.0 M the maximum shifts to ca. 390 nm. The band initially at 517 nm moves steadily to longer wavelengths through both concentration ranges. The complexes are assumed to be  $\text{Rh}_2(\text{OAc})_4\text{Cl}$  and  $\text{Rh}_2(\text{OAc})_4\text{Cl}_2^-$ . In order to avoid complications due to the latter, we kept the chloride concentration as low

- (1) (a) Taken from the M.Sc. and Ph.D. theses of K. Sarawek, University of East Anglia, 1974 and 1976. (b) Presented in part at the meeting of the Inorganic Mechanisms Group of the Chemical Society, Leicester, England, Dec 1976.
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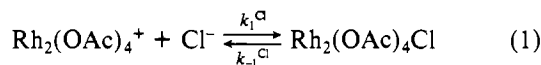
**Table I.** Kinetic Data for the Reactions  $\text{Rh}_2(\text{OAc})_4^+ + \text{Cl}^- \rightleftharpoons \text{Rh}_2(\text{OAc})_4\text{Cl}^a$ 

$10^3 a, ^b \text{ M}$	$10^3 b, ^c \text{ M}$	$k_{\text{obsd}}^0, \text{ s}^{-1}$	
		5 °C	25 °C
7.0	3.5	40.8	89
6.0	3.0	38.5	111
5.0	2.5	37.5	92
4.0	2.0	32.2	87
3.0	1.5	26.2	89
2.0	1.0	22.4	71
6.0	6.0	34.7	111
5.0	5.0	29.5	111
4.0	4.0	27.7	92
3.5	3.5	27.2	99
2.67	2.67	20.4	92
2.0	2.0	22.0	68
1.5	1.5	18.7	68
Anation Reactions			
2.5	2.5	21.0	
2.0	2.0	20.7	
3.5	3.5	19.8	

<sup>a</sup>  $\lambda = 415 \text{ nm}$ ,  $I = 1.0 \text{ M}$  ( $\text{HClO}_4$ ). The data in columns 1 and 2 are concentrations of the reagents in the mixing vessel, immediately after mixing. In the anation experiments the reagents were initially in separate syringes. In the aquation experiments they were initially in the same syringe, with 1 M  $\text{HClO}_4$  in the other syringe.

<sup>b</sup>  $a = [\text{Rh}_2(\text{OAc})_4^+]_{\text{T}}$ . <sup>c</sup>  $b = [\text{Cl}^-]_{\text{T}}$ .

as possible ( $[\text{Cl}^-] \leq 6 \text{ mM}$ ), while to maximize the absorbance change, we chose the rhodium dimer concentrations greater than or equal to the chloride concentration. Under these conditions, reaction 1 is reversible, and some reactions were



in fact run in reverse: a solution containing equal concentrations of  $\text{Rh}_2(\text{OAc})_4^+$  and  $\text{Cl}^-$  ion was mixed in the stopped-flow apparatus with a solution of 1 M  $\text{HClO}_4$  and thus diluted by a factor of 2.

In both directions, with low reagent concentrations, first-order kinetics were observed (eq 2, where  $A$  and  $A_\infty$  denote

$$-dA/dt = k_{\text{obsd}}(A - A_\infty) \quad (2)$$

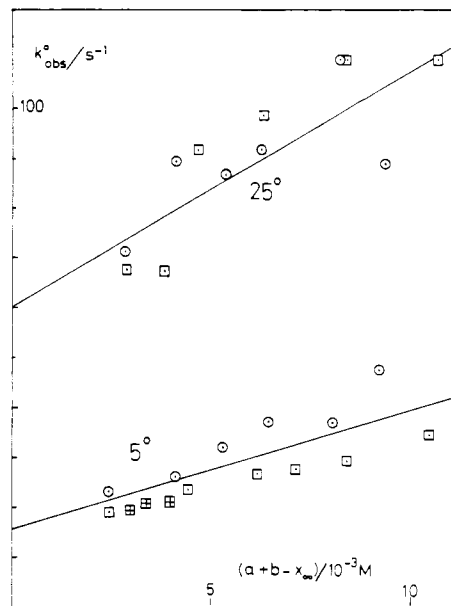
absorbances at time  $t$  and at equilibrium). For the anation reactions at higher concentrations, the plots of  $\log(A - A_\infty)$  against time were curved, consistent with second-order kinetics. Limiting specific rates  $k_{\text{obsd}}^0$  were obtained as the slopes of the logarithmic plots at time  $t = 0$ . Data are listed in Table I. Values of  $k_{\text{obsd}}$  (or  $k_{\text{obsd}}^0$ ) for the anation reactions were fitted to eq 3a and values for the aquation reactions were fitted

$$k_{\text{obsd}}^0 = k_{-1} + k_1(a + b - x_\infty) \quad (3a)$$

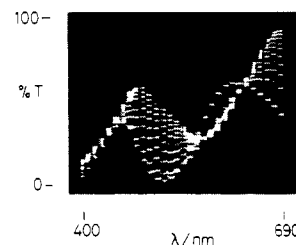
$$k_{\text{obsd}}^0 = k_{-1} + k_1(a + b - x_0 - x_\infty) \quad (3b)$$

to eq 3b, where  $a$  and  $b$  are total concentrations of rhodium dimer and chloride,  $x_\infty$  is the final concentration of  $\text{Rh}_2(\text{OAc})_4\text{Cl}$ , and  $x_0$  is the initial concentration of  $\text{Rh}_2(\text{OAc})_4\text{Cl}$ .

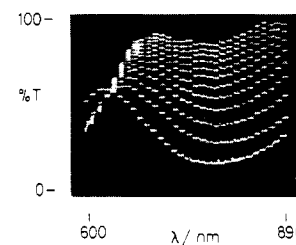
As a first approximation, values of  $k_{\text{obsd}}^0$  were plotted against  $(a + b)$ , to obtain the slope  $k_1$  and intercept  $k_{-1}$  at  $[\text{Cl}^-] \rightarrow 0 \text{ M}$ . From these values,  $K_1$  was calculated, whence the equilibrium concentrations  $x_0$  and  $x_\infty$  were obtained for each experiment, and the graphs were redrawn as plots of  $k_{\text{obsd}}^0$  against  $(a + b - x_0 - x_\infty)$  to obtain a second pair of values of  $k_1$  and  $k_{-1}$  (Figure 1). These were respectively greater and less than the first approximations, but a second recalculation made no further difference. The results are shown in Table V. Limits of error are twice the standard error of estimate of the ordinate (for  $k_{-1}$ ) and twice the standard error of estimate of the slope (for  $k_1$ ).<sup>12</sup>



**Figure 1.** Kinetic data for the reactions  $\text{Rh}_2(\text{OAc})_4^+ + \text{Cl}^- \rightleftharpoons \text{Rh}_2(\text{OAc})_4\text{Cl}$ :  $\circ$ ,  $a = [\text{Rh}_2(\text{OAc})_4^+]_{\text{T}} = 2b = 2[\text{Cl}^-]_{\text{T}}$ ;  $\square$  and  $\blacksquare$ ,  $a = b_0$ . Points  $\circ$  and  $\square$  represent reactions run in the forward direction,  $x_0 = 0$ ; points  $\blacksquare$  represent reactions run in the reverse direction.  $[\text{H}^+] = 1.0 \text{ M}$ ,  $I = 1.0 \text{ M}$  ( $\text{ClO}_4^-$ ), temperatures are as shown, and  $\lambda = 415 \text{ nm}$ .



**Figure 2.** Visible spectra of the system  $\text{Rh}_2(\text{OAc})_4^+ + \text{Br}^-$  as a function of time. Each spectrum consists of 30 horizontal lines at intervals of 10 nm. The time between the first and last reading of a single spectrum is 0.1 ms; the delay time between successive spectra is 5 s ( $[\text{H}^+] = 1.0 \text{ M}$ ,  $[\text{Br}^-]_{\text{T}} = 0.1 \text{ M}$ , room temperature, path length = 1 cm).



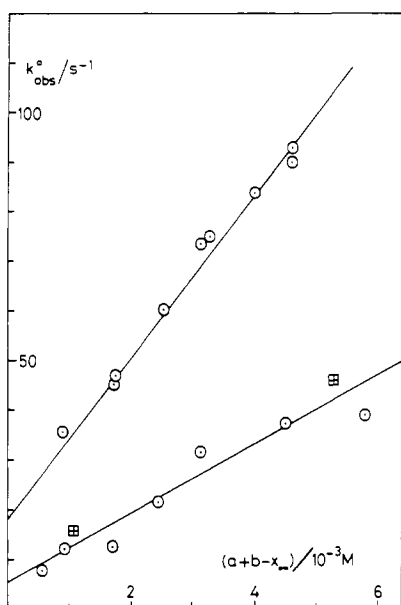
**Figure 3.** Visible-near-IR spectra of the same system as in Figure 2, under the same conditions.

**Anation Reaction  $\text{Rh}_2(\text{OAc})_4^+ + \text{Br}^-$ .** On mixing of solutions of  $\text{Rh}_2(\text{OAc})_4^+$  and bromide ion, two color changes are observed in succession: a rapid change from flesh pink to blood red and then a slower fading to apple green. The final spectrum is the same as that of  $\text{Rh}_2(\text{OAc})_4$  in the same bromide medium. With the aid of the Multiplex stopped-flow rapid-scanning device, the evolution of the whole of the visible and near-infrared spectrum was monitored (Figures 2 and 3). The first stage is characterised by isosbestic points ca. 570 and 630 nm and the second by an almost isosbestic region, from

**Table II.** Kinetic Data for the Reaction  $\text{Rh}_2(\text{OAc})_4^+ + \text{Br}^- \rightarrow \text{Rh}_2(\text{OAc})_4\text{Br}^a$ 

		$k_{\text{obsd}}^o, \text{s}^{-1}$	
$10^3 a, ^b \text{ M}$	$10^3 b, ^c \text{ M}$	5 °C	25 °C
0.3	0.3	7.7	
0.5	0.5	12.4	35.9
1.0	1.0	12.6	46.2
1.0	1.0		45.6
1.5	1.5	21.7	60.3
2.0	2.0	31.5	74.9
2.0	2.0		74.9
2.5	2.5		84.0
3.0	3.0	37.5	92.4
3.0	3.0		90.0
4.0	4.0	39.6	
1.0	0.1	15.8	
5.0	1.0	46.2	

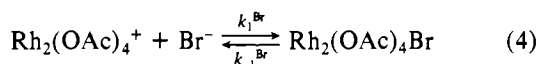
<sup>a</sup>  $\lambda = 525 \text{ nm}$ ,  $I = 1.0 \text{ M}$  ( $\text{HClO}_4$ ). <sup>b</sup>  $a = [\text{Rh}_2(\text{OAc})_4^+]_{\text{T}}$ . <sup>c</sup>  $b = [\text{Br}^-]_{\text{T}}$ .



**Figure 4.** Kinetic data for the reaction  $\text{Rh}_2(\text{OAc})_4^+ + \text{Br}^- = \text{Rh}_2(\text{OAc})_4\text{Br}$ :  $\blacksquare$ ,  $a = [\text{Rh}_2(\text{OAc})_4^+] > b = [\text{Br}^-]_{\text{T}}$  (5 or 10 times);  $\circ$ ,  $a = b$ .  $[\text{H}^+] = 1.0 \text{ M}$ ,  $I = 1.0 \text{ M}$  ( $\text{ClO}_4^-$ ), temperatures are as in Figure 1, and  $\lambda = 525 \text{ nm}$ .

590 to 650 nm. The spectrum of the intermediate has absorption maxima at 520–530 and 790–800 nm. The intermediate is evidently a bromide adduct of  $\text{Rh}_2(\text{OAc})_4^+$ , the first reaction stage being the anation reaction and the second stage a redox reaction.

For the study of the kinetics, low concentrations of bromide were chosen, with  $[\text{Rh}_2(\text{OAc})_4^+] \geq \text{Br}^-$  to favor the mono-adduct (eq 4). Data are listed in Table II. Plots of  $k_{\text{obsd}}$



against  $(a + b - x_{\infty})$ , where  $b = [\text{Br}^-]_{\text{T}}$ , were constructed as in the chloride case (Figure 4). Values of  $k_1^{\text{Br}}$ ,  $k_{-1}^{\text{Br}}$ , and  $K_1^{\text{Br}}$  are listed in Table V.

**Redox Reaction  $\text{Rh}_2(\text{OAc})_4^+ + \text{Br}^- = \text{Rh}_2(\text{OAc})_4 + \frac{1}{2}\text{Br}_2$ .** In this study,  $[\text{Br}^-]$  concentrations ranged from 40 to 50 mM. Good first-order kinetics were observed (eq 2). Values of  $k_{\text{obsd}}$  are listed in Table III. The plot of  $k_{\text{obsd}}$  against  $[\text{Br}^-]$  is markedly nonlinear, suggesting saturation of an equilibrium. From the values of  $K_1^{\text{Br}}$  obtained above, we know that the equilibrium 4 is already largely saturated at the lowest bromide

**Table III.** Kinetic Data for the Reaction  $\text{Rh}_2(\text{OAc})_4^+ + \text{Br}^- = \text{Rh}_2(\text{OAc})_4 + \frac{1}{2}\text{Br}_2^a$ 

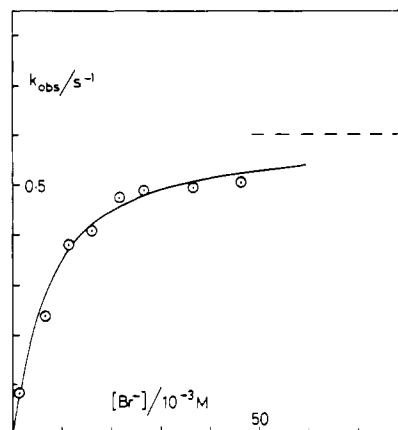
$10^3 [\text{Br}^-]_{\text{T}}, \text{ M}$	$10^3 [\text{Br}^-], ^b \text{ M}$	$k_{\text{obsd}}, \text{ s}^{-1}$
4	1.2	0.081
10	6.6	0.239
15	11.4	0.381
20	16.3	0.408
25	21.2	0.447
30	26.3	0.488
40	36.3	0.495
50	46.3	0.502

<sup>a</sup>  $\lambda = 525 \text{ nm}$ ,  $T = 25 \text{ }^\circ\text{C}$ ,  $I = 1.0 \text{ M}$  ( $\text{HClO}_4$ ). <sup>b</sup> Calculated value of  $[\text{Br}^-]_{\text{T}} - [\text{Rh}_2(\text{OAc})_4\text{Br}]$  are obtained by using  $K_1^{\text{Br}} = 900 \text{ M}^{-1}$ .

**Table IV.** Kinetic Data for the Reaction  $\text{Rh}_2(\text{OAc})_4 + \frac{1}{2}\text{Cl}_2 \rightarrow \text{Rh}_2(\text{OAc})_4^+ + \text{Cl}^-^a$ 

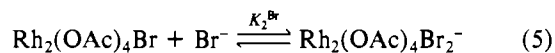
$10^3 \times [\text{Rh}_2(\text{OAc})_4]_0, \text{ M}$	$10^3 [\text{Cl}_2]_0, \text{ M}$	$10^3 [\text{Cl}^-]_0, \text{ M}$	$10^3 k_{\text{obsd}}, \text{ s}^{-1}$
0.315	6.67	0	1.18
0.315	13.3	0	2.06
0.315	20.0	0	2.26
0.315	26.7	0	3.30
0.315	33.3	0	4.12
0.315	38.1	0	4.50
0.163	33.3	0	4.07
0.163	36.1	0	3.96
0.157	3.33	33	0.99
0.157	6.77	33	1.08
0.157	10.0	33	1.80
0.157	13.3	33	1.52
0.157	16.7	33	1.54
0.163	30.0	33	5.10
0.163	33.3	33	2.89
0.350	26.7	0	3.15 <sup>b</sup>

<sup>a</sup>  $\lambda = 395 \text{ nm}$ ,  $[\text{H}^+] = 1.0 \text{ M}$ , counterion  $\text{ClO}_4^-$ . <sup>b</sup>  $[\text{H}^+] = 0.1 \text{ M}$ ,  $[\text{Li}^+] = 0.9 \text{ M}$ .



**Figure 5.** Kinetic data for the reaction  $\text{Rh}_2(\text{OAc})_4^+ + \text{Br}^- \rightarrow \text{Rh}_2(\text{OAc})_4 + \frac{1}{2}\text{Br}_2$ . Values of  $[\text{Br}^-]$  calculated with allowance for equilibrium 5, by using  $K_1^{\text{Br}} = 900 \text{ M}^{-1}$  ( $T = 25 \text{ }^\circ\text{C}$ ,  $[\text{H}^+] = 1.0 \text{ M}$ ,  $I = 1.0 \text{ M}$  ( $\text{ClO}_4^-$ ),  $\lambda = 525 \text{ nm}$ ). The curve is calculated from eq 6, by using  $K_2^{\text{Br}} = 150 \text{ M}^{-1}$  and  $k = 0.60 \text{ s}^{-1}$ .

concentrations used; hence we attribute the curvature to the second successive equilibrium (5). The data fit well to eq 6



$$k_{\text{obsd}} = \frac{kK_2^{\text{Br}}[\text{Br}^-]}{1 + K_2^{\text{Br}}[\text{Br}^-]} \quad (6)$$

with  $k = 0.60 \text{ s}^{-1}$  and  $K_2^{\text{Br}} = 150 \text{ M}^{-1}$  (Figure 5). Here  $[\text{Br}^-]$  denotes the concentration of bromide ion corrected for the

Table V. Summary of Rate and Equilibrium Constants<sup>a</sup>

reaction	$10^{-3}k, {}^b \text{M}^{-1} \text{s}^{-1}$		$k, {}^c \text{s}^{-1}$		$\log(K/\text{M}^{-1})$	
	5 °C	25 °C	5 °C	25 °C	5 °C	25 °C
$\text{Rh}_2(\text{OAc})_4^+ + \text{Cl}^- \rightleftharpoons \text{Rh}_2(\text{OAc})_4\text{Cl}$	$2.3 \pm 0.6$	$4.7 \pm 1.6$	$14 \pm 6$	$60 \pm 14$	$2.0 \pm 0.3$	$1.9 \pm 0.2$
$\text{Rh}_2(\text{OAc})_4^+ + \text{Br}^- \rightleftharpoons \text{Rh}_2(\text{OAc})_4\text{Br}$	$6.8 \pm 0.8$	$16.4 \pm 0.5$	$6 \pm 2$	$18 \pm 3$	$3.05 \pm 0.1$	$2.95 \pm 0.5$
$\text{Rh}_2(\text{OAc})_4\text{Br} + \text{Br}^- \rightleftharpoons \text{Rh}_2(\text{OAc})_4\text{Br}_2^-$						2.17
$\text{Rh}_2(\text{OAc})_4\text{Br}_2^- \rightarrow \text{Rh}_2(\text{OAc})_4 + \text{Br}_2^-$		0.60				
$\text{Rh}_2(\text{OAc})_4^+ + \text{Cl}_2 \rightleftharpoons \text{Rh}_2(\text{OAc})_4 + \text{Cl}_2$				0.12		

<sup>a</sup>  $I = 1.0 \text{ M}$  ( $\text{HClO}_4$ ). <sup>b</sup> Forward. <sup>c</sup> Reverse.

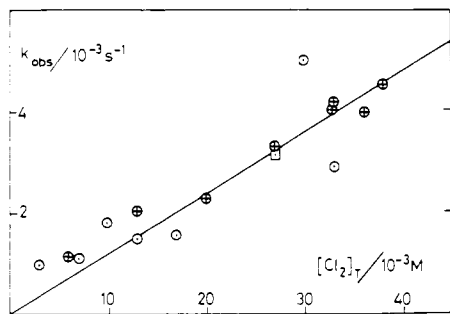
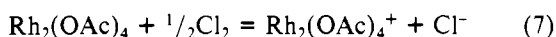


Figure 6. Kinetic data for the reaction  $\text{Rh}_2(\text{OAc})_4 + \frac{1}{2}\text{Cl}_2 \rightarrow \text{Rh}_2(\text{OAc})_4\text{Cl} + \text{Cl}^-$ :  $\bullet$ ,  $[\text{Cl}^-] = 0$  initially;  $\circ$ ,  $[\text{Cl}^-]_T = 33 \text{ mM}$  initially ( $[\text{H}^+] = 1.0 \text{ M}$ ,  $I = 1.0 \text{ M}$  ( $\text{ClO}_4^-$ ));  $\square$ ,  $[\text{Cl}^-] = 0$  initially ( $[\text{H}^+] = 0.1 \text{ M}$ ,  $I = 1.0 \text{ M}$  ( $\text{LiClO}_4$ ),  $T = 25^\circ\text{C}$ ,  $\lambda = 385 \text{ nm}$ ).

effects of equilibrium 4, i.e.,  $[\text{Br}^-] = [\text{Br}^-]_T - [\text{Rh}_2(\text{OAc})_4\text{Br}]$ . A further correction for the effect of equilibrium 5 made no significant difference to the results.

**Redox Reaction  $\text{Rh}_2(\text{OAc})_4 + \text{Cl}_2$ .** This reaction is rapid in solution, but the rate was found to be measurable by the stopped-flow method. For the main series of experiments, concentration ranges were 0.16–0.35 mM for  $[\text{Rh}_2(\text{OAc})_4]_T$  and 6–38 mM for  $[\text{Cl}_2]$ . Although the brown color of  $\text{Rh}_2(\text{OAc})_4\text{Cl}$  is noticeable in the final solution, the concentration of chloride ion produced is small enough for the stoichiometry to be eq 7. Good pseudo-first-order kinetics were obtained



(eq 2), and a first-order dependence on  $[\text{Cl}_2]$  was found (see Figure 6; data are listed in Table IV). Experiments with excess chloride ion gave rather scattered results but no significant difference in rate. Varying the acid concentration (one run) also had no effect; hence the rate law may be summarized as eq 8 with  $k = 0.12 \text{ M}^{-1} \text{ s}^{-1}$ ,  $25^\circ\text{C}$ ,  $I = 1.0 \text{ M}$  ( $\text{HClO}_4$ ).

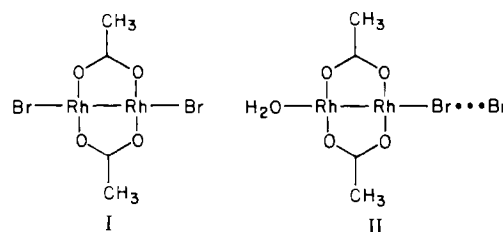
$$-d[\text{Rh}_2(\text{OAc})_4]/dt = k[\text{Rh}_2(\text{OAc})_4][\text{Cl}_2][\text{Cl}^-]^0[\text{H}^+]^0 \quad (8)$$

## Discussion

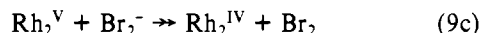
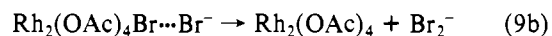
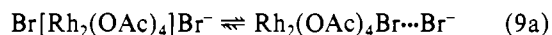
The anation and aquation rate data for the  $\text{Rh}_2(\text{OAc})_4^+$  complexes are, as far as we know, the first to be reported for ligand replacements in a symmetrical, class III,<sup>6</sup> mixed-valence complex. The corresponding rates of formation of rhodium(II) adducts are faster than these (outside the stopped-flow time range),<sup>13</sup> while reactions of rhodium(III) are well-known to be much slower. It seems likely that, in general, substitution reactions of class III mixed-valence compounds will be found to be intermediate between those of the corresponding oxidized and reduced species. It is of interest that the order of aquation rates and the order of anation rates both parallel the order of the equilibrium constants for the reactions concerned; i.e.,  $k_1^{\text{Br}} > k_1^{\text{Cl}}$  and  $k_{-1}^{\text{Br}} < k_{-1}^{\text{Cl}}$ . Data of this kind are usually cited in favor of an interchange as opposed to a mainly dissociative

or associative mechanism,<sup>15</sup> but extension to more systems is required before a discussion of this point becomes worthwhile. The low rates of anation do, however, confirm that in aqueous solution the  $\text{Rh}_2(\text{OAc})_4^+$  ion has axial water molecules and that these are more strongly bound than those of the  $\text{Rh}_2(\text{OAc})_4(\text{OH}_2)_2$  molecule.

There can be no doubt that the species  $\text{Rh}_2(\text{OAc})_4\text{Br}_2^-$  implied by eq 6 is predominantly in form I (where for clarity,



two of the bridging acetate ions are omitted). We propose, however, that the transition state for the redox reaction has form II and that the overall mechanism is as shown in eq 9a–c



in which the second step is rate determining and  $\text{Rh}_2^{\text{V}}$  denotes one or more of the complexes  $\text{Rh}_2(\text{OAc})_4\text{Br}_i^{(1-i)+}$ . This is in line with previously proposed mechanisms of oxidation of  $\text{Br}^-$  by one-electron oxidizing metal complexes. A variety of different rate laws have been reported, reflecting the differing coordination chemistry of the oxidants, but in most cases the radical ion  $\text{Br}_2^-$  is postulated as the primary product of the redox step. With  $\text{Ce}^{4+}$ <sup>16</sup> and  $\text{Mn}^{3+}$ <sup>17</sup>, rates are second order in  $\text{Br}^-$  ion, consistent with a labile equilibrium  $\text{M}^{n+} + \text{Br}^- \rightleftharpoons \text{MBr}^{(n-1)+}$  preceding the step  $\text{MBr}^{(n-1)+} + \text{Br}^-$ .<sup>18</sup> With  $\text{VO}_2^+$  as oxidant, a third-order bromide dependence<sup>19</sup> is similarly interpreted in terms of  $\text{VOBr}_2^+ + \text{Br}^- \rightarrow \text{VOBr}^+ + \text{Br}_2^-$ .<sup>20</sup> With  $\text{Co}^{3+}(\text{aq})$ <sup>21</sup> and *cis*- $\text{Co}(\text{NH}_3)_2^{3+}(\text{aq})$ ,<sup>22</sup> the bromide dependence is first order, and most authors agree in postulating the rate-determining step  $\text{Co}^{3+} + \text{Br}^- \rightarrow \text{Co}^{\text{III}}\text{Br}^{2+}$ , followed by rapid electron transfer  $\text{Co}^{\text{III}}\text{Br}^{2+} + \text{Br}^- \rightarrow \text{Co}^{2+} + \text{Br}_2^-$ .<sup>23</sup> In short, wherever an inner-sphere mechanism is possible, the main reaction path involves electron transfer in the directly bonded  $\text{M}^{n+}\text{-Br}$  unit, assisted by a second bromide ion. The

(15) A similar conclusion applies to the rates of formation and dissociation of amine adducts of  $\text{Rh}_2(\text{OAc})_4$ .<sup>14</sup>

(16) C. F. Wells and A. F. M. Nazer, *J. Chem. Soc., Faraday Trans. 1*, **75**, 816 (1979).

(17) C. F. Wells and D. Mays, *J. Chem. Soc. A*, 577 (1968).

(18) A term first order in  $\text{Br}^-$  is found at low  $\text{Br}^-$  concentrations,<sup>17</sup> interpreted as  $\text{MnBr}^{2+} \rightarrow \text{Mn}^{2+} + \text{Br}$ .

(19) K. Julian and W. A. Waters, *J. Chem. Soc.*, 818 (1962).

(20) The authors of ref 19 write these formulas with  $(\text{OH})_2$  in place of O.

(21) (a) M. N. Malik, J. Hill, and A. McAuley, *J. Chem. Soc. A*, 643 (1970); (b) G. Davies and K. O. Watkins, *J. Phys. Chem.*, **74**, 3388 (1970); (c) B. Šrámková, J. Zýka, and J. Doležal, *J. Electroanal. Chem.*, **30**, 177 (1971); (d) C. F. Wells, A. F. M. Nazer, and D. Mays, *J. Inorg. Nucl. Chem.*, **39**, 2001 (1977).

(22) I. Bodek, G. Davies, and J. H. Ferguson, *Inorg. Chem.*, **14**, 1708 (1975).

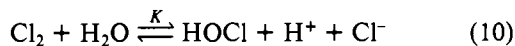
(23) Wells and co-workers<sup>21d</sup> dispute this interpretation and prefer to write the rate-determining step as  $\text{Co}^{\text{III}}\text{Br}^{2+} \rightarrow \text{Co}^{2+} + \text{Br}$ .

(13) By a temperature-jump method, rates of formation and dissociation of several amine adducts of  $\text{Rh}_2(\text{OAc})_4$  have been observed and the rates of water loss from  $\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2$  in aqueous solutions are concluded to be very high.<sup>14</sup>

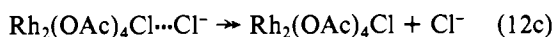
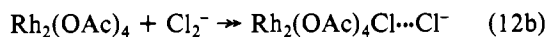
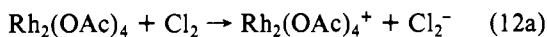
(14) K. Das, E. L. Simmons, and J. L. Bear, *Inorg. Chem.*, **16**, 1268 (1977).

reaction  $\text{Ni}(\text{bpy})_3^{3+} + \text{Br}^-$  is believed to be outer sphere.<sup>24</sup>

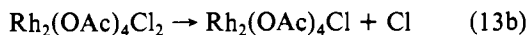
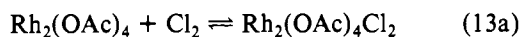
The oxidation of  $\text{Rh}_2(\text{OAc})_4$  by  $\text{Cl}_2$  also requires two halogen atoms in the transition state. Under the conditions of our experiments, hydrolysis of chlorine is slight and hypochlorous acid is undissociated (eq 10 and 11) ( $\log K = -3.4$ ,



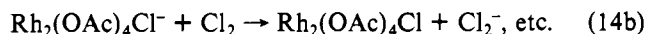
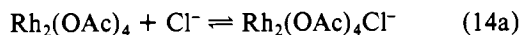
$\text{p}K_a = 7.5$ ).<sup>25</sup> Hence the lack of hydrogen ion or chloride dependence in the rate expression, eq 8, shows that neither HOCl nor  $\text{OCl}^-$  are effective oxidants, in comparison with  $\text{Cl}_2$ . A mechanism consistent with the rate law is shown in eq 12a-c



which is analogous to reactions 9a-c, in reverse, except that the first and not the middle step is rate determining. Step 12a could be written in other ways, including an inner-sphere process giving the mechanism as in eq 13a-c. It should be



noted, however, that one inner-sphere mechanism (eq 14a, b)



which might have been expected is definitely excluded by our data. At low chloride concentrations this sequence would require a first-order dependence on chloride concentration, which is not observed.

#### Appendix

For the mechanisms, eq 1 or 4, the rate of the forward reaction is given by

$$dx/dt = k_1(a-x)(b-x) - k_{-1}x \quad (A1)$$

where  $x$  is the concentration of  $\text{Rh}_2(\text{OAc})_4\text{X}$  at time  $t$  and  $a$  and  $b$  are the initial concentrations of  $\text{Rh}_2(\text{OAc})_4^+$  and  $\text{X}^-$  ( $\text{X} = \text{Cl}, \text{Br}$ ). At equilibrium

$$k_1(a-x_\infty)(b-x_\infty) - k_{-1}x_\infty = 0 \quad (A2)$$

whence

$$dx/dt = k_1(a+b)(x-x_\infty) + k_1(x^2-x_\infty^2) - k_{-1}(x-x_\infty) \quad (A3)$$

and

$$k_{\text{obsd}} = -(x-x_\infty)^{-1}dx/dt = k_1[(a+b) - (x+x_\infty)] + k_{-1} \quad (A4)$$

For a small extent of reaction the term  $(x+x_\infty)$  may be neglected. Equation 3a of the text is obtained by setting  $x = 0$  and retaining  $x_\infty$ . The latter is given by eq A5 or approximately, when  $x_\infty \ll (ab)^{1/2}$ , eq A6.

$$x_\infty = \frac{1}{2}\{(a+b+K_1^{-1}) - [(a+b+K_1^{-1})^2 - 4ab]^{1/2}\} \quad (A5)$$

$$x_\infty \simeq ab/(a+b+K_1^{-1}) \quad (A6)$$

For the case of a reaction run in reverse, let  $x_0$  be the initial concentration of  $\text{Rh}_2(\text{OAc})_4\text{X}$ , and let  $a$  and  $b$  be the total concentrations of rhodium dimer and chloride ion, so that at time  $t = 0$ ,  $[\text{Rh}_2(\text{OAc})_4]^+ = a - x_0$  and  $[\text{X}^-] = b - x_0$ . As before,  $x$  is the concentration of  $\text{Rh}_2(\text{OAc})_4\text{X}$  at time  $t$ , and eq A1-A4 are still applicable. Equation 3a of the text does not apply but eq 3b is obtained from eq A4 by setting  $x = x_0$ . For  $x_0$  to be obtained, it must be remembered that, before mixing, the total concentrations of rhodium dimer and of chloride ion in the syringe are  $2a$  and  $2b$ . The equilibrium concentration of  $\text{Rh}_2(\text{OAc})_4\text{Cl}$  is calculated accordingly, but this is halved immediately on mixing to give

$$x_0 = \frac{1}{4}\{(a+b + \frac{1}{2}K_1^{-1}) - [(a+b + \frac{1}{2}K_1^{-1})^2 - 4ab]^{1/2}\} \quad (A7)$$

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**Registry No.**  $\text{Rh}_2(\text{OAc})_4^+$ , 55569-93-2;  $\text{Cl}^-$ , 16887-00-6;  $\text{Br}^-$ , 24959-67-9.

(24) C. F. Wells and D. Fox, *J. Chem. Soc., Dalton Trans.*, 1502 (1977).

(25) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Wiley-Interscience, New York, 1972, p 476.