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Bimolecular Substitution Reactions of *trans*-Diacidobis(ethylenediamine)rhodium(III) Complexes with Some Univalent Anions

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The kinetics have been studied of the reactions *trans*-$Rh(en)_2LX^+ + Y^- \rightarrow Rh(en)_2LY^+ + X^-$ (L = I, X = Cl, Y = OH or Br; L = I, X = I, Y = Cl or Br) in aqueous solutions at an ionic strength of 1.00 M. All follow the rate equation $k_{obsd} = k_1 + k_2[Y^-]$. The activation parameters for the second-order path all lie on a good isokinetic plot together with parameters for the reactions where Y = OH and L = X = Cl, Br, or I and where Y = OH = L and X = Cl, Br, or I. The values of $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ cover ranges of ca. 90 kJ mol^{-1} and ca. 60 J K^{-1} mol^{-1}, respectively. The activation parameters also lie on an excellent *pseudoisokinetic plot* (i.e., one of $\Delta H_2^{\ddagger}-\Delta H_1^{\ddagger}$ against $\Delta S_2^{\ddagger}-\Delta S_1^{\ddagger}$). The values of $\Delta H_2^{\ddagger}-\Delta H_1^{\ddagger}$ and $\Delta S_2^{\ddagger}-\Delta S_1^{\ddagger}$ cover ranges of ca. 75 kJ mol^{-1} and ca. 60 J K^{-1} mol^{-1}. The very wide ranges of these activation parameter differences, when considered in conjunction with the extent of stereochemical change and with the exact significance of pseudoisokinetic plots, lead to the conclusion that the bimolecular reactions cover a mechanistic range from S_N1cB (for high values of $\Delta H_2^{\ddagger}-\Delta H_1^{\ddagger}$) through S_N1ip (for small values) and probably as far as S_N2 (for substantially negative values).

Introduction

We recently reported[1,2] that the base hydrolyses of *trans*-$Rh(en)_2X_2^+$ and *trans*-$Rh(en)_2(OH)X^+$ (X = Cl, Br, I), previously thought to be pH independent,[3] actually obey the rate equation

$$k_{obsd} = k_1 + k_2[OH^-] \qquad (1)$$

although the hydroxide concentration must be quite high for the small, second-order term to be observed. We also showed[1] that for the dihalogeno complexes substantial stereochemical rearrangement occurred during the bimolecular pathway. Subsequent work by Hancock and co-workers[4] has confirmed our results for L = X = Cl and extended the observations to other amine complexes of rhodium(III). The unexpectedness of our results for the base hydrolysis reactions led us to investigate whether other anions gave bimolecular pathways for substitution in such complexes. [Anion]-dependent substitution has been observed several times for complexes of cobalt(III)[5] and chromium(III)[6] but only once apparently for complexes of rhodium(III). Bowker et al.[7] reported that the rates for radiochloride exchange with *trans*-$Rh(en)_2Cl_2^+$ and *cis*-$Rh(trien)Cl_2^+$ rose to limiting values at high [Cl$^-$]. Ion-pairing constants of 25 and 60 M^{-1}, respectively, were derived. These values seem unreasonably large for association in aqueous solution, and a value considerably less than 1 has been obtained for *trans*-$[Rh(en)_2Cl_2,Cl]$ from spectroscopic studies.[8] We report here kinetic studies that show the occurrence of an [anion]-dependent path in reactions of the type shown in (2) (L = X = I and Y = Cl or Br; L = I, X = Cl, and Y = Br

$$trans\text{-}Rh(en)_2LX^+ + Y^- \rightarrow Rh(en)_2LY^+ + X^- \qquad (2)$$

or OH). Activation parameters for the anion-assisted and -unassisted pathways are also reported.

Experimental Section

Preparation of Complexes. The complexes *trans*-$[Rh(en)_2IX]ClO_4$ (X = Cl, I) were prepared by published methods.[9] Satisfactory elemental analyses were obtained,[8] and the electronic spectra, recorded in 0.1 M NaX, showed peaks at 490, ca. 440 (sh), 301, and 241 nm (X = Cl; ε 260, ca. 160, 4300, and 38 000 M^{-1} cm^{-1}) and 467 and 342 nm (X = I; ε 271 and 16 000 M^{-1} cm^{-1}), in good agreement with published values.[9]

Spectroscopic Changes and Kinetics. Spectra were recorded on a Perkin-Elmer 402 spectrophotometer. Solutions for kinetic studies were prepared as described previously.[2] The ionic strength, μ, was generally maintained constant at 1.0 M with sodium perchlorate. Kinetics were followed in 10-mm cells placed in the thermostated cell holder of a Perkin-Elmer 402 or Cary 16K spectrophotometer. In the first case four reactions could be followed simultaneously; in the second, five. Reaction mixtures came to constant temperature within 10 min, and exposure to the spectrophotometer light for different amounts of time had no effect on the rates. Temperatures were measured by a thermistor or a precision thermometer.[1]

The reactions of *trans*-$Rh(en)_2I_2^+$ with chloride and bromide showed spectroscopic changes consistent with those expected for formation of the *trans*-iodochloro and -iodobromo complexes, respectively,[10] and there was no evidence for any stereochemical rearrangement. The kinetics were followed at 342 nm. The spectroscopic changes for the reaction of *trans*-$Rh(en)_2ICl^+$ with bromide were consistent with formation of the *trans*-iodobromo complex.[9b,10] A close inspection of the spectroscopic changes during reaction with OH$^-$ suggested that a small amount (≲3%) of cis product[1] could have been formed. These reactions with Br$^-$ and OH$^-$ were followed at 315 and 341 nm, respectively, the latter being an isosbestic point for the subsequent hydrolysis of *trans*-$Rh(en)_2I(OH)^+$ to *trans*-$Rh(en)_2(OH)_2^+$.[2a] No evidence for any intermediate aquo complexes was observed in the reactions with Cl$^-$ or Br$^-$. The concentrations of halide were always such that the anation of any intermediate aquo complexes was fast and complete.[10]

Values of the pseudo-first-order rate constant, k_{obsd}, for all reactions are given in Table I. In all cases the rate equation (3) was obeyed.

$$k_{obsd} = k_1 + k_2[Y^-] \qquad (3)$$

Values of k_1 and k_2 (Table I) were obtained from a weighted linear least-squares analysis in which the percentage error $\sigma(k_{obsd})$ in k_{obsd} was assumed to be constant. The residuals for all the sets of rate

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[1] Poë, A. J.; Vuik, C. P. J. *J. Chem. Soc., Dalton Trans.* **1976**, 661.
[2] (a) Poë, A. J.; Vuik, C. P. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2250. (b) Poë, A. J.; Vuik, C. P. J. *Can. J. Chem.* **1975**, *53*, 1842.
[3] (a) Johnson, S. A.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 1741. (b) Klabunde, U. Ph.D. Thesis, Northwestern University, 1967.
[4] Hancock, M. P.; Heaton, B. T.; Vaughan, D. H. *J. Chem. Soc., Dalton Trans.* **1979**, 761.
[5] (a) Campbell, M. B. M.; Wendt, M. R.; Monk, C. B. *Chem. Soc., Dalton Trans.* **1972**, 1714. (b) Laurie, S. H.; Monk, C. B. *J. Chem. Soc.* **1965**, 724. (c) Muscat, V. I.; Walker, J. B. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2765. (d) Pearson, R. G.; Henry, P. M.; Basolo, F. *J. Am. Chem. Soc.* **1957**, *79*, 5382. (e) Bosnich, B.; Ingold, C.; Tobe, M. L. *J. Chem. Soc.* **1965**, 4074. (f) Fitzgerald, W. R.; Watts, D. W. *Aust. J. Chem.* **1966**, *19*, 1411.
[6] Walker, J. B.; Monk, C. B. *J. Chem. Soc. A* **1966**, 1372. (b) Palmer, D. A.; Watts, D. W. *Inorg. Chim. Acta* **1972**, *6*, 197.
[7] Bowker, K. W.; Gardner, E. R.; Burgess, J. *Trans. Faraday Soc.* **1971**, *67*, 3076.
[8] Vuik, C. P. J. Ph.D. Thesis, London University, 1974.
[9] (a) Johnson, S. A.; Basolo, F. *Inorg. Chem.* **1962**, *1*, 925. (b) Bounsall, E. J.; Poë, A. J. *J. Chem. Soc. A* **1966**, 286. (c) Burgess, J.; Hartley, F. R.; Rogers, D. E. *Inorg. Chim. Acta* **1975**, *13*, 35.
[10] Bott, H. L.; Bounsall, E. J.; Poë, A. J. *J. Chem. Soc. A* **1966**, 1275.

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Table I. Pseudo-First-Order Rate Constants for the Reaction of *trans*-$Rh(en)_2IX^+$ with Y^- (the Values are 10^5k_{obsd} in s^{-1}) at $\mu = 1.0$ M

(a) X = I, Y = Cl, [Complex] = 6 × 10^{-5} M

	$[Cl^-]$, M							
T, °C	0.100	0.300	0.550	0.800	1.00	10^5k_1, s^{-1}	10^5k_2, M^{-1} s^{-1}	$\sigma(k_{obsd})$, %
34.8	1.79	1.85	1.91	1.98	1.99	1.774 ± 0.015	0.235 ± 0.025	0.96
42.0	4.66	4.81	5.04	5.12	5.32	4.602 ± 0.040	0.707 ± 0.066	
45.4	6.97	7.21	7.59	7.89	8.21	6.819 ± 0.060	1.373 ± 0.095	
49.9	12.6	13.2	13.8	14.3	15.1	12.36 ± 0.11	2.63 ± 0.18	
55.0	22.9	23.2	25.0	26.2	26.9	22.21 ± 0.20	4.80 ± 0.33	

(b) X = I, Y = Br, [Complex] = 6 × 10^{-5} M

	$[Br^-]$, M							
T, °C	0.100	0.300	0.550	0.800	1.00	10^5k_1, s^{-1}	10^5k_2, M^{-1} s^{-1}	$\sigma(k_{obsd})$, %
35.5	2.11	2.13	2.26	2.34	2.46	2.040 ± 0.026	0.396 ± 0.044	1.4
42.0	4.57	4.68	5.00	5.21	5.40	4.449 ± 0.058	0.951 ± 0.096	
45.3	6.96	7.22	7.77	8.14	8.28	6.808 ± 0.088	1.569 ± 0.147	
50.0	12.8	13.8	14.5	15.0	15.4	12.75 ± 0.16	2.80 ± 0.27	
54.2	21.7	23.1	24.1	25.5	25.7	21.45 ± 0.28	4.68 ± 0.46	

(c) X = Cl, Y = OH, [Complex] = 1.6 × 10^{-3} M

	$[OH^-]$, M							
T, °C	0.0093	0.251	0.500	0.749	1.00	10^5k_1, s^{-1}	10^5k_2, M^{-1} s^{-1}	$\sigma(k_{obsd})$, %
25.60	4.08	4.04	4.15	4.35	4.68	3.96 ± 0.07	0.59 ± 0.11	1.9
30.48	7.28	7.37	7.45	7.89	8.20	7.16 ± 0.12	0.94 ± 0.20	
34.28	11.4	11.5	11.8	11.7	12.5	11.3 ± 0.2	0.98 ± 0.31	
38.98	18.8	19.4	19.3	20.2	20.5	18.8 ± 0.3	1.74 ± 0.51	
44.48	34.9	34.3	36.8	37.3	39.8	34.0 ± 0.6	5.09 ± 0.97	
48.57	57.6	59.7	62.1	65.2	67.3	57.3 ± 0.9	10.0 ± 1.6	
53.96	104	105	108	113	117	102.5 ± 1.7	13.6 ± 2.9	

(d) X = Cl, Y = Br, [Complex] = 1.4 × 10^{-4} M

	$[Br^-]$, M						
T, °C	0.100	0.400	0.700	1.00	10^5k_1, s^{-1}	10^5k_2, M^{-1} s^{-1}	$\sigma(k_{obsd})$, %
30.83	8.03	9.42	9.74	10.2	8.02 ± 0.27	2.40 ± 0.46	
34.62	14.1	14.6	15.8	15.8	13.9 ± 0.5	2.09 ± 0.75	3.0
40.00	23.5	25.9	27.2	28.9	23.2 ± 0.8	5.90 ± 1.31	
40.23	24.6	26.5	25.8	28.9	24.4 ± 0.8	3.66 ± 1.33	
44.34	42.6	44.6	47.0	46.3	42.6 ± 1.4	4.57 ± 2.24	
50.4	77.7	84.8	86.0	86.2	78.5 ± 2.6	9.17 ± 4.13	

Table II. Kinetic Parameters[a] for the Reaction *trans*-$Rh(en)_2LX^+ + Y^- \rightarrow Rh(en)_2LY^+ + X^-$

	L	X	Y	$\Delta H_1^‡$	$\Delta H_2^‡$	$\Delta S_1^‡$	$\Delta S_2^‡$	10^5k_1[d]	10^5k_2[d]	ref
1[b]	Cl	Cl	OH	109.0 ± 2.6	146.7 ± 5.9	−21.5 ± 7.7	87.9 ± 17.3	0.12	0.06	1
2	Br	Br	OH	107.9 ± 1.4	140.0 ± 2.7	−13.4 ± 4.0	84.8 ± 7.7	0.6	0.4	1
3	I	I	OH	102.0 ± 0.5	130.5 ± 3.0	−5.6 ± 1.6	73.9 ± 9.0	12.0	4.0	1
4	OH	Cl	OH	105.2 ± 0.6	108.1 ± 2.9	−2.8 ± 1.9	−2.1 ± 8.8	4.7	2.0	2a
5	OH	Br	OH	108.7 ± 0.8	104.9 ± 5.4	8.0 ± 2.4	−13.0 ± 16.2	4.7	1.5	2a
6	OH	I	OH	116.4 ± 0.8	122.8 ± 3.6	21.0 ± 2.2	33.2 ± 10.4	1.2	0.44	2b
7	I	Cl	OH	90.2 ± 0.5	94.6 ± 5.9	−27.3 ± 1.7	−30 ± 19	62	9.6	this work
8	I	I	Cl	102.7 ± 0.5	123.7 ± 4.5	−2.8 ± 1.5	49 ± 14	12.3	2.51	this work
9	I	I	Br	103.7 ± 0.8	108.7 ± 5.7	0.6 ± 2.3	4 ± 18	12.7	2.79	this work
10	I	Cl	Br	93.4 ± 1.8	56 ± 14	−15.9 ± 5.4	−150 ± 46	79	7.9	this work
11	I	Cl	Br		79[c]		−75[c]			

[a] Enthalpies in kJ mol^{-1}, entropies in J K^{-1} mol^{-1}, k_1 in s^{-1}, and k_2 in M^{-1} s^{-1}. [b] Numbering of complexes defines points in figures. [c] Upper limits (95% confidence). [d] At 50 °C.

constants for a particular reaction were pooled. This increased the number of degrees of freedom so that only small corrections had to be applied to the estimated standard deviations to give those characteristic of an infinite number of degrees of freedom. Previous studies[2,8] have shown that this approach is valid. Values of the activation parameters, obtained from a suitably weighted linear least-squares analysis of log (k_1/T) or log (k_2/T) vs. $1/T$, are given in Table II. Parameters obtained previously for the base hydrolysis of similar complexes are also given in Table II for comparison.

Discussion

The results reported here show that the anion assistance revealed by the term $k_2[Y^-]$ in the rate equation is not limited to Y = OH but can also occur when Y = Cl or Br. In all cases reported here and elsewhere[1,2,4] k_{obsd} is accurately proportional to $[Y^-]$ up to 1.0 M at an ionic strength of 1.0 M maintained with sodium perchlorate. Excellent Eyring plots were obtained from the values of k_1 and k_2. The values of k_{obsd} are unaffected[1,11] by $[ClO_4^-]$ and μ at low $[Y^-]$ (when $k_{obsd} \simeq k_1$), and the activation parameters obtained from the temperature dependence of k_1 are essentially independent of the nature of Y^- within the experimental uncertainties. The [anion]-independent path, therefore, involves simple aquation, the aquo complex produced undergoing either rapid proton transfer when $Y^- = OH^-$ or anation when Y^- is a halide.

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(11) When L = I, Y = Cl, [complex] = 6 × 10^{-5} M, $[Cl^-]$ = 0.0502 M, T = 55.3 °C, and $[ClO_4^-]$ = 0, 0.302, 0.604 and 0.906 M, 10^5k_{obsd} = 23.4, 23.3, 23.3, and 23.1, respectively.

The activation parameters for the anion-assisted path are strongly dependent on the nature of Y^-. When $L^- = X^- =$ halide and $Y^- = OH^-$, this path is accompanied by trans → cis isomerization, the extent of which decreases along the series $LX = Cl_2 > Br_2 > I_2 > ICl$. When $L^- = OH^-$, $X^- =$ halide, and $Y^- = OH^-$, no isomerization is detectable, nor is it when $LX = I_2$ or ICl and $Y^- = Cl^-$ or Br^-.

By its very nature the anion-assisted path involves the coming together of an anion and a cation, but high values of $[Y^-]$ were necessary for it to be detected. The question of ion pairing therefore arises, and its extent must depend on the activities of the participating ions. In view of the difficulty of estimating activity coefficients for values of $[Y^-]$ varying up to 1.0 M the reactions were studied at a constant ionic strength maintained with sodium perchlorate. Whether competitive ion pairing by ClO_4^- occurs or not in such mixtures has been a matter for discussion recently.[12] As far as our results are concerned, however, all the evidence[8,12a,13] suggests that ion pairing between unipositive complexes and chloride, bromide, or perchlorate in aqueous solution is small or negligible at $\mu = 1.0$ M. It follows that at $[Y^-] = 1.0$ M (when $[ClO_4^-] = 0$) k_2 will be a good measure of the product k_YK_Y where K_Y is the equilibrium constant for formation of the encounter complex[14] (the ion pair) and k_Y is the rate constant for the slow reaction of the encounter complex to form the products. The fact that k_2 is unaffected (within experimental error) by the composition of the solution when $[Y^-] < 1.0$ M suggests that ClO_4^- ions have no detectable effect on k_YK_Y and that the activation parameters do describe the difference in enthalpy and entropy between the separated reactants and the transition state involving the associated reactants.[15] The nature of the transition state will define the intimate mechanism,[14] and consideration of the detailed energetics of such reactions should enable mechanistic conclusions to be drawn.

A mechanism that has been found to operate for anion-assisted substition reactions of some octahedral d^6 complexes of Pt(IV) is the reductive elimination–oxidative addition (REOA) mechanism.[16] This involves two-electron reduction of the complex to a four-coordinate d^8 species followed by reoxidation and incorporation of new ligands as indicated in eq 4 and 5. (The equatorial ligands have been omitted for

$$Y^- + L\text{–}Pt^{IV}\text{–}X \rightarrow Y\text{–}L + Pt^{II} + X^- \qquad (4)$$

$$Y\text{–}L + Pt^{II} + Y^- \rightarrow L\text{–}Pt^{IV}\text{–}Y + Y^- \qquad (5)$$

clarity.) Although a d^8 Rh(I) intermediate could conceivably be formed in our reactions, we do not believe this is at all likely. Oxidative addition to d^8 complexes in aqueous solution appears always to form trans products,[17] and it is difficult to see why overall trans to cis isomerization should occur only for the base hydrolysis of the dihalogeno complexes. Further, the REOA reactions of Pt(IV) show a clear correlation of free energies of activation with standard free energies for reduction.[16b] No such correlations exist for the bimolecular reactions of these Rh(III) complexes. Thus ΔG_2^* at 25 °C for reaction of *trans*-$Rh(en)_2I_2^+$ with OH^-, Br^-, and Cl^- are 108, 109, and 108 kJ mol^{-1}, respectively, whereas the values of $\Delta G°$ for reduction with Br^- and Cl^- would be 39 and 54 kJ mol^{-1} less favorable, respectively, than for reduction with OH^-.[18] Similarly the values of ΔG_2^* for reaction of *trans*-$Rh(en)_2ICl^+$ with OH^- and Br^- at 25 °C are identical. Furthermore, anion assistance is also known with sulfate and phosphate[8] which are unlikely to act as reducing agents.

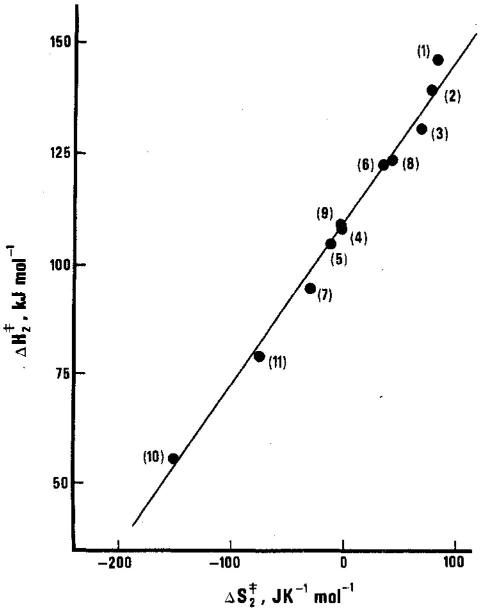

Figure 1. Isokinetic plot for bimolecular reactions of *trans*-$Rh(en)_2LX^+$ with Y^-. Numbering and data were taken from Table II. 5.8 J K^{-1} mol^{-1} has been subtracted from each value of ΔS_2^* for complexes with L = X.

Although specific trends indicative of a REOA mechanism are obviously not apparent, some very regular relationships between enthalpies and entropies of activation for these reactions are evident and are useful in helping to delineate the mechanisms. Thus, all the activation parameters for the anion-assisted path fall on a good isokinetic plot as shown in Figure 1. (The values of ΔS_2^* have been corrected to allow for the different number of potential leaving groups in each complex.) Although some of the activation parameters are quite imprecise (Table II), the fact that the uncertainties in ΔH_2^* and ΔS_2^* are closely interdependent means that the error contours for each point take the form of a very eccentric elipse with the major axis lying almost parallel to the isokinetic plot.[19] Point 11 is plotted to illustrate this. There is less than a 1 in 20 chance that the parameters for the reaction of *trans*-$Rh(en)_2ICl^+$ with Br^- should lie further away than this from point 10 along the line joining points 10 and 11. The linearity and gradient of the isokinetic plot are therefore quite well defined. The correlation coefficient is 0.9927, and the slope corresponds to an isokinetic temperature of 100 °C, i.e., the relative rates as measured are enthalpy controlled.

Isokinetic plots are usually assumed to have mechanistic significance only when one reactant is systematically changed, e.g., by varying a substituent in a position remote from the reaction site.[20] The parameters in Figure 1 correspond to

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[12] (a) Van Eldick, R.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1979**, *18*, 1520 and references therein. (b) Pavelich, M. J.; Maxey, S. M.; Pfaff, R. C. *Ibid.* **1978**, *17*, 564. (c) Pavelich, M. J. *Ibid.* **1975**, *14*, 982. Burnett, M. G. *J. Chem. Soc. A* **1970**, 2480, 2486, 2490.

[13] Bott, H. L.; Poë, A. J.; Shaw, K. *J. Chem. Soc. A* **1970**, 393.

[14] Langford, C. H.; Gray, H. B. "Ligand Substitution Processes", Benjamin: New York, 1976. Langford, C. H. *J. Chem. Educ.* **1969**, *46*, 557.

[15] Even if k_2 is not an exact measure of k_YK_Y, it is virtually impossible for the large changes in ΔH_2^* and ΔS_2^* in Table II to be attributable to *differences* in ion-pairing effects when all the complexes involved are so similar.

[16] (a) Vuik, C. P. J.; Poë, A. J. *Inorg. Chim. Acta* **1979**, *34*, 129. (b) Poë, A. J.; Vaughan, D. H. *J. Am. Chem. Soc.* **1970**, *92*, 7537. (c) Elding, L. I.; Gustafson, L. *Inorg. Chim. Acta* **1976**, *19*, 165. Peloso, A. *Coord. Chem. Rev.* **1973**, *10*, 123.

[17] Halpern, J.; Cozens, R. *Coord. Chem. Rev.* **1975**, *16*, 141.

[18] Calculated from data in: Latimer, W. M. "Oxidation Potentials", 2nd ed.; Prentice-Hall: Englewood Cliffs, N.J., 1952.

[19] Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; p 323. This means that the linearity of the plot is much more closely defined than if the errors in ΔH_2^* and ΔS_2^* were quite independent of each other when considerable curvature, or even major discontinuities, in the plot would have been possible.

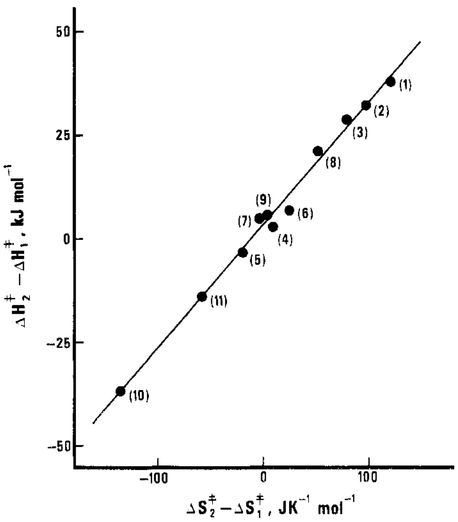

Figure 2. Pseudoisokinetic plot for reactions of *trans*-Rh(en)$_2$LX$^+$ with Y$^-$. Numbering was taken from Table II.

reactions involving a series of different ligands immediately trans to the reaction site and a series of different entering and leaving groups. The fact that data for both OH$^-$ and halide as entering groups lie on the line is surprising at first sight, but the linearity of the plot must indicate at least that there is some regularity in the mechanistic path or paths being followed. In order, however, to minimize the effects of the different natures of the groups L and X, we have plotted in Figure 2 what we have called[1] a *Pseudoisokinetic plot*, i.e., a plot of $\Delta H_2^{\ddagger}-\Delta H_1^{\ddagger}$ against $\Delta S_2^{\ddagger}-\Delta S_1^{\ddagger}$. This provides some compensation for changes in the inherent reactivity of the complex toward substitution as the natures of L and X are changed. The linearity of this line is also excellent, the correlation coefficient being 0.9987 and the pseudoisokinetic temperature 32 °C. The values of $\Delta H_2^{\ddagger}-\Delta H_1^{\ddagger}$ and $\Delta S_2^{\ddagger}-\Delta S_1^{\ddagger}$ are the standard enthalpies ($\Delta H°$) and entropies ($\Delta S°$), respectively, for the equilibrium shown in eq 4. $[Rh(en)_2LX^+]^{\ddagger}$

$$[Rh(en)_2LX^+]^{\ddagger} + Y^- \rightleftharpoons [Rh(en)_2LX,Y]^{\ddagger} \qquad (4)$$

and $[Rh(en)_2LX,Y]^{\ddagger}$ are the transition states for the aquation and anion-assisted reactions, respectively.[21] $\Delta H°$ and $\Delta S°$ are, therefore, a measure of how much Y$^-$ in $[Rh(en)_2LX,Y]^{\ddagger}$ interacts with, and perturbs, the Rh(en)$_2$LX$^+$ which is itself energetically excited. If the aquation reaction has any associative, I$_a$, character, $[Rh(en)_2LX^+]^{\ddagger}$ would also contain an H$_2$O molecule and there would be some Rh···OH$_2$ bonding. If the anion-assisted path has any I$_a$ character, then either there would be an H$_2$O molecule present, with some Rh···OH$_2$ bonding (if reaction was anion-assisted aquation), or there would be some Rh···Y bonding (if the anion assisting the reaction were the one that ends up in the inner sphere). The pseudoisokinetic temperature corresponds to the temperature at which the values of k_2/k_1 are the same for all the reactions.

The values of $\Delta H°$ for the base hydrolysis of the dihalogeno complexes decrease from +36 to +4 kJ mol^{-1} along the series LX = Cl$_2$ > Br$_2$ > I$_2$ > ICl, and along with this decrease in the enthalpy involved is a decrease in the amount of stereochemical rearrangement. Thus there is virtually complete trans → cis isomerization when LX = Cl$_2$ and Br$_2$, only 50% when LX = I$_2$, and less than ca. 20% (and quite possibly none[24]) when LX = ICl. The large positive values for $\Delta H°$ and $\Delta S°$ when LX = Cl$_2$ or Br$_2$, and (to a lesser extent) I$_2$ and the extensive stereochemical changes that occur are both compatible with formation of a conjugate base intermediate so that $[Rh(en)_2LX,Y]^{\ddagger}$ can be written $[Rh(en)(en\text{-}H)LX,OH_2]^{\ddagger}$; i.e., the overall mechanism is S$_N$1cB.[25]

However, the low value of $\Delta H°$, and the small or negligible amount of stereochemical change, when LX = ICl is more suggestive of an S$_N$1ip mechanism. This is true for the hydroxyhalogeno complexes as well, the interaction of OH$^-$ with Rh(en)$_2$LX$^+$ within $[Rh(en)_2LX,OH]^{\ddagger}$ being very small and much more compatible with a weaker ion-pairing interaction than with one involving complete proton transfer. This belief is confirmed by the fact that the interaction of Cl$^-$ with Rh(en)$_2$I$_2$$^+$ in $[Rh(en)_2I_2,Cl]^{\ddagger}$ involves a significantly higher value of $\Delta H°$ and $\Delta S°$ and yet cannot involve conjugate base formation. The closeness of the values of $\Delta H°$ and $\Delta S°$ for formation of $[Rh(en)_2I_2,OH]^{\ddagger}$ and $[Rh(en)_2I_2,Cl]^{\ddagger}$ shows that the borderline between the S$_N$1cB and S$_N$1ip mechanisms may lie between the reactions of OH$^-$ and Cl$^-$ with *trans*-Rh(en)$_2$I$_2$$^+$. This is also a borderline between reactions that involve clear stereochemical change and those that do not. The association of stereochemical rearrangement with the S$_N$1cB mechanism has been rationalized[1] in terms of what is known about trans effects in such complexes. The absence of isomerization and the small values of $\Delta H°$ and $\Delta S°$, in the reactions assigned an S$_N$1ip mechanism, is consistent with there being no proton transfer and no loss of ligand field stabilization energy such as would occur on formation of a trigonal-bipyramidal intermediate. It has been pointed out[26] that the ion-pairing ability of OH$^-$ is very close[27] to that of Cl$^-$, Br$^-$, etc., but that the uniquely pronounced ability of OH$^-$ to catalyze many aquation reactions is a good indicator of the S$_N$1cB mechanism. Apart from those cases where $\Delta H°$ is large and stereochemical rearrangement occurs, OH$^-$ is clearly not unique in the reactions reported here, and this is excellent evidence that an ion-pairing mechanism is operative in some cases.

The very substantially negative values of $\Delta H°$ and $\Delta S°$ for interaction of Br$^-$ with Rh(en)$_2$ICl$^+$ in $[Rh(en)_2ICl,Br]^{\ddagger}$ do not seem to be consistent with simple ion pairing. The strength of the interaction is such as to suggest the possibility of considerable bond making in the transition state for the Br$^-$-assisted reaction, i.e., an S$_N$2ip mechanism. This does not imply that it is necessarily a Rh–Br bond that is being formed because it is conceivable that the Br$^-$ ion in the outer sphere might disturb the solvent sheath in such a way as to activate a water molecule and make it more energetically suited to nucleophilic attack.

The occurrence of I$_a$ mechanisms[28] in aquation and anation reactions of some Rh(III) complexes has been disputed recently.[12,29] It is, however, hard to see how else to explain these

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(20) Reference 19, Chapter 9.

(21) This approach resembles the use of transition-state acidity parameters by Kurz.[22] A similar consideration of equilibria involving transition states was also found useful in discussing the mode of operation of the trans effect in octahedral rhodium(III) complexes.[10,23]

(22) Kurz, J. L. *Acc. Chem. Res.* **1972**, *5*, 1. Kurz, J. L.; Lee, Y.-N. *J. Am. Chem. Soc.* **1975**, *97*, 3841.

(23) Bott, H. L.; Poë, A. J. *J. Chem. Soc. A* **1967**, 205.

(24) The maximum amount of isomerization was estimated to be ca. 3% when 14% of the reaction was proceeding by the second-order path during which isomerization occurs.[1]

(25) It is unlikely to be S$_N$2cB because the sterically more conjested complex *trans*-Rh(udmen)$_2$Cl$_2$$^+$ (udmen = *N*,*N*-dimethylethylenediamine) undergoes base hydrolysis ca. 30 times faster than *trans*-Rh(en)$_2$Cl$_2$$^+$ at 80 °C.[4]

(26) Buckingham, D. A.; Clark, C. R.; Lewis, T. W. *Inorg. Chem.* **1979**, *18*, 2041.

(27) Watts, D. W. *Rec. Chem. Prog.* **1968**, *29*, 131. Boreham, C. J.; Buckingham, D. A.; Clark, C. R. *Inorg. Chem.* **1979**, *18*, 1990.

(28) (a) Johnson, S. A.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 1741. (b) Bott, H. L.; Poë, A. J.; Shaw, K. *Chem. Commun.* **1968**, 793. (c) Monacelli, F. *Inorg. Chim. Acta* **1968**, *2*, 263. (d) Bott, H. L.; Poë, A. J.; Shaw, K. *J. Chem. Soc. A* **1970**, 1745. (e) Powell, H. K. J. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 891. Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217.

energetics especially since the alternative REAO mechanism seems inoperative (see above). The reactions therefore cover a mechanistic spectrum from S_N1cB through S_N1ip and, possibly, to S_N2,[30] this range[31] of mechanisms being made evident by the variation in the stereochemical changes, the 90 kJ mol^{-1} range of $\Delta H_2^{\ddagger}$ and the 75 kJ mol^{-1} range of $\Delta H_2^{\ddagger}-\Delta H_1^{\ddagger}$.

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Registry No. *trans*-Rh(en)$_2$ICl$^+$, 55721-97-6; *trans*-Rh(en)$_2$I$_2$$^+$, 24444-41-5; OH$^-$, 14280-30-9; Cl$^-$, 16887-00-6; Br$^-$, 24959-67-9.

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[29] Pavelich, M. J. *Inorg. Chem.* **1975**, *14*, 982.

[30] The ip in S_N2ip is redundant since any S_N2 reaction must inevitably occur via an encounter complex of some kind.

[31] The possibility of an S_N1cB–S_N1ip mechanistic spectrum was, of course, suggested some time ago by Chan and Lau.[32] This is the first time that the possibility has been so strongly indicated by detailed and systematic variations of energetic and stereochemical behavior for a series of closely related reactions.

[32] Chan, S. C.; Lau, O. W. *Aust. J. Chem.* **1969**, *22*, 1851.

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Chromium(III) Products from the Reduction of 1,4-Benzoquinone by Chromous Ion. Synthesis of the μ-Oxo-bis(pentaaquochromium(III)) Ion

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The chromium(III) products resulting from the reduction of 1,4-benzoquinone (BQ) by chromous ion in weakly and strongly acidic solutions have been isolated through cation-exchange chromatography on SP-Sephadex C-25 resin. Five chromium-containing products were obtained from the anaerobic addition of 1.25 mL of 0.460 M $Cr(ClO_4)_2$–0.117 M $HClO_4$ to 0.60 mmol of benzoquinone dissolved in 50 mL of water: $Cr(H_2O)_6^{3+}$ (42%); a 2:1 ratio chromium(III)–hydroquinone complex (35%), proposed to be $[(H_2O)_4Cr(OH)(HQ)Cr(H_2O)_4]^{4+}$; an oxo-bridged binuclear complex (4%), $[(H_2O)_5CrOCr(H_2O)_5]^{4+}$; a 3:1 Cr^{III}–H_2Q complex (15%); and a small amount of a golden yellow product which could not be eluted from SP-C-25 resin. A much larger initial yield of $[(H_2O)_5CrOCr(H_2O)_5]^{4+}$ was obtained from the addition of Cr^{2+}(aq) to benzoquinone dissolved in 0.1 M $HClO_4$, but this product is unstable in acidic solution, yielding $Cr(H_2O)_6^{3+}$ as the predominant (75%) chromium species eluted from the cation-exchange column. Much less of the 2:1 Cr^{III}–H_2Q complex was formed from the Cr^{II}–BQ reaction in 0.1 M $HClO_4$ (3%), and a second 3:1 Cr^{III}–H_2Q complex (19%) was produced under these conditions. The UV–visible absorption spectra of the chromium(III) products are reported, and the implications of the product distribution studies for the mechanism of electron transfer from chromium(II) to benzoquinone are discussed.

Introduction

Kinetic studies of the reduction of *Rhus vernicifera* laccase type 1 copper by substituted hydroquinones[1] prompted our interest in the effect of coordination on the electron-transfer reactivity of these organic substrates. We planned, therefore, to examine the oxidation mechanism of chromium(III)-complexed hydroquinone (H_2Q) in the (hydroquinonato)pentaaquochromium(III) ion and related species. Reduction of 1,4-benzoquinone (BQ) by the (pentacyano)cobaltate(II) ion yields a binuclear cobalt(III) complex, $[(NC)_5CoOC_6H_4OCo(CN)_5]^{6-}$, containing a bridging group isoelectronic with the dianion of hydroquinone.[2] The mononuclear $[(NC)_5CoOC_6H_4OH]^{3-}$ ion was obtained through partial hydrolysis of the binuclear complex.[2] By analogy with these results for $Co(CN)_5^{2-}$ as the reductant, we expected to obtain $[(H_2O)_5CrOC_6H_4OCr(H_2O)_5]^{4+}$ and $[(H_2O)_5CrOC_6H_4OH]^{2+}$ as the predominant chromium(III) products in the reaction of 1,4-benzoquinone with chromous ion in aqueous solution. This expectation was in fact not realized, but a number of other interesting products, including the μ-oxo-bis(pentaaquochromium(III)) ion, were obtained through the reduction of benzoquinone by Cr^{2+}(aq). In this paper we report product distribution studies for the reaction of Cr^{2+}(aq) with benzoquinone in both weakly and strongly acidic solutions. The implications of these distribution studies for the mechanism of electron transfer from Cr(II) to BQ are discussed.

Experimental Section

Materials. Reagent grade chemicals were used throughout. Reactions were carried out in solutions prepared with triply distilled water, and eluant solutions were prepared with doubly distilled water. $Cr(ClO_4)_3 \cdot 6H_2O$, $Ce(ClO_4)_3 \cdot 6H_2O$, $LiClO_4$, and 0.5 N $Ce(ClO_4)_4$ in 6 N $HClO_4$ were used as supplied by G. F. Smith. Practical grade 1,4-benzoquinone was purified through vacuum sublimation. SP-Sephadex C-25-120 resin was used in all cation-exchange experiments. Acidic solutions of the di-μ-hydroxo-bis(tetraaquochromium(III)) ion were obtained through the aerobic oxidation of chromous ion, as described by Ardon and Plane.[3]

Solutions in serum-capped bottles were made anaerobic by purging with chromous-scrubbed nitrogen for at least 40 min. Teflon needles were used in purging solutions, while stainless-steel needles and Hamilton gastight syringes were employed in transferring anaerobic solutions. A chromous perchlorate stock solution was prepared by reducing anaerobic 0.460 M $Cr(ClO_4)_3$ in 0.117 M $HClO_4$ over 4% zinc amalgam.

Analyses. Chromium(II) stock solutions were assayed by injecting aliquots into an excess of acidic Fe(III). The Fe(II) produced was then titrated with standard $Cr_2O_7^{2-}$ to a diphenylaminesulfonate end point. Hydroquinone ($\epsilon_{288} = 2.30 \times 10^3$ M^{-1} cm^{-1})[4] and benzoquinone ($\epsilon_{246} = 2.18 \times 10^4$ M^{-1} cm^{-1})[5] concentrations were determined spectrophotometrically in solutions containing no Cr. Correction was made for the absorption of benzoquinone at 288 nm[5] when [H_2Q]

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[1] Clemmer, J. D.; Gilliland, B. L.; Bartsch, R. A.; Holwerda, R. A. *Biochim. Biophys. Acta* **1979**, *568*, 307–20.

[2] Vlcek, A. A.; Hanzlik, J. *Inorg. Chem.* **1967**, *6*, 2053–9.

[3] Ardon, M.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3197–200.

[4] Baxendale, J. H.; Hardy, H. R. *Trans. Faraday Soc.* **1953**, *49*, 1140–4.

[5] Baxendale, J. H.; Hardy, H. R.; Sutcliffe, L. H. *Trans. Faraday Soc.* **1951**, *47*, 963–73.

0020-1669/80/1319-1775$01.00/0