known that $Co(CN)_4(SO_3)OH_2^{3-}$ is generated by aquation of $Co(CN)_4(SO_3)_2^{5-}$, a complex known to have a *trans* configuration, and that *trans*-$Co(CN)_4(SO_3)_2^{5-}$ is regenerated in the reaction of $Co(CN)_4(SO_3)OH_2^{3-}$ with SO_3^{2-}. If these processes occur with retention of configuration, then the assumption under consideration is valid. Indirect evidence for a *trans* configuration is also provided by the similarity in kinetic behavior of $Co(CN)_y(SO_3)OH_2^{3-}$ and $Co(NH_3)_4(SO_3)_x$, where x may be one of a variety of ligands.[4] In the complex where x is NH_3, exchange studies using $N^{15}H_3$ have established that labilization does occur only in the *trans* position.

The kinetic behavior of $Co(CN)_4(SO_3)OH_2^{3-}$ and $Co(NH_3)_4(SO_3)OH^{4-}$ is remarkable in two respects. First, reactions 1 and 7 occur with unusual rapidity, an indication that the presence of the SO_3^{2-} ligand lowers the free energy of activation for formation of an activated complex which presumably still has a coordination number of six. Of even greater importance from the standpoint of mechanistic interpretation of the kinetic data is the fact that the active intermediate generated by these complexes reacts much more readily with NH_3, CN^-, and other ligands than it does with H_2O, a species present at much higher concentration. An unpublished study of the displacement of H_2O in $Co(DH)_2(SO_3)OH_2^+$ by SCN^- suggests that, at least for SCN^-, this latter behavior may vary considerably, depending upon the ligands other than SO_3^{2-} present in the complex. Preliminary experiments[13] for this system at 25° and unit ionic strength yield the numerical values of $k_1 = 11$ sec^{-1} and $k_2/k_3 = 0.85\ M$.

In view of the sparsity of data, any detailed discussion of the origin of the kinetic behavior under discussion is probably premature. However, it may be noted that Ballhausen and Gray have predicted that the kinetic phenomenon known as the *trans* effect should be observed in octahedral complexes where a ligand undergoes strong metal-to-ligand π bonding.[14,15] It is possible that π bonding of this sort is of importance, but the rather extensive organic literature of the SO_3^- functional group suggests that other ligands such as NO_2^- or CN^- would accept electrons much more effectively in this type of bonding. A limiting type of SN1 mechanism has been proposed for the displacement of H_2O in $Co(CN)_5OH_2^{2-}$, but *trans* activation by the CN^- ligand in this complex[16] is certainly less effective than that found in the sulfite complexes. In addition, it may be noted that the rate of exchange[17] of the axial CN^- ligand in $Cr(CN)_5NO^{2+}$ with labeled CN^- is only a factor of 14 greater than with the equational CN^-. This result is of some importance, since the prediction of *trans* activation by Ballhausen and Gray was based, in part, upon a consideration of the spectral properties of $Cr(CN)_5NO^{2-}$. A factor of 14 is, of course, not insignificant, but it hardly provides an overwhelming confirmation of the theory.

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[13] This work and analogous studies of the substitution reactions of $Co(DH)_2(NO_2)OH_2$ and $Co(DH)_2(CN)OH_2$ are being carried out by Hon-Gee Tsiang.

[14] C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **2**, 426 (1963). The SO_3^{2-} ligand is effective in *trans* activation of square-planar complexes, but it is generally assumed that these reactions involve an SN2 mechanism.

[15] By contrast, C. K. Ingold, R S. Nyholm, and M. L. Tobe, *Nature*, **187**, 477 (1960), have suggested that metal-to-ligand π bonding promotes SN2 reaction mechanisms.

[16] A summary of this work has been published by A. Haim, R. J. Grossi, and W. K. Wilmarth, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 31.

[17] R. B. Spencer and R. J. Myers, *J. Am. Chem. Soc.*, **86**, 522 (1964).

Contribution from the National Chemical Research
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Kinetics of Aquation of Aquopentachlororhodium(III) and Chloride Anation of Diaquotetrachlororhodium(III) Anions

By W. ROBB and M. M. de V. STEYN

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The kinetics of the reactions

$$RhCl_5(H_2O)^{2-} + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} RhCl_4(H_2O)_2^- + Cl^-$$

were investigated. The process of equilibration is described by the rate law

$$\frac{-d[RhCl_5(H_2O)^{2-}]}{dt} = k_3[RhCl_5(H_2O)^{2-}] - k_4[RhCl_4(H_2O)_2^-][Cl^-]$$

Values for k_3 and k_4 were obtained at several temperatures in perchloric–hydrochloric acid media of ionic strength $\mu = 4.00$. At 30°, $k_3 = 8.0 \times 10^{-5}$ sec^{-1} and $k_4 = 6.4 \times 10^{-4}\ M^{-1}$ sec^{-1}. The Arrhenius energies of activation, E_a, are 26 and 22 kcal/mole, respectively. The corresponding PZ factors are 1.6×10^{14} sec^{-1} and $3.7 \times 10^{12}\ M^{-1}$ sec^{-1}.

Introduction

A paper by Johnson, Basolo, and Pearson[1] on the reactions of acidoamminerhodium(III) complexes suggested that some of the reactions of rhodium(III) conformed more to an SN2 type of mechanism than do

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[1] S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 1741 (1963).

the well-known Co(III) systems. The first hint of a possible bimolecular reaction came from the work of Lamb[2] in 1939 in his kinetic studies on the hydrolysis of $[Rh(NH_3)_5Cl]^{2+}$ and $[Rh(NH_3)_5Br]^{2+}$ but the interpretation of the results was complicated by uncontrolled salt effects.

More recently the study of the chloride ligand exchange reaction of hexachlororhodium(III) in acid medium reported by Robb and Harris[3] raised the question as to whether some of the radioactively "tagged" chloride entered the octahedral $RhCl_6^{3-}$ by a path that was independent of the aquation reaction

$$RhCl_6^{3-} + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} RhCl_5(H_2O)^{2-} + Cl^- \qquad (1)$$

Garner and co-workers[4,5] have published the results of studies on the analogous chloro complexes of iridium(III) that serve as a useful guide to what can be expected in the reactions of the chlororhodium(III) complexes. This paper presents kinetic data on the reaction of aquopentachlororhodium(III) in acid medium and these data are discussed in terms of the existing reports on the reactions of rhodium(III) and iridium(III) complexes.

Some evidence is presented that points to the existence of possible isomers of diaquotetrachlororhodium(III).

Experimental Section

A.—Potassium aquopentachlororhodium(III) was prepared as described previously[6,7] from pure metallic rhodium.[8]

Potassium diaquotetrachlororhodium(III) was made from potassium hexachlororhodium(III) by boiling an aqueous solution containing 0.07 *M* hydrochloric acid for 5 min and then cooling to 0° prior to adsorption on a Bio-Rad AG1-X8, 100–200 mesh, anion-exchange column in an ice jacket.[9] The $RhCl_3(H_2O)_3$ fraction was washed off the column with 0.001 *M* $HClO_4$ and discarded. The $RhCl_4(H_2O)_2^-$ was then eluted with 4 *M* $HClO_4$, collected, and used immediately for chloride anation studies.

All other chemicals used were of AR grade.

B.—The spectrophotometric kinetic studies were carried out using a Cary Model 15 spectrophotometer fitted with a thermostatable cell holder. The graph of optical density *vs.* time of a prepared sample containing the desired amount of $RhCl_5(H_2O)^{2-}$, HCl, and $HClO_4$ was analyzed in the conventional manner. Observations were made at wavelengths of 507 and 402 mμ, the absorption maxima for $RhCl_5(H_2O)^{2-}$. The aquation reaction of $RhCl_4(H_2O)_2^-$, being very much slower[10] than that of $RhCl_5(H_2O)^{2-}$, did not interfere with the infinite time values for optical density chosen for the $RhCl_5(H_2O)^{2-}$–$RhCl_4(H_2O)_2^-$ equilibration. Also, the chloride ion concentrations for the aquation study were chosen to be small enough to eliminate complications due to anation of $RhCl_5(H_2O)^{2-}$ to $RhCl_6^{3-}$, yet large enough to make the reaction pseudo first order for the $RhCl_5(H_2O)^{2-}$–$RhCl_4(H_2O)_2^-$ equilibration.

Chloride anation studies of $RhCl_4(H_2O)_2^-$ were largely thwarted by the complication of $RhCl_5(H_2O)^{2-}$ anation at the same chloride concentration. It was nearly impossible to obtain an equilibrium value for the optical density and hence straight-line semilogarithmic plots of concentration *vs.* time. The use of relatively higher chloride concentrations in the anation work than those used in aquation studies was necessary to obtain appreciable changes in optical density with time.

C.—The spectrum of the reaction mixture was taken during the aquation runs to find isosbestic points.

Results and Discussion

The results of the experiments in which the conditions were chosen so as to conform to a pseudo-first-order equilibration for the reactions

$$RhCl_5(H_2O)^{2-} + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} RhCl_4(H_2O)_2^- + Cl^- \qquad (2)$$

are given in Table I. The rate expression[11] was

$$\ln \frac{D_0 - D_\infty}{D_t - D_\infty} = (k_3 + k_4[Cl^-])t \qquad (3)$$

where D_0, D_t, and D_∞ refer to the concentrations of $RhCl_5(H_2O)^{2-}$ at times zero, *t*, and infinity, respectively. From a plot of ln $(D_t - D_\infty)$ *vs.* time, the value for $t_{1/2}$ was obtained and used in eq 3, reduced to the form

$$\frac{0.693}{t_{1/2}} = k_3 + k_4[Cl^-] \qquad (4)$$

As depicted in Figure 1, plots of $0.693/t_{1/2}$ *vs.* $[Cl^-]$ gave values for k_3, the intercepts, and k_4, the slopes, at any temperature. These values for k_3 and k_4 are given in Table II.

TABLE I

AQUATION–ANATION EQUILIBRATION OF $RhCl_5(H_2O)^{2-}$ [a] WHERE μ = 4.0 *M*, ADJUSTED WITH $HClO_4$

$[Cl^-]$,[b] *M*	*T*, °C	10^4k_{obsd}, sec^{-1}	$[Cl^-]$,[b] *M*	*T*, °C	10^4k_{obsd}, sec^{-1}
0.1	45	9.6	0.1	35	2.7
0.2	45	14.2	0.2	35	3.8
0.3	45	16.9	0.3	35	4.9
0.4	45	20.9	0.4	35	6.0
0.1	40	4.5	0.1	30	1.4
0.2	40	8.1	0.2	30	2.2
0.3	40	8.1	0.3	30	2.6
0.4	40	9.9	0.4	30	3.4

[a] Initial concentration of $RhCl_5(H_2O)^{2-}$ varied with no effect on k_{obsd}. [b] All runs at various Cl^- concentrations, at least duplicated. Values reported for k_{obsd} are mean values of several measurements.

It is of interest that the value for Δ*H* for the equilibrium shown in eq 2 is 5 kcal/mole. This corresponds to the small positive value reported for Δ*H* by Chang and Garner[5] for the

$$IrCl_5(H_2O)^{2-} + H_2O \rightleftharpoons IrCl_4(H_2O)_2^- + Cl^-$$

reactions. It would appear that the Δ*H* values for the successive equilibria in the aquochlororhodium(III) system would go from positive, as in the hexachloroaquopentachlororhodium(III) case where a value of 8 kcal/mole was found, to negative as the coordinated

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[2] A. B. Lamb, *J. Am. Chem. Soc.*, **61**, 699 (1939).

[3] W. Robb and G. M. Harris, *ibid.*, **87**, 4472 (1965).

[4] I. A. Poulsen and C. S. Garner, *ibid.*, **84**, 2032 (1962).

[5] J. C. Chang and C. S. Garner, *Inorg. Chem.*, **4**, 209 (1965).

[6] G. H. Ayers and F. Young, *Anal. Chem.*, **24**, 165 (1952).

[7] S. N. Anderson and F. Basolo, *Inorg. Syn.*, **7**, 214 (1963).

[8] Supplied by Koch-Light Laboratories Ltd. and stated to be 99.9% pure.

[9] W. C. Wolsey, C. A. Reynolds, and J. Kleinberg, *Inorg. Chem.*, **2**, 463 (1963).

[10] Preliminary experiments have shown that this reaction is less than 10% of the rate of the reaction under investigation.

[11] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p 186.

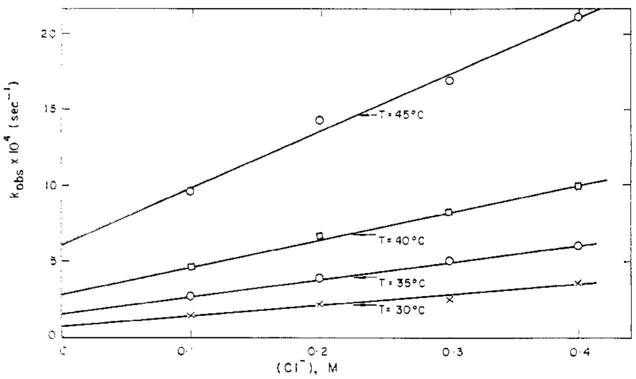

Figure 1.—Chloride ion concentration dependence of $RhCl_5(H_2O)^{2-}$-$RhCl_4(H_2O)_2^-$ equilibration. Ionic strength = 4.00 and [H^+] = 4.00 *M*.

Table II

Values of k_3 and k_4 for the Reactions

$$RhCl_5(H_2O)^{2-} + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} RhCl_4(H_2O)_2^- + Cl^-$$

T, °C	10^4k_3, sec^{-1}	10^4k_4, M^{-1} sec^{-1}
45	6.2	36.8
40	2.8	17.8
35	1.6	10.9
30	0.8	6.4

	E_a, kcal/mole	PZ
k_3	25.8	1.6×10^{14} sec^{-1}
k_4	21.9	3.7×10^{12} M^1 sec^{-1}

water content in the complex increases. This would be in accord with the findings of King, *et al.*,[12] for the reactions

$$Cr(H_2O)_5Cl^{2+} + H_2O \rightleftharpoons Cr(H_2O)_6^{3+} + Cl^-$$
$$Cr(H_2O)_4Cl_2^+ + H_2O \rightleftharpoons Cr(H_2O)_5Cl^{2+} + Cl^-$$

where negative enthalpies of equilibration were measured.

The linearity of the rate *vs.* chloride concentration plots as shown in Figure 1, especially over such a wide range of chloride concentrations, contrasts with the observations of Swaminathan and Harris[13] on the chloride anation reaction of hexaaquorhodium(III). In the latter case the rate dependence on chloride ion concentration falls off steadily from first order when the chloride ion concentration exceeds a few tenths molar, being consistent with an ion-pair formation mechanism followed by the rate-determining dissociation of water which is then replaced by chloride ion.

The absence of any convincing evidence for the formation of an ion-pair intermediate between the two negatively charged reactants in the anation reaction leads to the belief that the outer-sphere water also can react bimolecularly with the aquopentachlororhodium(III) anion in the aquation process. This point of view is further substantiated when the exchange reaction of chloride ligands in hexachlororhodium(III) is considered.[3] The rate of ligand exchange reported in ref 3 cannot be fully accounted for by the expression

$$R_{ex} = k_1[RhCl_6^{3-}] + k_3[RhCl_5(H_2O)^{2-}] \qquad (5)$$

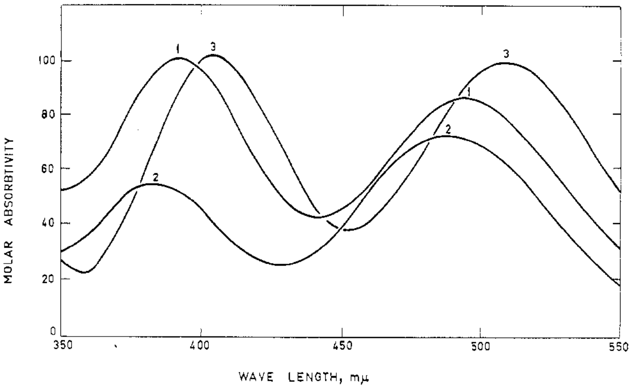

Figure 2.—Spectra of (1) $RhCl_4(H_2O)_2^-$ obtained in this study by hydrolysis of $RhCl_6^{3-}$; (2) $RhCl_4(H_2O)_2^-$ from ref 9 where $Rh(H_2O)_6^{3+}$ was heated with HCl; (3) $RhCl_5(H_2O)^{2-}$ measured in this study.

The excess amount of exchange, when expressed as a second-order rate constant, that takes place at each of the three temperatures studied is quite substantial and is comparable in magnitude to the rate constants of anation k_2 and k_4. Moreover, at 25° with the value of 10×10^{-5} M^{-1} sec^{-1}, it is certainly greater than the value of 4×10^{-5} M^{-1} sec^{-1} for k_1 divided by the water concentration.

Without entering a discussion on the nature or configuration for the transition state[1,14] in such a bimolecular process, it is clear that acceptable evidence is emerging to justify the argument that the rhodium(III) complexes exhibit more SN2 character in their reactions than was found for Co(III) systems. When k_1 and k_3 are treated as pseudo-first-order rate constants it is obvious that chloride ion is at least as effective as a nucleophile as the water molecule in replacing a ligand in the octahedral hexachlororhodium(III) anion. A thorough study on the effectiveness of different nucleophilic groups in competition with the water for the first chloride ligand that is replaced in hexachlororhodium(III) in aqueous media is under way. Preliminary results show that the findings of Johnson, Basolo, and Pearson,[1] that substitutions of chloride in the *trans*-bis(ethylenediamine)dichlororhodium(III) cation by hydroxy, nitrite, iodo, thiourea, and amino groups all appear to be governed by hydrolysis of the complex and hence react at the same rate and independent of their concentrations, do not apply in the case of the $RhCl_6^{3-}$ system.

It is of interest at this stage to compare the different measured rate constants in the aquochlororhodium(III) system. At 25° $k_1 = 1.8 \times 10^{-3}$, $k_3 = 3.7 \times 10^{-5}$ sec^{-1}, and the rate constants for water entering the coordination sphere of the complex become progressively smaller as the number of chloride ligands present decreases, until finally, in the case of hexaaquorhodium(III), water exchanges with a half-time of several months. On the other hand, at the same temperature, the anation rate constants $k_2 = 2.1 \times 10^{-4}$ M^{-1} sec^{-1} and $k_4 = 3.3 \times 10^{-4}$ M^{-1} sec^{-1} imply that a change in mechanism takes place in such a reaction in going from

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[12] K. Schug and E. L. King, *J. Am. Chem. Soc.*, **80**, 1089 (1958).

[13] Private communication.

[14] N. S. Hush, *Australian J. Chem.*, **15**, 378 (1962).

$RhCl_5(H_2O)^{2-}$ to $Rh(H_2O)_6^{3+}$ because the increase must cease and be reversed for the entry of chloride into $Rh(H_2O)_6^{3+}$, a very slow process occurring *via* an ion-pair intermediate. The aquation of $Rh(H_2O)_5Cl^{2+}$ must necessarily be very slow indeed to give a formation constant greater than 10^3 M^{-1}, as reported in the literature.[9] This point of view is confirmed by the fact that prolonged boiling of $RhCl_3(H_2O)_3$ with concentrated $HClO_4$ is required to expel all coordinated chloride in the preparation[15] of $Rh(H_2O)_6^{3+}$.

The ever-present question of *cis–trans* isomers of $RhCl_4(H_2O)_2^-$ deserves a comment. Kleinberg, *et al.*,[9] found no evidence for the existence of *cis* and *trans* isomers in their chromatographic studies nor did Garner, *et al.*,[5] in the chloroiridium(III) system. Figure 2 also gives the spectrum of pure $K_2RhCl_5(H_2O)$ in aqueous acid medium of ionic strength 4. There are three distinct isosbestic points at 398, 443, and 493 mμ, respectively. The full spectral change occurring upon aquation of the aquopentachlororhodium(III) exhibited three isosbestic points at 399, 445, and 494 mμ, respectively, for more than 60% of the equilibrium hydrolysis reaction. It is clear that the aquopentachlororhodium(III) anion hydrolyzes to a single product which may be one isomer only or an equilibrium mixture of *cis*- and *trans*-diaquotetrachlororhodium(III). Considering the experimental conditions used by Kleinberg, *et al.*,[9] it is more likely that, in fact, they obtained the equilibrium mixture whose spectrum is given here in Figure 2.

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[15] G. H. Ayres and J. S. Forrester, *J. Inorg. Nucl. Chem.*, **3**, 365 (1957).

Notes

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The *cis-trans* Isomers of Tetrachlorodiaquorhodate(III) Anion[1a]

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Although Wolsey, Reynolds, and Kleinberg[2] had isolated a series of chloroaquorhodium(III) complexes by ion-exchange chromatography, they reported only one tetrachloro species. Robb and Harris[3] studied the aquation of hexachlororhodate(III) anion but did not isolate any tetrachloro complex produced by the secondary aquation. Since Fine[4] had found the *cis–trans* isomers of tetrachlorodiaquoruthenate(III) anion and Garner and co-workers[5] recently isolated the *cis–trans* isomers of tetrachlorodiaquoiridate(III) anion, both by ion-exchange chromatography, we decided that it should also be possible to obtain the *cis–trans* isomers of tetrachlorodiaquorhodate(III) anion by ion-exchange chromatography. Furthermore, the aquation of pentachloroaquorhodate(III) anion cannot be studied until the product of this aquation is identified.

Procedure and Results

The tetrachlorodiaquorhodate(III) anion was produced by two methods: the aquation of hexachlororhodate(III) anion and the chloride anation of hexaaquorhodium(III) cation. In the aquation method, 5 ml of a 50 mF solution of $Na_3RhCl_6 \cdot 12H_2O$ in 1 F $HClO_4$ was heated at about 100° for 1.5 min, and the resulting solution, after cooling in ice–water, was chromatographed on a 15-cm NO_3^- Dowex AG 1-X8 (100–200 mesh) column at 2°, using a jacketed condenser-type column with ice water circulated through the jacket. After eluting the cationic and neutral species completely with 0.001 F $HClO_4$, a pink band was eluted next by 0.3 F HNO_3. Only one pink band was eluted by 0.3 F HNO_3, and all fractions of this effluent gave similar visible absorption spectra. The Cl:Rh atom ratio of this complex, designated as complex X, was found to be essentially 4 (3.93–4.12 for seven different samples). Rh was determined spectrophotometrically by the method of Ayres, *et al.*,[6] and ligand chloride was determined by the method of Clarke[7] after decomposing the complex with excess NaOH.[8] Chromatography of the aquation solution on an HSO_4^- Dowex AG 1-X8 column at 2° gave the same result: one pink complex, which has essentially the same Cl:Rh atom ratio (4.01–4.10 for three different samples) and the same visible absorption spectrum as complex X, was eluted by 0.3 F H_2SO_4. The visible absorption spectrum of this complex was the same, within experimental error, both in the original effluent and in a solution made 6 F in HCl: λ_{max} 492 ± 2 and 392 ± 2 mμ (ϵ 101 and 113 M^{-1} cm^{-1}, $\epsilon_{392}/\epsilon_{492} = 1.12$) and λ_{min} 440 ± 2 mμ (ϵ 48.3 M^{-1} cm^{-1}).

In the chloride-anation method, about 0.3 g of hexaaquorhodium(III) perchlorate, prepared by the method of Ayres and Forrester,[9] was boiled in 2 F HCl until the color of the solution was changed from yellow to red.

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[1] (a) Abstracted in part from the M.A. thesis of K. L. Bridges, State College of Iowa, Cedar Falls, Iowa, July 1966; (b) NSF-AYI participant, 1965–1966.

[2] W. C. Wolsey, C. A. Reynolds, and J. Kleinberg, *Inorg. Chem.*, **2**, 463 (1963).

[3] W. Robb and G. M. Harris, *J. Am. Chem. Soc.*, **87**, 4472 (1965).

[4] D. A. Fine, U. S. Atomic Energy Commission Report UCRL-9050, 1960.

[5] C. S. Garner, private communications.

[6] G. H. Ayres, B. L. Tuffly, and J. S. Forrester, *Anal. Chem.*, **27**, 1742 (1955).

[7] F. E. Clarke, *ibid.*, **22**, 553 (1950).

[8] J. C. Chang and C. S. Garner, *Inorg. Chem.*, **4**, 209 (1965).

[9] G. H. Ayres and J. S. Forrester, *J. Inorg. Nucl. Chem.*, **3**, 365 (1957).