Kinetics of Aquation of the Hexabromorhenate(IV) and Hexachlororhenate(IV) Ions

By **John Burgess,*** **Raymond D. Peacock,** and **Alexander M. Petric,** Chemistry Department, University of Leicester, Leicester LE1 7RH

The kinetics of aquation of the hexabromorhenate(IV) ion in aqueous solution and aqueous organic media, and those of the hexachlororhenate(IV) ion in aqueous solution in the presence of mercury(II) ions, are reported. Activation parameters for the aquation of the hexabromorhenate(IV) ion in aqueous solution are $\Delta H^\ddagger = 26{\cdot}0$ kcal mol^{-1} and $\Delta S^\ddagger = -6$ cal K^{-1} mol^{-1}.

THERE have been relatively few kinetic studies of substitution in rhenium complexes in solution. The kinetics of oxygen exchange in tetraoxorhenate(VII) ions in water and in aqueous methanol,[1] and of substitution in $Re_2Cl_8^{2-}$, $Re_2Br_8^{2-}$, and related species in methanol,[2] have been described. Kinetic studies of substitution in rhenium(IV) complexes appear to be restricted to those of chloride-ion exchange with hexachlororhenate(IV) [3] and of bromide-ion exchange with hexabromorhenate(IV) [4] ions in aqueous solution, and of ligand exchange in solid K_2ReCl_6 and K_2ReBr_6.[5] There are also some qualitative observations, derived from calorimetric studies, on the effect of hypochlorite ions on the rate of reaction of hexachlororhenate(IV) with hydroxide ions.[6] It is perhaps surprising that there have been so few kinetic studies of substitution in rhenium(IV), for the ion is a kinetically inert d^3 centre which should be amenable to study by conventional techniques, like the extensively investigated chromium(III) [7] and the less extensively studied vanadium(II) [8] d^3 centres.

We report the results of our investigation of the uncatalysed and mercury(II)-catalysed hydrolysis of hexabromorhenate(IV) and of hexachlororhenate(IV) ions in acid and in alkaline media, in water and in mixed aqueous organic solvents.

RESULTS AND DISCUSSION

At concentrations of *ca.* 0·1M, both hexabromorhenate(IV) and hexachlororhenate(IV) ions hydrolyse in alkaline, neutral, or weakly acidic solution to give a dark brown precipitate of hydrated rhenium dioxide. However at much lower concentrations, *ca.* 10^{-4}M, there is no such precipitation. As the hydrolysis proceeds the colour of the solution fades; the u.v. spectrum of the product solution is identical with that reported [9] for tetraoxorhenate(VII) ions. For hydrolysis of hexachlororhenate(IV) ions there is an isosbestic point at 247 nm; the extinction coefficient of tetraoxorhenate(VII) ion is lower than that of hexabromorhenate(IV) throughout the range 205—700 nm and we have therefore not observed an isosbestic point associated with the hydrolysis of the latter.

It is known that rhenium dioxide is fairly susceptible to oxidation; [10] the redox potential (I.U.P.A.C. sign convention) for the ReO_4^-, $4H^+$–$ReO_2,2H_2O$ couple is probably [11] $+0{\cdot}51$ V, so oxidation by dissolved oxygen is thermodynamically favourable in 1N-acid. Whereas it has been speculated that in the absence of oxygen hexachlororhenate(IV) ion disproportionates into lower oxidation states of rhenium plus rhenium(VII), in the presence of oxygen rhenium(VII) appears to be produced readily.[12] We cannot tell whether oxidation follows the loss of all six halide ligands from the rhenium(IV) ion, which would produce the unlikely but not impossible intermediate $Re(OH_2)_6^{4+}$ or a hydroxo-equivalent $Re(OH)_n(OH_2)_{6-n}^{(4-n)+}$, or takes place at some earlier stage in the halide-replacement sequence. The $ReCl_5(OH)^{2-}$ anion is oxidised in about the timescale of

---

[1] R. K. Murmann, *J. Amer. Chem. Soc.*, 1971, **93**, 4184.

[2] M. J. Hynes, *J. Inorg. Nuclear Chem.*, 1972, **34**, 366.

[3] J. D. Woods, J. Gruca, and C. M. Pietrzak, *Proc. Iowa Acad. Sci.*, 1970, **76**, 119.

[4] G. Schmidt and W. Herr, *Z. Naturforsch.*, 1961, **16a**, 748.

[5] R. Bell, K. Rössler, G. Stöcklin, and S. R. Upadhyay, *J. Inorg. Nuclear Chem.*, 1972, **34**, 461.

[6] R. H. Busey, K. H. Gayer, R. A. Gilbert, and R. B. Bevan, *J. Phys. Chem.*, 1966, **70**, 2609.

[7] See, for example, (*a*) 'Inorganic Reaction Mechanisms,' ed. J. Burgess, Chem. Soc. Specialist Periodical Report, London, vol. 1, 1971, pp. 169—174, 183; (*b*) *ibid.*, vol. 2, 1972, pp. 157—166, 172—175; (*c*) C. H. Langford and V. S. Sastri in 'Reaction Mechanisms in Inorganic Chemistry,' ed. M. L. Tobe, M.T.P. International Review of Science, Butterworths, London, series 1, vol. 9, 1971, pp. 228—235.

[8] See, for example, J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, 1968, **7**, 250; W. Kruse and D. Thusius, *ibid.*, p. 464; R. G. Pearson and O. A. Gansow, *ibid.*, p. 1373; M. V. Olsen, Y. Kanazawa, and H. Taube, *J. Phys. Chem.*, 1969, **51**, 289.

[9] N. Bailey, A. Carrington, K. A. K. Lott, and M. C. R. Symons, *J. Chem. Soc.*, 1960, 290.

[10] R. D. Peacock, 'The Chemistry of Technetium and Rhenium,' Elsevier, Amsterdam, 1966, p. 28.

[11] Ref. 6, p. 2612.

[12] I. Noddack and W. Noddack, *Z. anorg. Chem.*, 1933, **215**, 129 (see especially pp. 168—169).

our experiments to tetraoxorhenate(VII) ion,[13] and this and other halogenohydroxo- or halogeno-oxo-rhenium(IV) complexes are known to be considerably more labile than hexahalogenorhenium(IV) anions.

In the light of the previous and present evidence detailed above, we believe that the rate-determining step whose kinetics we are monitoring is loss of the first halide ligand from the rhenium(IV) complex [equation (1)].

$$\mathrm{ReX_6}^{2-} + \mathrm{H_2O} \longrightarrow \mathrm{ReX_5(OH_2)}^{-} + \mathrm{X}^{-} \qquad (1)$$

Hexachlororhenate(IV) *Ion.—Aquation in acidic aqueous solution.* This reaction is extremely slow at normal temperatures; at 35·0 °C the first-order rate constant is 9×10^{-9} s^{-1}. We have therefore not studied the kinetics of this reaction further, but have concentrated our attention on the mercury(II)-catalysed aquation of this anion, and on the aquation of the hexabromorhenate(IV) anion, both of which reactions have much more convenient half-lives.

Hexabromorhenate(IV) *Ion.—Aquation in acidic aqueous solution.* The disappearance of this ion in acidic aqueous solution followed first-order kinetics up to at least 90% completion of reaction; the rate law is thus simply as in equation (2). Values of the rate constant

$$-\mathrm{d}[\mathrm{ReBr_6}^{2-}]/\mathrm{d}t = k[\mathrm{ReBr_6}^{2-}] \qquad (2)$$

k, as a function of acid concentration, ionic strength, and temperature, are reported in Table 1. Aquation rates varied only slightly with acid concentration and the small variation that was observed can be ascribed mainly to the variation of ionic strength. The trend of observed rate constant with increasing ionic strength suggests that at low ionic strengths the gradient of a plot of the logarithm of the rate constant against the square root of the ionic strength would have a gradient of less than *ca.* 0·02; a value approximating to zero is expected for hydrolysis of a charged ion [compare, for example, the aquation of the complex $\mathrm{Cr(urea)_6}^{3+}$].[14]

TABLE 1

First-order rate constants (k) for hydrolysis of the hexabromorhenate(IV) ion in aqueous solution: $[\mathrm{ReBr_6}^{2-}]_0 = 6 \times 10^{-5}$—$20 \times 10^{-5}$M

Temp./°C	[HClO$_4$]/M	10^7k/s^{-1}
25·0	0·20	4·7
30·0	0·20	10·0
35·0	0·20	17·8
40·0	0·20	37
45·0	0·20	68
50·0	0·20	148
55·0	0·20	293
	0·50	310
	1·00	345
	2·00	360
	0·20 [a]	300
	0·20 [b]	310

[a] [NaClO$_4$] = 0·25M. [b] [NaClO$_4$] = 0·50M.

Activation parameters were calculated from the rate constants reported in Table 1. The activation enthalpy for the aquation is 26·0 kcal mol^{-1}, the standard error being 0·57 kcal mol^{-1}.* As the latter was derived from seven points (five degrees of freedom), the 90% confidence limits can be set[15] at ±1·1 kcal mol^{-1}. The activation entropy is -6 ± 3 cal K^{-1} mol^{-1}. These activation parameters are compared with those for the aquation of some similar complexes in Table 2. Activation parameters for substitution in the analogous d^6 platinum(IV) complexes $\mathrm{PtX_6}^{2-}$ (X = Cl or Br) are not directly comparable, for substitution at this centre also involves a redox process and generally has a much lower activation enthalpy in the range 12—16 kcal mol^{-1}.[4,16,17]

TABLE 2

Activation parameters for aquation of hexahalogenometallate anions in aqueous solution

Complex	Configuration	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	Conditions	Ref.
$[\mathrm{ReBr_6}]^{2-}$	d^3	26·0	−6	0·20M-HClO$_4$	This work
$[\mathrm{IrBr_6}]^{3-}$	d^5	22·6	−3	1M-HClO$_4$	*a*
$[\mathrm{IrCl_6}]^{3-}$	d^6	27·5	+15	0·1M-HClO$_4$; I = 0·13M	*b*
$[\mathrm{RhCl_6}]^{3-}$	d^6	24·4	+10	[H$^+$] = I = 4M	*c*

[a] V. I. Kravtsov, N. V. Titova, and G. P. Tsayun, *Elektrokhimiya*, 1970, **6**, 573. [b] A. J. P. Domingos, A. M. T. S. Domingos, and J. M. P. Cabral, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2563. [c] W. Robb and G. M. Harris, *J. Amer. Chem. Soc.*, 1965, **87**, 4472.

The higher activation enthalpy for aquation of $\mathrm{ReBr_6}^{2-}$ compared with that of $\mathrm{IrBr_6}^{3-}$ (Table 2) may be ascribed to the larger formal positive charge on the rhenium (4+) than on the iridium (3+) ion. The difference between the d^3 and d^6 configurations for these two metal centres would, from intercomparison of pairs of chromium(III) and cobalt(III) complexes, be expected to make a difference of only one or two kcal mol^{-1} in the activation enthalpy. Activation enthalpies for bromide exchange in $\mathrm{ReBr_6}^{2-}$, $\mathrm{OsBr_6}^{2-}$, and $\mathrm{IrBr_6}^{2-}$ are all, within experimental error, 29·4 kcal mol^{-1}.[4] The activation entropy values in Table 2 suggest that these are dominated by interactions between the halide ligands and the solvent, rather than by the nature of the central metal cation. The activation enthalpy for aquation of $\mathrm{ReBr_6}^{2-}$ appears to be somewhat less than that for bromide-ion exchange, whereas a common dissociative mechanism requires the same activation enthalpy. Unfortunately confidence limits are not reported for the bromide-ion exchange activation energy

---

* 1 cal = 4·184 J.

[13] B. Jezowska-Trzebiatowska and S. Wajda, *Bull. Acad. polon. Sci., Classe III*, 1954, **2**, 249.

[14] See, for example, K. J. Laidler, ' Reaction Kinetics,' vol. 2, Pergamon, Oxford, 1963, pp. 18—22.

[15] E. S. Swinbourne, ' Analysis of Kinetic Data,' Nelson, London, 1971, pp. 7—9.

[16] R. Dreyer, *Z. phys. Chem.* (*Frankfurt*), 1961, **29**, 347.

[17] R. Dreyer, I. Dreyer, and D. Rettig, *Z. phys. Chem.* (*Leipzig*), 1964, **227**, 105.

so a statistical test of the hypothesis that the two processes have the same activation enthalpy is not possible. The differences in experimental conditions, both in reagent concentration and in the temperature range studied ($\Delta C_p^{\ddagger}$ is unlikely to be zero so $\Delta H^{\ddagger}$ will vary with temperature to some small extent), may contribute significantly to the small difference between the reported activation enthalpies for the aquation and exchange reactions.

Aquation in mixed aqueous organic solvents. The variation of rate constant with solvent composition often gives some evidence relating to the mechanism of a solvolysis reaction. In particular, for the solvolysis of organic halide compounds a linear correlation of the logarithm of the rate constant against solvent Y values, for a variety of mixed aqueous solvents, indicates a dissociative mechanism; the scale of Y values is based on solvolysis rates for t-butyl chloride, the solvolysis of which is taken as the reference dissociative reaction.[18] For the dissociative aquation of ammine- or amino-halogenocobalt(III) complexes, linear correlations of the logarithms of aquation rate constants with solvent Y values, at least in water-rich solvent mixtures, have been reported.[19] The gradient (m) of this correlation is about 0·3 for the cobalt(III) complexes, 1·0 (by definition) for t-butyl chloride. It is the linearity of the correlation which is significant; the m value merely reflects the widely different solvation requirements of the initial and transition states.

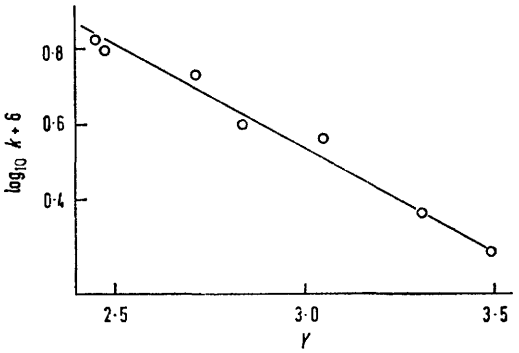
Rate constants for aquation of the hexabromorhenate(IV) ion in a variety of aqueous organic solvent mixtures are reported in Table 3. Logarithms of these rate constants correlate well with the respective solvent Y values, which suggests a dissociative mechanism. It is particularly significant that the point corresponding to acetic acid (30%) lies on the correlation line (see the Figure), for whereas the solvating powers (Y values) of aqueous acetic acid and of aqueous alcohols are similar, the nucleophilicity of water, a key parameter if the mechanism of aquation is associative in character, is very different in these two types of solvent.[20] The gradient (m) of the plot of the logarithms of the rate constants against solvent Y values is ***negative***, -0.55 ± 0.07,* which indicates very different solvation requirements of the 'non-leaving' group $ReCl_5^-$ compared to those of Me_3C^+ or $Co(en)_2Cl^{2+}$ (en = ethylenediamine).

TABLE 3

Variation of the first-order rate constant (k) for hydrolysis of hexabromorhenate(IV) ion in mixed aqueous solvents at 35 °C and $[HClO_4] = 0.20$M

Non-aqueous component	% (v/v)	Y [a]	$10^7k/s^{-1}$
Ethanol	10	3·31	23
	20	3·05	36
	30	2·72	54
Acetone	30	2·48	65
Dioxan	30	2·46	68
Acetic acid	30	2·84	40

[a] From ref. 18.



Grunwald–Winstein mY plot for the aquation of the hexabromorhenate(IV) ion in mixed aqueous solvents

Hexachlororhenate(IV) *Ion.—Mercury*(II)*-catalysed aquation.* Mercury(II) ion is an efficient catalyst for the aquation of a wide range of halogeno-complexes of transition-metal cations. Kinetic studies of such aquation reactions have concentrated on chromium(III) and cobalt(III) complexes.[21] We have studied the kinetics of aquation of the hexachlororhenate(IV) ion in the presence of mercury(II) ions;† observed first-order rate constants are reported, for aquation both in aqueous solution and in ethanol (20% v/v), in Table 4. The mercury(II) ion was present in considerable excess; the kinetics of each run were first-order. The variation of observed first-order rate constants with mercury(II)-ion concentration indicates a second-order rate law of the form (3). Values of k_2, determined graphically, are

$$-d[ReCl_6^{2-}]/dt = k_2[ReCl_6^{2-}][Hg^{II}] \qquad (3)$$

also quoted in Table 4.

TABLE 4

Observed first-order rate constants (k_{obs}) and derived second-order rate constants (k_2) for the mercury(II)-catalysed aquation reaction of the hexachlororhenate(IV) ion at 35·0 °C

Solvent	$10^3[Hg(NO_3)_2]/M$				$k_2/l\ mol^{-1}\ s^{-1}$
	1·2	2·4	3·6	4·8	
	$10^4k_{obs}/s^{-1}$				
Water [a]	4·2	9·8	14·7	19·0	0·40
Water [b]	3·6	8·1	13·4	16·6	0·35
Ethanol (20%) [b]	22	47	68		1·9

[a] Ionic strength maintained with magnesium nitrate. [b] Ionic strength maintained with calcium nitrate.

---

* 90% Confidence limits.

† An isosbestic point is observed at 260 nm for this reaction.

[18] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846; P. R. Wells, 'Linear Free Energy Relationships,' Academic Press, London, 1968, ch. 4.

[19] See, for example, C. H. Langford, *Inorg. Chem.*, 1964, **3**, 228; J. Burgess, *J. Chem. Soc.* (*A*), 1970, 2703.

[20] J. C. Lockhart, 'Introduction to Inorganic Reaction Mechanisms,' Butterworths, London, 1966, pp. 34—35.

[21] Ref. 7*a*, pp. 167, 173; ref. 7*b*, pp. 153—154, 164—165.

As expected, the nature of the cation used to maintain the ionic strength constant (the nitrate salt was employed) had only a small effect (which could be zero within the probable experimental errors of the Table 4 values) on the rate constants. The aquation took place considerably more rapidly in ethanol (20%) than in water; this trend is in the same direction as that recorded for the mercury(II)-catalysed aquation reactions of the $Co(NH_3)_5Cl^{2+}$ and $Rh(NH_3)_5Cl^{2+}$ cations.[22] These mercury(II)-catalysed aquation reactions are dissociative as far as the metal ion is concerned [though associative, S_E2, at the mercury(II) ion], so the logarithms of the rate constants correlate linearly with solvent Y values. For the $Co(NH_3)_5Cl^{2+}$ and $Rh(NH_3)_5Cl^{2+}$ cations m values for mercury(II)-assisted aquation reactions are $-0{\cdot}35$ and $-0{\cdot}25$ respectively.[22] For $ReCl_6^{2-}$, values of k_2 in water and in ethanol (20%) define an mY plot of gradient $-1{\cdot}7$. Thus for both the cobalt(III) and rhodium(III) complexes, and for $ReCl_6^{2-}$, the m value for mercury(II)-assisted aquation is much more negative than that for the uncatalysed aquation reaction.

Aquation Mechanism.—Whilst one can suggest with considerable confidence that the mechanism of the mercury(II)-catalysed aquation reaction is dissociative with respect to the rhenium(IV)–halide bond, it is not possible to make an unequivocal assignment of mechanism to the uncatalysed reaction. Substitution reactions of cobalt(III) complexes of the $Co(NH_3)_5Cl^{2+}$ type seem to be purely dissociative in mechanism, but there is a considerable body of rather indirect evidence that suggests that there may be at least some associative character to substitution in similar d^3 chromium(III) complexes,[23] and at similar complexes of the larger d^6 rhodium(III) and iridium(III) centres.[24] In fact the rhenium(IV) ion has the same estimated ionic radius, 0·63 Å,[25] as that of cobalt(III), and is thus smaller than the ions chromium(III), rhodium(III), and iridium(III), but it does have the same electronic configuration, d^3, as chromium(III). The lower electron density at a d^3 centre compared with a d^6 centre should make nucleophilic attack slightly easier, in other words make an associative contribution to the substitution mechanism slightly less unlikely.

We have very little information available to assist in deciding whether there is any associative character in the mechanism of aquation of hexachlororhenate(IV) anions. The mY correlation described above does suggest a predominantly dissociative mechanism. The activation entropies of Table 2 are not helpful, as their variation with metal centre and halide ligand can be explained either by variation of the solvation requirements in a dissociative mechanism or by some variable associative contribution. A dissociative mechanism has been proposed for ligand-exchange reactions in solid K_2ReCl_6 and K_2ReBr_6;[5] such a mechanism may well obtain for the aquation of these complexes in solution.

Base Hydrolysis.—As mentioned earlier, very dilute solutions (*ca.* 10^{-4}M) of hexachlororhenate(IV) or of hexabromorhenate(IV) ions do not give a precipitate of hydrated rhenium dioxide on addition of hydroxide ions. In fact the colours of the solutions fade entirely; the optical densities of the charge-transfer bands decrease to zero. We therefore attempted to determine the kinetics of base hydrolysis of these very dilute hexahalogenorhenate(IV) solutions. In the presence of an excess of hydroxide ion, the order with respect to hexachlororhenate(IV) ion was found to be *ca.* 3·5; variation of the concentration of hydroxide ion showed a similar dependence of initial rates on hydroxide-ion concentration. Thus the overall order of reaction is about seven; we are unable to propose a plausible mechanism to account for these observations.

EXPERIMENTAL

Potassium hexabromorhenate(IV) and potassium hexachlororhenate(IV) were prepared by reducing solutions of potassium tetraoxorhenate(VII) in hydrochloric and hydrobromic acids, respectively, with iodide ions.[26] The kinetics of hydrolysis of these complexes were monitored spectrophotometrically. The hexabromorhenate(IV) anion has two charge-transfer bands in the near u.v. region, at 28 200 (ε 9 900) and 30 700 cm^{-1} (ε 8 790 l mol^{-1} cm^{-1}); the former band was monitored in the kinetic experiments. The hexachlororhenate(IV) anion has only one band in the near u.v. region, at 35 300 cm^{-1} (ε 12 100 l mol^{-1} cm^{-1}).

First-order rate constants were calculated from the decreases in absorption with time using a standard least-mean-squares program.[27] Activation parameters for the aquation of the hexabromorhenate(IV) anion were computed from the temperature variation of observed rate constants, using the same program for determining the gradient of the appropriate plot and its standard error. The value of m, and its standard error, were also computed, from the variation of rate constants with solvent Y values, using the same program.

[2/1826 *Received, 2nd August,* 1972]

---

[22] J. Burgess and M. G. Price, *J. Chem. Soc. (A)*, 1971, 3108.

[23] See, for example, T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, 1968, **7**, 1915; T. P. Jones and J. K. Phillips, *J. Chem. Soc. (A)*, 1968, 674; ref. 7*b*, pp. 157—159.

[24] See, for example, H. K. J. Powell, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 891 and references therein.

[25] N. N. Greenwood, 'Ionic Crystals, Lattice Defects, and Non-stoichiometry,' Butterworths, London, 1968, p. 40.

[26] Ref. 10, p. 64.

[27] Ref. 15, pp. 38—42.