Kinetics of Metal-ion-catalysed Aquation of the Hexachlororhenate(IV) and Hexabromorhenate(IV) Anions in Aqueous Solution†

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Kinetic parameters are reported for catalysis of the aquation of the hexachlororhenate(IV) anion by mercury(II), thallium(III), cadmium(II), and indium(III), and of the hexabromorhenate(IV) anion by thallium(III), in aqueous solution. Correlation of these kinetic results with stability constants for halogeno-complexes of the respective metal cations is discussed.

RATES of spontaneous aquation of amminehalide, aminehalide, and related complexes of d^3 and low-spin d^6 transition-metal ions are very slow. Aquation of these complexes can be greatly accelerated by catalysis using a metal cation whose chloride complex has a high stability constant. Examples of systems for which kinetic data are available include the reactions of the $[CoCl(NH_3)_5]^{2+}$ cation with Hg^{2+}(aq),[1] Tl^{3+}(aq),[2] or Ag^+(aq),[2] of $[CrCl(NH_3)_5]^{2+}$ with Cu^{2+}(aq) [3] or with Hg^{2+}(aq),[4] and of $[RhCl(NH_3)_5]^{2+}$ with Hg^{2+}(aq).[5] A correlation of rate constants for such metal-ion catalysed aquations with the stability constants for the respective monochloro-complexes formed has been attempted.[6] The amount of extant data for inclusion in this correlation is limited. A more impressive correlation of solvolysis rate constants with metal complex stability constants has been described for metal-ion catalysed solvolysis of 2-chloro-2-methylpropane (t-butyl chloride).[7]

The rate of spontaneous aquation of the hexachloro-complex of the d^3 cation rhenium(IV), $[ReCl_6]^{2-}$, is very slow. A rate constant of *ca.* 9×10^{-9} s^{-1} has been estimated for this reaction at 308 K.[8] Preliminary experiments suggested that Hg^{2+}(aq) is an effective catalyst for this aquation.[8] In the present paper we report the results of a systematic study, yielding rate constants and activation parameters, of the mercury(II)-catalysed aquation of $[ReCl_6]^{2-}$. We have also examined the catalytic effect of thallium(III), indium(III), and cadmium(II) on the aquation of $[ReCl_6]^{2-}$, and of mercury(II) and thallium(III) on the aquation of $[ReBr_6]^{2-}$. We compare the kinetic characteristics of metal-ion catalysis here with those reported for cobalt(III), chromium(III), and rhodium(III) complexes, and examine the relation between rate constants for metal-ion catalysed aquation of the $[ReCl_6]^{2-}$ and $[ReBr_6]^{2-}$ anions and stability constants for the monochloro- and monobromo-complexes of the metal ions concerned.

EXPERIMENTAL

Reagents.—Potassium hexachlororhenate(IV) and potassium hexabromorhenate(IV) were prepared by reducing solutions of potassium tetraoxorhenate(VII) in hydrochloric and hydrobromic acids respectively with hypophosphorous acid,[9] and purified by recrystallisation from the relevant hydrohalogenic acid. Mercury(II) perchlorate (K and K), mercury(II) nitrate (Hopkins and Williams), and cadmium(II) perchlorate (Alfa) were used as supplied. Solutions of thallium(III) perchlorate and indium(III) perchlorate were prepared by stirring thallium(III) oxide or indium(III) oxide in the appropriate strength (see below) perchloric acid at *ca.* 325 K overnight. The resulting solutions were filtered to remove unchanged oxide, and the filtrate was used for kinetic runs and analysed as soon as possible. Thallium(III) solutions were analysed by liberation of iodine from potassium iodide solution (containing sodium hydrogencarbonate), followed by titration of the liberated iodine with sodium thiosulphate solution, itself standardised against AnalaR potassium iodate.[2,10] Indium(III) solutions were analysed by use of ethylenediaminetetra-acetate and back titration against nickel(II).[11]

Kinetics.—The mercury(II)- and thallium(III)-catalysed aquations of $[ReCl_6]^{2-}$ were carried out in 1 cm cells in the thermostatted cell compartment of a Unicam SP 800A recording spectrophotometer. The very slow aquations of $[ReCl_6]^{2-}$ were conducted in sealed vessels immersed in a thermostat bath; aliquot portions were removed at intervals for spectrophotometric assay of the content of hexachlororhenate(IV). Hexachlororhenate(IV) concentrations were monitored at 283 nm, the wavelength of maximum absorption of the main charge-transfer peak of this anion.[12,13]

The thallium(III)-catalysed aquation of $[ReBr_6]^{2-}$ was too fast to monitor by these conventional techniques, and was therefore studied in a stopped-flow apparatus. This consisted of an Applied Photophysics stopped-flow device built into a Unicam SP 500 spectrophotometer fitted with a photomultiplier and storage oscilloscope. Technical restrictions dictated that the aquation of $[ReBr_6]^{2-}$ be

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† No reprints available.

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monitored at 385 nm, on the shoulder of the main charge-transfer band ($\lambda_{max.}$ 350 nm) for this species.[12] The stopped-flow unit and reservoirs were thermostatted at 298 K by water circulated from an external thermostatted tank.

Concentrations of reagents are indicated in the Tables of experimentally determined rate constants. First-order rate constants were computed using a standard least-mean-squares program for the metal-ion catalysed aquations of $[ReCl_6]^{2-}$. For the thallium(III)-catalysed aquation of $[ReBr_6]^{2-}$, rate constants were calculated from half-lives estimated from the oscilloscope traces.

RESULTS AND DISCUSSION

The product of the spontaneous aquation of the hexachloro- and hexabromo-rhenate(IV) anions in dilute (*ca.* 10^{-4} mol dm^{-3}) acidic solutions containing dissolved oxygen is the tetraoxorhenate(VII) anion, $[ReO_4]^-$.[8] Whether this is produced *via* oxidation of the reasonable but as yet uncharacterised * species $Re^{4+}(aq)$, or by oxidation and hydrolysis of mixed aquahalogeno-intermediates, is not known. The same final product, $[ReO_4]^-$, is obtained in the metal-ion catalysed aquations that we have examined in the present work.

Preliminary non-kinetic experiments established which systems were worth studying kinetically. Silver(I) was ruled out as a catalyst by the known insolubility of both its hexachloro- and hexabromo-rhenate(IV) salts. Mercury(II) forms a precipitate with $[ReBr_6]^{2-}$ but not with $[ReCl_6]^{2-}$, thus permitting an examination of the kinetics of mercury(II)-catalysed aquation of the latter. Thallium(III) was found to be an effective catalyst for both the hexachloro- and the hexabromo-complex; no precipitation of complex salts was observed here. Cadmium(II) and indium(III) had very little or no catalytic action. It was impossible to include mercury(II)-catalysed aquation of the pseudohalide complex $[Re(NCS)_6]^{2-}$ in our investigations {*cf.*, for example, mercury(II) catalysis of aquation of the $[Cr(NCS)_6]^{3-}$ anion[14] and of the $[Co(NH_3)_5(SCN)]^{2+}$ cation[15]}, since Hg^{II} produced a precipitate with this complex anion in aqueous solution {*cf.* the generation of $[Co(NH_3)_5(NCSAg)]^{3+}$ from $[Co(NH_3)_5(NCS)]^{2+}$ and silver(I)[16]}.

TABLE 1

Observed first-order rate constants, $k_{obs.}$, and derived second-order rate constants, k_2,* for mercury(II)-catalysed aquation of $[ReCl_6]^{2-}$ in aqueous soluton (perchlorate medium); $[H^+] = 0.05$ mol dm^{-3} and $I = 0.065$ mol dm^{-3} (maintained with sodium perchlorate), initial $[ReCl_6{}^{2-}] = 5.4 \times 10^{-5}$ mol dm^{-3}

$10^3[Hg(ClO_4)_2]$/ mol dm^{-3}	1.3	2.7	4.0	5.0	
	$10^4k_{obs.}$/s^{-1}				k_2/
T/K					dm^3 mol^{-1} s^{-1}
298.3	0.64	1.26	1.87	2.2	0.045 ± 0.002
	0.65	1.29	1.90	2.2	0.044 ± 0.002
303.2	1.55	3.3	4.7	5.8	0.117 ± 0.002
308.2	3.3	7.4	10.2	12.6	0.26 ± 0.01
313.1	7.7	16.2	24	29	0.59 ± 0.01
317.0	11.9	19.3	40	48	0.98 ± 0.09
	12.2	27	37	45	0.92 ± 0.03

* Uncertainties given are the standard errors of the values cited.

TABLE 2

Observed first-order rate constants, $k_{obs.}$, and derived second-order rate constants, k_2,* for thallium(III)-catalysed aquation of $[ReCl_6]^{2-}$ in aqueous solution (perchlorate medium); $[H^+] = 1.25$ mol dm^{-3} and $I = 1.25$ mol dm^{-3}, initial $[ReCl_6{}^{2-}] = 5.4 \times 10^{-5}$ mol dm^{-3}

$10^3[Tl(ClO_4)_3]$/ mol dm^{-3}	2.0	4.0	6.0	7.5	
	$10^4k_{obs.}$/s^{-1}				k_2/
T/K					dm^3 mol^{-1} s^{-1}
297.0			0.33	0.50	
297.1			0.42	0.66	
304.3			1.04	1.51	
309.0	0.76	1.12	1.85	2.5	0.032 ± 0.004
314.1	1.50	3.4	4.9	6.5	0.089 ± 0.004
314.3	1.82	3.9	6.0	7.4	0.102 ± 00052
319.4	3.3	6.7	10.5	13.2	0.181 ± 0.003
319.5	3.9	8.4	12.3	15.5	0.210 ± 0.004

* Uncertainties given are the standard errors of the values cited.

TABLE 3

Observed first-order rate constants, $k_{obs.}$,[a] for cadmium(II)- and indium(III)-catalysed aquation of $[ReCl_6]^{2-}$ and for thallium(III)-catalysed aquation of $[ReBr_6]^{2-}$ in aqueous solution (perchlorate medium); initial $[ReCl_6{}^{2-}] =$ 5.4×10^{-5} mol dm^{-3}, initial $[ReBr_6{}^{2-}] = 7.5 \times 10^{-5}$ mol dm^{-3}

$[ReCl_6]^{2-} + Cd^{2+}$ [b]				
$10^3[Cd(ClO_4)_2]$/mol dm^{-3}	250	375	500	
$10^7k_{obs.}$/s^{-1} (323.2 K)	7	9	11	
$[ReCl_6]^{2-} + In^{3+}$ [c]				
$10^3[In(ClO_4)_3]$/mol dm^{-3}	220	330	450	560
$10^7k_{obs.}$/s^{-1} (323.2 K)	4	3	3	4
$[ReBr_6]^{2-} + Tl^{3+}$ [d]				
$10^3[Tl(ClO_4)_3]$/mol dm^{-3}	3.5	6.9	10.4	13.8
$k_{obs.}$/s^{-1} (300.2 K)	1.4	4.5	7.4	9.4

[a] Derived second-order rate constants are $k_2 = 1.6 \times 10^{-6}$ dm^3 mol^{-1} s^{-1} for $[ReCl_6]^{2-} + Cd^{2+}$, $k_2 = 0$ for $[ReCl_6]^{2-} + In^{3+}$, and $k_2 = 780$ dm^3 mol^{-1} s^{-1} for $[ReBr_6]^{2-} + Tl^{3+}$. [b] $[H^+] = 2.5$ mol dm^{-3} and $I = 4.5$ mol dm^{-3} (maintained by $Na[ClO_4]$). [c] $[H^+] = I = 2.5$ mol dm^{-3}. [d] $[H^+] = I = 3.0$ mol dm^{-3}.

All kinetic runs were in the presence of a large excess of the metal-ion catalyst. Under these conditions first-order kinetics were observed over at least three half-lives. Observed first-order rate constants, $k_{obs.}$, for the aquation of the hexachloro- and hexabromo-rhenate(IV) anions in the presence of various concentrations of the metal-ion catalysts are reported in Tables 1—3. All these results can be accommodated by one general rate law [equation (1)] for catalysis by a

$$-d[ReX_6{}^{2-}]/dt = \{k_1 + k_2[M^{n+}(aq)]\}[ReX_6{}^{2-}] \quad (1)$$

metal-ion $M^{n+}(aq)$. In this rate law k_1 is the rate constant for spontaneous aquation and k_2 that corresponding to catalysed aquation. As the results in Tables 1 and 2 show, $k_2[M^{n+}(aq)] \gg k_1$ for mercury(II) and thallium(III) catalysis, which thus effectively obey a

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* Despite the lack of definite evidence for the existence of the $Re^{4+}(aq)$ cation in aqueous solution, a pK_a value for this species has been published (*Special Publ.* No. 17, The Chemical Society, 1964, p. 52).

[14] See, for example, J. N. Armor and A. Haim, *J. Amer. Chem. Soc.*, 1971, **93**, 867.

[15] A. Adegite, M. Orhanović, and N. Sutin, *Inorg. Chim. Acta*, 1975, **15**, 185.

[16] G. C. Lalor and H. Miller, *J. Inorg. Nuclear Chem.*, 1975, **37**, 307.

simple second-order rate law [equation (2)] except at

$$-\mathrm{d}[\mathrm{ReX_6}^{2-}]/\mathrm{d}t = k_2[\mathrm{M}^{n+}(\mathrm{aq})][\mathrm{ReX_6}^{2-}];\quad \mathrm{M}^{n+} = \mathrm{Hg}^{2+} \text{ or } \mathrm{Tl}^{3+} \qquad (2)$$

extremely low concentrations of metal ion. At the other extreme, $k_1 \gg k_2[\mathrm{M}^{n+}(\mathrm{aq})]$ for indium(III) (Table 3). Here there is only spontaneous aquation and a first-order rate law [equation (3)] at all accessible concentrations of indium(III). The case of cadmium(II) (Table 3) is intermediate between these two extremes, with $k_1 \sim k_2[\mathrm{Cd}^{2+}(\mathrm{aq})]$ at the concentrations used. The cadmium(II) results in Table 3 indicate a value of k_1 of 3×10^{-6} s^{-1}

$$-\mathrm{d}[\mathrm{ReX_6}^{2-}]/\mathrm{d}t = k_1[\mathrm{ReX_6}^{2-}];\ \text{for } \mathrm{M}^{n+} = \mathrm{In}^{3+} \qquad (3)$$

at 323.2 K, which agrees well with the value of k_1 between 3×10^{-6} and 4×10^{-6} s^{-1} at 323.2 K for the indium(III) experiments. Thus the sequence of catalytic effectiveness is $\mathrm{Hg}^{2+} > \mathrm{Tl}^{3+} \gg \mathrm{Cd}^{2+} > \mathrm{In}^{3+}$. Greater catalytic activity of Hg^{2+} than of Tl^{3+} is the order of effectiveness found for aquation of the majority of chlorocobalt(III) complexes, although interestingly the exceptional order $\mathrm{Hg}^{2+} < \mathrm{Tl}^{3+}$ has been reported for some anionic chlorocobalt(III) species.[17]

The mechanism of mercury(II)-catalysed aquation of several chlorocobalt(III),[2,18] chlorochromium(III),[19] and chlororhodium(III) complexes[4] involves equilibrium formation of a chloride-bridged binuclear complex [equation (4) †] followed by relatively slow dissociative breakdown of this intermediate [equation (5) †] to give

$$[\mathrm{M{-}Cl}]^{2+} + \mathrm{Hg}^{2+} \overset{\text{fast}}{\rightleftharpoons} [\mathrm{M{-}Cl{-}Hg}]^{4+} \qquad (4)$$

$$[\mathrm{M{-}Cl{-}Hg}]^{4+} \xrightarrow{\text{slow}} \mathrm{M}^{3+} + [\mathrm{HgCl}]^{+} \qquad (5)$$

the aqua-complex and the $[\mathrm{HgCl}]^+$ cation. A similar mechanism has been proposed for the thallium(III)-[20] and lead(II)-catalysed[21] aquation of chlorocobalt(III) complexes. On the other hand, several examples exist of reactions of this type in which there is no evidence for a persistent chloro-bridged intermediate.[2] In the case of mercury(II) and thallium(III) catalysis of aquation of hexachloro- and of hexabromo-rhenate(IV), the linear dependence of $k_{\mathrm{obs.}}$ on the concentration of metal-ion catalyst, and the linearity and zero intercept of $1/k_{\mathrm{obs.}}$ against reciprocal metal-ion catalyst concentration,[22] are consistent with a direct one-step attack by the metal ion at the co-ordinated halogen. They are also consistent with the intermediacy of a transient binuclear intermediate of low stability, but not with the mechanism detailed in equations (4) and (5). In our discussion of our results we have therefore assumed a one-step mechanism as the simplest hypothesis consistent with our experimental observation. If these reactions do involve a transient intermediate, then our rate constants and activation parameters are composite quantities containing contributions from both the equilibrium formation of such a transient intermediate and its subsequent decomposition.

Values of k_2, derived second-order rate constants for attack of metal-ion catalysts at the hexahalogenorhenate(IV) anions, with their standard errors, obtained from $k_{\mathrm{obs.}}$ values by a standard least-mean-squares computation, are also given in Tables 1—3. Activation parameters derived from the rate constants in Tables 1 and 2 are reported in Table 4. The Table 4 values, with their standard errors, were computed from the quotient $k_{\mathrm{obs.}}/[\mathrm{M}^{n+}(\mathrm{aq})]$ for each appropriate $k_{\mathrm{obs.}}$ in Tables 1 and 2. The activation parameters may be (see above) composite quantities, referring to $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ of formation of transient $[\mathrm{Cl_5Re}\cdots\mathrm{Cl}\cdots\mathrm{Hg}]^{\ddagger}$ and $[\mathrm{Cl_5Re}\cdots\mathrm{Cl}\cdots\mathrm{Tl}]^{+\ddagger}$ species and to $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of their breakdown. However, it is likely that $\Delta H^{\ominus}$ values for the formation of the mercury(II) and thallium(III) intermediates are very similar, as $\Delta H^{\ominus}$ values for the formation of the complexes $[\mathrm{HgCl}]^+$ and $[\mathrm{TlCl}]^{2+}$ have been reported as -5.8 and -5.45 kcal mol^{-1} respectively.[23] As for mercury(II)- and thallium(III)-catalysed aquation of cobalt(III) complexes,[24] the different effects of these cations on rates of aquation resides mainly in the entropy rather than in the enthalpy of activation.

TABLE 4

Activation parameters for metal-ion-catalysed aquation of $[\mathrm{ReCl_6}]^{2-}$ in aqueous solution (perchlorate media)

Catalyst	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
Hg^{2+}(aq)	123 ± 2	142 ± 4
Tl^{3+}(aq)	116 ± 3	105 ± 8

We used all the metal-ion catalysts in the form of their perchlorate salts (in acid solution) so that the catalytic species is simply M^{n+}(aq). In the case of $\mathrm{Hg^{II}}$ we attempted to obtain confirmatory results by using solutions of mercury(II) nitrate in nitric acid. Surprisingly, the consistency of the results was poorer, and the rate constants obtained were slightly lower, than for analogous experiments with $\mathrm{Hg^{II}}$ in perchlorate media. Typically, six or seven determinations of a given rate constant gave values ranging between that obtained in the analogous perchlorate medium and about one half of that value.

The relative effectiveness of $\mathrm{Hg^{II}}$ as a catalyst for aquation of $\mathrm{Re^{IV}{-}Cl}$, $\mathrm{Co^{III}{-}Cl}$, $\mathrm{Rh^{III}{-}Cl}$, and $\mathrm{Cr^{III}{-}Cl}$ complexes is assessed in Table 5. It appears that $\mathrm{Hg^{II}}$

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† Other ligands, *e.g.* ammonia or water, co-ordinated to the metal ions have been omitted for the sake of clarity.

[17] S. F. Chan and S. L. Tan, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 435.

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[22] S. F. Chan and S. L. Tan, *Austral. J. Chem.*, 1975, **28**, 1133.

[23] S. W. Foong, J. D. Edwards, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1975, 277 and refs. therein.

[24] S. C. Chan and S. F. Chan, *Austral. J. Chem.*, 1973, **26**, 1235.

TABLE 5

Comparisons of the effectiveness of Hg^{II}, and of Tl^{III}, as catalysts for the aquation of metal chloro-complexes

Complex (T/K)	k_2(M^{n+} catalysed) $dm^3\,mol^{-1}\,s^{-1}$	k_1 (aquation) s^{-1}	k_2/k_1 $dm^3\,mol^{-1}$	Ref.
Mercury(II)				
$[ReCl_6]^{2-}$ (323.2)	2.41 [a]	3.5×10^{-7}	6.9×10^{6}	*b*
$[CoCl(NH_3)_5]^{2+}$ (308.2)	0.55	6.0×10^{-6}	9.2×10^{4}	6
$[RhCl(NH_3)_5]^{2+}$ (298.2)	2.3×10^{-4} 6.1×10^{-4}	1.5×10^{-8} 8.6×10^{-8}	1.5×10^{4} 7×10^{3}	5
$[CrCl(NH_3)_5]^{2+}$ (298.2)	8.7×10^{-2}	7.3×10^{-6}	1.2×10^{4}	4, 6
Thallium(III)				
$[ReCl_6]^{2-}$ (323.2)	0.25 [c]	3.5×10^{-7}	7×10^{5}	*b*
$[CoCl(NH_3)_5]^{2+}$ (298.2)	1.2×10^{-2}	1.7×10^{-6}	7×10^{3}	2

[a] Extrapolated from results in Table 1. [b] This work. [c] Extrapolated from results in Table 2.

is at its most effective as an aquation-promoting catalyst for Re^{IV}–Cl. It is tempting to ascribe this to the favourable charge interaction in this case, but such a simple explanation is rendered suspect by the observation that Pb^{II} is known to be a comparably effective catalyst for negatively and positively charged complexes of Co^{III}.[21] Comparative assessments of the effectiveness of Tl^{III}, Cd^{II}, or In^{III} are precluded by the lack of appropriate kinetic results.

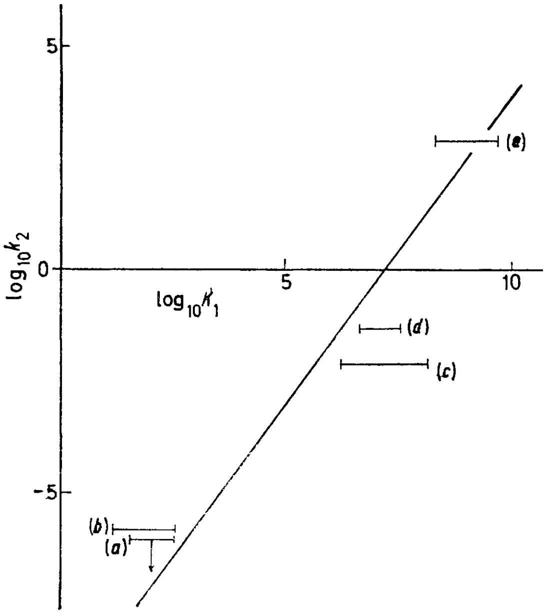
TABLE 6

Relation between second-order rate constants (k_2) for metal-ion-catalysed aquation of hexahalogenorhenate(IV) anions and stability constants (K_1) for formation of monohalogeno-complexes of these metal ions

	k_2/dm^3 mol^{-1} s^{-1} (T/K)	$\log_{10}K_1$ *
$[ReCl_6]^{2-}$		
Hg^{2+}(aq)	4.8×10^{-2} (298.2)	6.6—7.5
Tl^{3+}(aq)	7.5×10^{-3} (298.2)	6.2—8.1
Cd^{2+}(aq)	2×10^{-6} (323.2)	1.2—2.5
In^{3+}(aq)	$<10^{-6}$	1.5—2.5
$[ReBr_6]^{2-}$		
Tl^{3+}(aq)	780 (300.2)	8.3—9.7

* From ref. 25, normally at 298.2 K.

The relation between rate constants for metal-ion-catalysed aquation of hexahalogenorhenate(IV) complexes and stability constants for the respective monohalogeno-complexes of the metal-ion catalysts is detailed in Table 6 and illustrated in the Figure. It is not possible to cite a single definitive stability constant appropriate to the conditions of our experiments, as the results quoted in the standard reference source[25] are for a variety of conditions and themselves vary over rather wide ranges. We have therefore simply cited the range of reported stability constants for each monohalogeno-complex in Table 6. The Figure shows a strong indication of at least some degree of correlation between the rate constants and stability constants; the gradient of the correlation line in the Figure is *ca.* 1.4. It is disappointing that this correlation cannot be made more definite by obtaining further experimental points. As stated earlier, results for silver(I) catalysis are precluded by the insolubility of $Ag_2[ReCl_6]$ and of $Ag_2[ReBr_6]$. Stability constants for the formation of halogeno-complexes of other M^{n+}(aq) cations are generally too low; both $[SnCl]^+$ and $[PbCl]^+$ have formation constants which are significantly lower than those for $[CdCl]^+$ or for $[InCl]^{2+}$. Nonetheless, the relatively small number of results that we do have are sufficient to suggest that these M^{n+}-catalysed aquations of $[ReX_6]^{2-}$ anions follow the same reactivity pattern as the other M^{n+}-catalysed solvolyses mentioned in the introduction, with interaction between the M^{n+} cation and the potential leaving ligand in the transition state an important factor in determining reaction rates.



Correlation between rate constants (k_2/dm^3 mol^{-1} s^{-1}) for metal-ion catalysed aquation of hexahalogenorhenate(IV) anions and stability constants (K_1/mol dm^{-3}) for the formation of the respective monohalogenometal ion complexes: (*a*) $[ReCl_6]^{2-} + In^{3+}$; (*b*) $[ReCl_6]^{2-} + Cd^{2+}$; (*c*) $[ReCl_6]^{2-} + Tl^{3+}$; (*d*) $[ReCl_6]^{2-} + Hg^{2+}$; (*e*) $[ReBr_6]^{2-} + Tl^{3+}$

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[25] *Special Publ.* Nos. 17 and 25, The Chemical Society, 1964 and 1971.