entropy in forming the compact chromate ions ($S^\circ = +9.2$ e.u.) from dichromate ions ($S^\circ = +70.5$ e.u.). Therefore the flow of charge toward one end of the transition-state complex (the "chromate end") must be hindered by a considerable degree of electrostriction. The larger (negative) value for ΔS_1° than ΔS^* must mean that the gain of a translational degree of freedom from the dissociation of the transition-state complex is offset by a considerable amount of electrostriction when the chromate ion is finally released. Similar considerations apply to the ammonia reaction. However, in this case an estimation of the standard entropy of the postulated intermediate ($NH_3 \cdot CrO_3$) must be made. We have used the equations

$$S^\circ_{NH_3 \cdot CrO_3} = S^\circ_{NH_3} + S^\circ_{CrO_3} - (\Delta S_t^\circ)_1$$
$$S^\circ_{H_2O \cdot CrO_3} = S^\circ_{H_2O} + S^\circ_{CrO_3} - (\Delta S_t^\circ)_2$$

where ΔS_t° is approximately the entropy of one translational degree of freedom.[22] We have made the reasonable assumption that $(\Delta S_t^\circ)_1 \approx (\Delta S_t^\circ)_2$ for these similar molecules and that $S^\circ_{H_2O \cdot CrO_3} \approx S^\circ_{H_2CrO_4}$, and this enables us to estimate $S^\circ_{NH_3 \cdot CrO_3} \approx 27$ e.u. It is obvious with all reactions examined that the large negative entropy of activation arises from an associated large entropy of formation of the intermediates which are postulated in the SN2 mechanism. Correlation with the over-all entropy of reaction is not possible.

Finally, we can compare the behavior of $Cr_2O_7^{2-}$ with the formally analogous $S_2O_7^{2-}$. Only recently[23,24] has the hydrolysis of pyrosulfate been measured ($S_2O_7^{2-} + H_2O \rightarrow 2H^+ + 2SO_4^{2-}$). The first-order rate constant at 20° (3.8×10^{-3} or 9.8×10^{-3} sec.$^{-1}$)[25] and the energy of activation (11.3[23] or 11.1[24]) are remarkably similar to those for dichromate hydrolysis. The reaction does not appear to have been studied at pH values higher than 10 so that the question of an OH^- catalyzed reaction analogous to $Cr_2O_7^{2-}$ remains unanswered at present.

P. M. proposes to study other bases and salt effects to elucidate further the mechanism of the dichromate base hydrolysis.

Acknowledgment.—We thank the Department of Scientific and Industrial Research for a grant (to P. M.).

[23] H. K. Hofmeister and J. R. Van Wazer, *Inorg. Chem.*, **1**, 811 (1962).

[24] E. Thilo and F. V. Lampe, *Z. anorg. allgem. Chem.*, **319**, 387 (1963); *Ber.*, **97**, 1775 (1964).

[25] There appears to be disagreement over the rate constant; however, there is known to be strong cationic catalysis and this may explain the differences.

CONTRIBUTION FROM THE CHEMICAL LABORATORY OF
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS

Mechanism of the Acid Hydrolysis of the Iodopentaaquochromium(III) Ion. Evidence for a *trans* Effect of Iodide in a Chromium(III) Complex

BY PETER MOORE, FRED BASOLO, AND RALPH G. PEARSON

Received September 2, 1965

Tracer studies with $H_2{}^{18}O$ in perchloric acid solutions have shown that the hexaaquochromium(III) ion produced from aquation of the iodopentaaquochromium(III) ion, $[CrI]^{2+}$, contains *two* labeled water molecules.

$$[Cr(H_2O)_5I]^{2+} + 2H_2{}^*O \rightarrow [Cr(H_2O)_4(H_2{}^*O)_2]^{3+} + H_2O + I^-$$

It has been shown that considerable exchange of *one* water molecule in $[CrI]^{2+}$ occurs prior to hydrolysis. These facts, plus our observation that the chloropentaaquochromium(III) ion, $[CrCl]^{2+}$, only undergoes very slow water exchange, lead us to suggest that iodide ion in $[CrI]^{2+}$ has a labilizing influence on the water molecule *trans* to it: *trans*-$[H_2OCr(H_2O)_4I] + H_2{}^*O \rightleftharpoons$ *trans*-$[H_2{}^*OCr(H_2O)_4I] + H_2O$. This mechanism can also account for a previous observation that more than 10% $[CrCl]^{2+}$ is formed when $[CrI]^{2+}$ is hydrolyzed in 1 *M* hydrochloric acid. Exchange of $H_2{}^{18}O$ with the complex $[Cr(H_2O)_5NO]^{2+}$ is also reported.

Introduction

It is known that iodide ion exhibits a *trans* effect in Pt(II) and Rh(III) complexes.[1] The possibility that a similar effect might occur in a chromium(III) complex such as $[CrI]^{2+}$[2] has not been investigated. However, recent observations by Ardon[3] that the acid hydrolysis of $[CrI]^{2+}$ in the presence of 1 *M* chloride or bromide ions produces more than 10% of the respective complex $[CrX]^{2+}$ ($X = Cl^-, Br^-$) in addition to $[Cr(H_2O)_6]^{3+}$ led us to suspect that iodide might have a strong *trans* effect in $[CrI]^{2+}$ also. If this were the case, we might expect reaction 1 to proceed at a rate comparable to or greater than the rate of hydrolysis (reaction 2). It would then be possible to explain

$$trans\text{-}[H_2OCr(H_2O)_4I]^{2+} + H_2{}^*O \underset{}{\overset{k_{H_2O}}{\rightleftharpoons}} trans\text{-}[H_2{}^*OCr(H_2O)_4I]^{2+} + H_2O \quad (1)$$

$$[Cr(H_2O)_4(H_2{}^*O)I]^{2+} + H_2{}^*O \xrightarrow{k} [Cr(H_2O)_4(H_2{}^*O)_2]^{3+} + I^- \quad (2)$$

---

[1] For a review of the *trans* effect in metal complexes see F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962); F. Basolo, E. J. Bounsall, and A. J. Poë [*Proc. Chem. Soc.*, 366 (1963)] discuss the *trans* effect of iodide in Rh(III).

[2] We shall abbreviate all [ligandpentaaquochromium(III)] complexes as $[CrX]^{2+}$ (X = ligand).

[3] M. Ardon, *Inorg. Chem.*, **4**, 372 (1965).

Ardon's observations by the following reaction scheme ($X^- = Cl^-, Br^-$)

$$[Cr(H_2O)_5I]^{2+} + X^- \overset{K}{\rightleftharpoons} X^-,[Cr(H_2O)_5I]^{2+} \text{ (ion pair)} \quad (3)$$

$$X^-,[Cr(H_2O)_5I]^{2+} \xrightarrow{k_{H_2O}} trans\text{-}[XCr(H_2O)_4I]^+ + H_2O \quad (4)$$

$$trans\text{-}[XCr(H_2O)_4I]^+ \xrightarrow{\text{fast}} [Cr(H_2O)_5X]^{2+} + I^- \quad (5)$$

It is not unreasonable to expect reaction 5 to be rapid compared with reaction 4 since by analogy *trans*-dichlorotetraaquochromium(III) ion, $[CrCl_2]^+$, hydrolyzes 15 times as fast as $[CrCl]^{2+}$ under similar conditions.[4,5] If reaction 5 proceeds *ca.* 15 times as fast as reaction 2,[5] it would be impossible to detect measurable amounts of the intermediate *trans*-$[CrClI]^+$.

The exchange of coordinated water molecules in $[Cr(H_2O)_6]^{3+}$ with solvent water only occurs over a period of days in perchloric acid at 25°.[6] Therefore, except for the possibility of a *trans* effect in $[CrI]^{2+}$, we might expect that the water molecules coordinated in this complex would only undergo exchange slowly.[7] Hence it is possible to test our proposals by means of tracer studies with $H_2{}^{18}O$ in acidic solutions. Reactions 1 and 2 were investigated by hydrolyzing $[CrI]^{2+}$ in 1 *M* $HClO_4$ containing $H_2{}^{18}O$ tracer and analyzing the product, $[Cr(H_2O)_6]^{3+}$, for labeled water content. The proposed reaction scheme of eq. 3–5 was examined by hydrolyzing $[CrI]^{2+}$ in 1 *M* HCl containing $H_2{}^{18}O$ tracer, extracting the $[CrCl]^{2+}$ produced by ion exchange, and examining this for ^{11}O enriched water content. Reaction 1 was also examined with $H_2{}^{18}O$ tracer in 1 *M* $HClO_4$ without extensive hydrolysis, and the complexes $[CrCl]^{2+}$ and $[CrNO]^{2+}$ were examined in the same way.

Experimental Section

Materials.—Preparations of the solid complex sulfates used in this study have been described previously.[8] ^{18}O-labeled water (1.55 atom %) was obtained from Yeda Research and Development Company Ltd. at the Weizmann Institute of Science, Rehovoth, Israel. Guanidine hydrochloride (Eastman Kodak) was recrystallized once from methanol and dried in an oven at 110° before use.

Preparation of 1 *M* $HClO_4$ Containing $H_2{}^{18}O$ Tracer.—A solution of 1 *M* $HClO_4$ in 1.44 ± 0.01 atom % ^{18}O-labeled water was prepared by diluting 2.14 ml. of 70% $HClO_4$ to 25 ml. with 1.55 atom % ^{18}O-labeled water. The solution was allowed to stand for 1 week to allow the perchlorate oxygen atoms to equilibrate with those of the $H_2{}^{18}O$. The acidity was checked by titrating 1 ml. of this solution with 0.1 *M* NaOH, and the ^{18}O content of the water was measured after equilibration by distilling some water from a sample on a *dry* vacuum line[9] and treating this as described below.

Preparation of 1 *M* HCl Containing $H_2{}^{18}O$ Tracer.—A solution of 1 *M* HCl in 1.44 ± 0.01 atom % ^{18}O-labeled water was prepared by diluting 2.06 ml. of concentrated HCl (12.1 *M*) to 25 ml. with 1.55 atom % ^{18}O-labeled water. The acidity was checked by titrating 1 ml. of this solution with 0.1 *M* NaOH and the ^{18}O content obtained by adding *ca.* 20 mg. of the solution to dry guanidine hydrochloride (*ca.* 20 mg.) and treating this as described below.

Conversion of H_2O to CO_2 for ^{18}O Analysis.—Approximately equal weights of water and guanidine hydrochloride (20 mg.), frozen at −180°, were sealed under high vacuum (10^{-5} mm. pressure) in a U-tube fitted with a break-seal. The U-tube and contents were then heated to 260° in a furnace for 8 hr. to convert the H_2O to CO_2 and NH_3. This procedure and the extraction of the CO_2 from NH_3 have been described elsewhere.[10] Unlike previous workers,[10] larger quantities of H_2O and guanidine hydrochloride were used since these were found to give better size samples of CO_2 for analysis with our mass spectrophotometer. The CO_2 samples were analyzed with a Consolidated Electronic Corp. mass spectrometer (Model 130), and the heights of the peaks of m/e 44, 45, and 46 were measured. The ratio, $R = 46/(44 + 45)$, was taken and the atom % ^{18}O in the sample (n) obtained from the formula[11] $n = 100R/2(1 + R)$. Duplicate samples were run when possible to check reproducibility.

Tracer Studies. (a) **Hydrolysis of $[CrI]^{2+}$ in 1 *M* $HClO_4$ with $H_2{}^{18}O$ Tracer.**—A 5-ml. solution of 0.2 *M* $[CrI]^{2+}$ was prepared by dissolving $[Cr(H_2O)_5I]SO_4 \cdot H_2O$ (0.3831 g.) in 1 *M* $HClO_4$ containing $H_2{}^{18}O$ tracer. This solution was kept at 25.0° in the dark[13] for 9 hr. (5–6 times the hydrolysis half-life[5]). The product, $[Cr(H_2O)_6]^{3+}$, was precipitated as the phosphate and dried by the methods described by Hunt and Plane.[14] There was no trace of unhydrolyzed $[CrI]^{2+}$ in the precipitate obtained. (Reaction of a portion of the precipitate with HIO_3 in H_2SO_4 gave no trace of iodine.) Dried $[Cr(H_2O)_6]PO_4$ (*ca.* 70 mg.) was heated under high vacuum[9] (10^{-5} mm. pressure) at 140–150° for 20 min.[6,12] and the liberated water trapped onto guanidine hydrochloride (*ca.* 20 mg.) for conversion to CO_2 and ^{18}O analysis as already described. A glass wool plug was placed in the vacuum line above the sample of $[Cr(H_2O)_6]PO_4$ to prevent this from shooting into the guanidine hydrochloride. This plug was carefully dried (before heating the phosphate) by flaming it with a bunsen burner while under high vacuum.

(b) **Hydrolysis of $[CrI]^{2+}$ in 1 *M* HCl with $H_2{}^{18}O$ Tracer.**—A 20-ml. solution of 0.2 *M* $[CrI]^{2+}$ was prepared by dissolving $[Cr(H_2O)_5I]SO_4 \cdot H_2O$ (1.4604 g.) in 1 *M* HCl containing $H_2{}^{18}O$ tracer. This solution was kept at 25.0° in the dark[13] for 9 hr. Using the known rate constants[3,5] we calculate that after this time the solution contains approximately 1% $[CrI]^{2+}$, 14% $[CrCl]^{2+}$, and 85% $[Cr(H_2O)_6]^{3+}$. The unhydrolyzed $[CrI]^{2+}$ was removed, together with free iodide, by adding a slight excess of HIO_3 (1.48 g.), and the liberated iodine was extracted with carbon tetrachloride. This procedure converts the unreacted $[CrI]^{2+}$ rapidly to $[Cr(H_2O)_6]^{3+}$.[15] The solution of $[CrCl]^{2+}$ and $[Cr(H_2O)_6]^{3+}$ was then placed on a Dowex 50W-X8 (100–200 mesh) cation-exchange column cooled to below 1° and the $[CrCl]^{2+}$ eluted with ice-cold 0.5 *M* H_2SO_4. The eluent of $[CrCl]^{2+}$ was concentrated by the method described previously[8] and the $[CrCl]^{2+}$ was eventually precipitated as the sulfate and dried overnight in a vacuum desiccator over $CaCl_2$; yield *ca.* 50 mg. Dry $[Cr(H_2O)_5Cl]SO_4 \cdot H_2O$ (*ca.* 50 mg.) was heated under high vacuum at 110–120° for 20 min. and the liberated water trapped onto guanidine hydrochloride (*ca.* 10 mg.). ^{18}O analysis was then carried out as already described.

(c) **Exchange of $H_2{}^{18}O$ with $[CrI]^{2+}$.**—Separate experiments were run for 15, 60, and 100 min. A 5-ml. solution of 0.4 *M* $[CrI]^{2+}$ was prepared in each case by dissolving $[Cr(H_2O)_5I]SO_4 \cdot H_2O$ (0.7662 g.) in 1 *M* $HClO_4$ containing $H_2{}^{18}O$, and the solution was kept at 25.0° in the dark for the requisite time. Then the

---

(4) C. W. Meridith, W. D. Mathews, and E. F. Orlemann, *Inorg. Chem.*, **3**, 320 (1964).

(5) T. W. Swaddle and E. L. King, *ibid.*, **4**, 532 (1965).

(6) J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954).

(7) The effect of reduced charge in $[CrI]^{2+}$ compared with $[Cr(H_2O)_6]^{3+}$ should not be very important. Thus, water molecules coordinated in $[CrCl]^{2+}$ only undergo exchange with solvent water very slowly (this work).

(8) P. Moore and F. Basolo, *Inorg. Chem.*, **4**, 1670 (1965).

(9) The vacuum line was always dried before use by flaming with a bunsen burner while evacuating. Apiezon T grease was used.

(10) P. D. Boyer, D. J. Graves, C. H. Suelter, and M. E. Dempsey, *Anal. Chem.*, **33**, 1906 (1961).

(11) The formula given in ref. 12 is wrong.

(12) G. Gordon [*Inorg. Chem.*, **2**, 1278 (1963)] uses a lower temperature than Hunt and Plane.[6]

(13) The hydrolysis is photoaccelerated; see ref. 5.

(14) See ref. 6. Less than 1% induced exchange results from this procedure.

(15) J. H. Espenson, *Inorg. Chem.*, **3**, 968 (1964).

solution was quickly frozen by cooling in a Dry Ice–acetone bath for a few seconds. The frozen mixture was allowed to warm up to 0° and the unhydrolyzed $[CrI]^{2+}$ was extracted by ion exchange (below 1°) and precipitated as the sulfate by methods already described.[8] A sample of the product, $[Cr(H_2O)_5I]SO_4 \cdot H_2O$ (*ca.* 0.1 g.) was heated under high vacuum at 100–110° for 20 min. to liberate water which was trapped onto guanidine hydrochloride (*ca.* 20 mg.) as described before. It was found that some iodine distilled over with the water, presumably because of the formation of HI and the decomposition of this. The iodine was removed by allowing the frozen water–iodine at $-180°$ to slowly warm while evacuating. The iodine sublimed off well before the ice distilled. Traces of iodine did not interfere with the conversion of H_2O to CO_2.

(d) **Exchange of $H_2{}^{18}O$ with $[CrCl]^{2+}$.**—The procedure was the same as that described for the iodo complex [procedure (c)]. Runs were carried out for 1 and 4 hr. In the former case ion-exchange extraction was not necessary because there is less than 1% hydrolysis in this time.[5] However, in this case it was necessary to recrystallize the precipitated complex from 0.5 *M* H_2SO_4 containing water of natural abundance to prevent the water of crystallization from being labeled. The $[Cr(H_2O)_5Cl]SO_4 \cdot H_2O$ was treated as described in procedure (b) for conversion of its water content to CO_2, although twice as much complex and guanidine hydrochloride were used to give larger yields of CO_2.

(e) **Exchange of $H_2{}^{18}O$ with $[CrNO]^{2+}$.**—Runs were carried out for 15 and 60 min. The method was identical with procedure (d). Ion-exchange extraction was not necessary since there is no hydrolysis in this time.[16] The precipitated complex was recrystallized from ice-cold 0.5 *M* H_2SO_4 containing water of natural abundance (see reason above) and then heated *in vacuo* to liberate bound water which was trapped onto guanidine hydrochloride as described for the chloro complex. A blank run was carried out by heating a sample of the complex before exchange to check that NO was not evolved with the H_2O, since NO might have interfered with the CO_2 mass spectral analysis because of possible NO_2 formation. However, the CO_2 analyzed was of natural abundance and contained no NO_2.

Results

The rate and mechanism of the acid hydrolysis of $[CrI]^{2+}$ has received considerable attention recently.[3,5,15] All of these studies showed the rate law to be $-d[CrI^{2+}]/dt = k[CrI^{2+}]$, where $k = k_0 + k_a/[H^+]$; k_0 and k_a are acid-independent and acid-dependent rate constants, respectively. The acid-dependent path is attributed to the very reactive species $[Cr(H_2O)_4(OH)I]^+$. At 30° in 1 *M* $HClO_4$ the reaction still proceeds *ca.* 36% by the acid-dependent path.

Hydrolysis of $[CrI]^{2+}$ in 1 *M* $HClO_4$ Containing $H_2{}^{18}O$ Tracer.—If reaction 1 proceeds at a rate comparable to or greater than reaction 2, then the $[Cr(H_2O)_6]^{3+}$ produced when $[CrI]^{2+}$ is hydrolyzed in $H_2{}^{18}O$ should contain between one and two labeled water molecules depending upon the relative rates of exchange (k_{H_2O}) and hydrolysis (k). If $k_{H_2O} \gg k$ then the product would be $[Cr(H_2O)_4(H_2{}^*O)_2]^{3+}$.

TABLE I

RATE OF EXCHANGE OF $H_2{}^{18}O$ WITH $[CrX]^{2+}$ IN 1 *M* $HClO_4$ AT 25.0° ($I = 2.6$)

Run	X^-	Time, min.	CO_2 mass spectral peaks, m/e 44	45	45	10^3R[a]	n_p,[b] %	x[c]
1	I^-	15	5040	56.8	25.3	5.16	0.257	0.28
2	I^-	50	2409	27.4	15.9	6.53	0.324	0.60
3	I^-	60	5520	62.5	39.0	6.99	0.347	0.66
4	I^-	100	5390	60.7	40.1	7.35	0.365	0.80
5	Cl^-	60	3520	39.7	14.8	4.16	0.207	0.03
6	Cl^-	240	5260	60.1	27.1	5.09	0.253	0.26
7	NO^-	15	4300	50.7	33.4	7.68	0.381	0.88
8	NO^-	60	3990	47.6	70.9	17.56	0.863	3.20

[a] $R = 46/(44 + 45)$. [b] n_p = atom % ^{18}O in product $= 100R/2(1 + R)$. [c] x = fraction of a water molecule to exchange; calculated from the equation $n_p = [xn_e + (6 - x)n_a]/6$, where n_e and n_a are atom % ^{18}O in the enriched solvent water and in water of natural abundance, respectively; $n_e = 1.44\%$; $n_a = 0.20\%$. It is assumed that all six H_2O molecules are randomly released on heating $[Cr(H_2O)_5X]SO_4 \cdot H_2O$.

If x is the number of ^{18}O-enriched water molecules to enter the product, $[Cr(H_2O)_6]^{3+}$, and if n_p is the atom % ^{18}O found in this product, $n_p = [xn_e + (6 - x)n_a]/6$, where n_e and n_a are the atom % ^{18}O in enriched solvent water and in water of natural abundance, respectively. The quantity n_e does not vary significantly during the course of the experiment and was determined by the method already described; found, $n_e = 1.44\%$. n_a was determined by hydrolyzing a sample of $[CrI]^{2+}$ in 1 *M* $HClO_4$ containing water of natural abundance. The $[Cr(H_2O)_6]^{3+}$ was then examined for ^{18}O content in the usual way; found, $n_a = 0.20\%$. This value is in good agreement with published values. Hence, for x = 1, 2, or 3 the calculated values of n_p under the conditions of our experiment are 0.41, 0.61, and 0.82%, respectively. In each of four experiments run for 9 hr. at 25° the observed value of n_p was $0.64 \pm 0.01\%$.[17] The calculated value of x, the number of labeled water molecules in the product, is therefore 2.1 ± 0.05. This value is in excellent agreement with reactions 1 and 2 if $k_{H_2O} \gg k$. A value of x slightly greater than 2 is reasonable because of the subsequent slow exchange

$$[Cr(H_2O)_4(H_2{}^*O)_2]^{3+} + H_2{}^*O \rightleftharpoons [Cr(H_2O)_3(H_2{}^*O)_3]^{3+} + H_2O$$

If one assumes this reaction proceeds at two-thirds the rate of exchange of all six water molecules,[6] the calculated value of x is *ca.* 2.05 under the conditions of our experiment (assuming $k_{H_2O} \gg k$).

Exchange of $H_2{}^{18}O$ with Coordinated Water Molecules in $[CrI]^{2+}$.—From the above results it would appear that iodide ion does have a strong labilizing influence on *one* water molecule in $[CrI]^{2+}$, and this is most likely because of a *trans* effect of iodide. To find out how rapidly this reaction occurs $[CrI]^{2+}$ was allowed to hydrolyze at 25° in 1 *M* $HClO_4$ (containing $H_2{}^{18}O$ tracer) for various times after which the reaction was frozen and the unhydrolyzed $[CrI]^{2+}$ extracted by ion exchange below 1°. The $[CrI]^{2+}$ was precipitated[8] as the complex sulfate, $[Cr(H_2O)_5I]SO_4 \cdot H_2O$, and this was analyzed for its $H_2{}^{18}O$ content. The results for exchange after various times are shown in Table I (runs 1–4).

A plot of log $(1 - x)$ against time (t) gives a reasonable straight line which passes through the point $x = 0$ when $t = 0$. The slope of this line gives $k_{H_2O} = 2.7 \times 10^{-4}$ sec.$^{-1}$. Hence, at 25° it would appear that the half-life for the exchange of one water molecule in

---

[16] There was no change in the spectrum of $[CrNO]^{2+}$ in 1 *M* $HClO_4$ after 6 hr. at 25° in the dark.

[17] Some of our CO_2 samples were checked with a high resolution, isotope ratio mass spectrometer by R. Kent Murmann (Argonne National Laboratory), whom we thank. Agreement was better than 2% of our value in this case (0.01 in n_p).

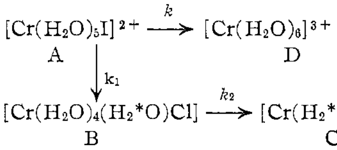
$[CrI]^{2+}$ is *ca.* 43 min. However, since the half-life for hydrolysis under similar conditions is *ca.* 101 min., it is apparent that the measured value of k_{H_2O} is too small to account for our previous results, which show $k_{H_2O} \gg k$. If our measured value of k_{H_2O} were correct, then in our previous experiment the product $[Cr(H_2O)_6]^{3+}$ could only contain *ca.* 1.7 labeled water molecules and not 2.1 as measured. A value of $k_{H_2O} = 1.2 \times 10^{-3}$ sec.$^{-1}$ ($k_{H_2O} \sim 10k$) would be needed to account for the 2.1 figure.

There are several possible reasons for this discrepancy. During the extraction of $[CrI]^{2+}$ by ion exchange and its subsequent slow precipitation as the sulfate, the labeled water molecule could reexchange to some extent with water of natural abundance. In all cases the separation procedure took more than 1 hr. although it was carried out at 0–5° to minimize the possible reexchange. It is also possible that induced exchange could occur on the ion-exchange column. Another possible error occurs in calculating the values of x. We have assumed that upon heating $[Cr(H_2O)_5I]SO_4 \cdot H_2O$ under high vacuum all six water molecules are randomly released. (Not all the water is evolved.) This assumption is probably not justified since it is likely that the water of crystallization is released in preference to the other five coordinated water molecules. The water of crystallization was not labeled since the $[CrI]^{2+}$ was eluted from the ion-exchange column with acid containing water of natural abundance. Also, upon heating $[Cr(H_2O)_6]PO_4$ under high vacuum at temperatures up to 150°, it is known that the phosphate oxygen atoms do not exchange with those of the coordinated water.[6,12] However, we have no evidence that heating $[Cr(H_2O)_5I]SO_4 \cdot H_2O$ does not cause the oxygen atoms of the sulfate to exchange with those of the water molecules. Unfortunately, we were unable to precipitate $[CrI]^{2+}$ with other, more suitable anions to check this point.

In view of all these possible sources of error we prefer to regard our measured value of k_{H_2O} as a minimum rate constant, since all the likely errors would tend to produce a value smaller than the true rate constant. In any case it is correct to say that there is good evidence for exchange of up to one water molecular prior to hydrolysis. We believe $1.2 \times 10^{-3} > k_{H_2O} > 2.7 \times 10^{-4}$ sec.$^{-1}$.

Hydrolysis of $[CrI]^{2+}$ in 1 *M* HCl with $H_2{}^{18}O$ Tracer.—$[CrI]^{2+}$ was hydrolyzed at 25° for 9 hr. in 1 *M* HCl with $H_2{}^{18}O$ present. After this time the solution contains $[CrI]^{2+}$ (*ca.* 1%), $[CrCl]^{2+}$ (*ca.* 14%), and $[Cr(H_2O)_6]^{3+}$ (*ca.* 85%) calculated from the known rate constants.[3,5] Unhydrolyzed $[CrI]^{2+}$ was removed rapidly by oxidation to $[Cr(H_2O)_6]^{3+}$ with HIO_3.[15] The $[CrCl]^{2+}$ was then extracted from the $[Cr(H_2O)_6]^{3+}$ with HIO_3.[15] The $[CrCl]^{2+}$ was then extracted from the $[Cr(H_2O)_6]^{3+}$ by ion exchange and precipitated as the sulfate. The water in the $[Cr(H_2O)_5Cl]SO_4 \cdot H_2O$ was examined for its $H_2{}^{18}O$ content in the usual way; found, $n_p = 0.55\%$. As before, in this experiment $n_e = 1.44\%$ and $n_a = 0.20\%$ (see definition of symbols in Table I). If we assume that all six water molecules in $[Cr(H_2O)_5Cl]SO_4 \cdot H_2O$ are randomly released upon heating this solid under high vacuum (see previous discussion), $n_p = [xn_e + (6 - x)n_a]/6$, where x is the number of labeled water molecules in the product $[CrCl]^{2+}$. Hence, the experimental value of x is *ca.* 1.7 ($n_p = 0.55\%$).

Unfortunately this experiment is complicated by the subsequent slow exchange B → C in the following reaction scheme.



$$\begin{tikzcd}
\underset{A}{[Cr(H_2O)_5I]^{2+}} \arrow[r, "k"] \arrow[d, "k_1"] & \underset{D}{[Cr(H_2O)_6]^{3+}} \\
\underset{B}{[Cr(H_2O)_4(H_2{}^*O)Cl]} \arrow[r, "k_2"] & \underset{C}{[Cr(H_2{}^*O)_5Cl]^{2+}}
\end{tikzcd}$$

We have assumed the mechanism is that given by eq. 3–5 and have made an estimate of the rate of reaction B → C. If we equate k_2 to four-fifths the rate constant for exchange of all five water molecules in B, k_2 is *ca.* 3.07×10^{-6} sec.$^{-1}$ at 25° (see below). Also, at 25° $k = k_0 + k_a/[H^+]$ where $k_0 = 8.41 \times 10^{-5}$ sec.$^{-1}$ and $k_a = 3.43 \times 10^{-5}$ *M* sec.$^{-1}$.[5] Hence, in 1 *M* H^+, $k = 1.18 \times 10^{-4}$ sec.$^{-1}$. At 30°, Ardon has shown[3] $k_1/k_0 = 0.24$. If we assume this is approximately the ratio of these rate constants at 25°, $k_1 = 2.02 \times 10^{-5}$ sec.$^{-1}$ at 25° and in 1 *M* Cl^-. It is easy to show that if the initial concentration of $[CrI]^{2+}$ is $[A]_0$, t is time, and $[B] = [C] = [D] = 0$ at $t = 0$, then for the above reaction scheme

$$[A]/[A]_0 = e^{-(k_1+k)t}$$

$$[B]/[A]_0 = k_1[e^{-(k_1+k)t} - e^{-k_2t}]/(k_2 - k_1 - k)$$

$$[C]/[A]_0 = k_1/(k_1 + k)\{1 + [(k_1 + k)e^{-k_2t} - k_2e^{-(k_1+k)t}]/(k_2 - k_1 - k)\}$$

$$[D]/[A]_0 = k/(k_1 + k)[1 - e^{-(k_1+k)t}]$$

Using these equations and the rate constants already mentioned, we calculate that after 9 hr. $[A]/[A]_0 = 0.010$, $[B]/[A]_0 = 0.133$, $[C]/[A]_0 = 0.011$, $[D]/[A]_0 = 0.845$. Hence, with this reaction scheme the calculated value of x, the number of moles of labeled water per mole of $[CrCl]^{2+}$, is $x = ([B] + 5[C])/([B] + [C]) =$ *ca.* 1.3. The fact that the experimental value of x (*ca.* 1.7) is larger than the calculated value (*ca.* 1.3) would suggest that our estimate of k_2 is too small. This is possible since our measured rate of exchange of $H_2{}^{18}O$ with $[CrI]^{2+}$ was also too small. Also, the nature of the experiment makes the estimation of $x = 1.7$ only a rough figure.

Exchange of $H_2{}^{18}O$ with Coordinated Water Molecules in $[CrCl]^{2+}$.—An estimate of the rate of this reaction was made as a control for the previous experiment. It was also of interest to compare this rate with the known rate of exchange of solvent water with coordinated water molecules in $[Cr(H_2O)_6]^{3+}$. It was not expected that chloride ion would have a significant *trans* effect and any differences in the exchange rate in $[CrCl]_2^+$ compared with $[Cr(H_2O)_6]^{3+}$ we would attribute to the differences in the charge on these cations.

The procedure was similar to that described for the iodo complex. Runs were carried out at 25°, for 1 and

4 hr. in 1 *M* $HClO_4$, and the results are summarized in Table I (runs 5 and 6). A plot of log $(5 - x)$ with time (t), including the point $x = 0$ at $t = 0$, gives an approximate value for the rate constant of 3.8×10^{-6} sec.$^{-1}$. This is the rate at which all five coordinated water molecules exchange. Hence, the rate constant for release of *one* water molecule is *ca.* 7.6×10^{-7} sec.$^{-1}$. The rate constant[18] for release of *one* water molecule in $[Cr(H_2O)_6]^{3+}$ is *ca.* 4.5×10^{-7} sec.$^{-1}$ at 25°. Hence, it would appear that the reduced charge in $[CrCl]^{2+}$ compared with $[Cr(H_2O)_6]^{3+}$ does not have any large effect on the rate of water exchange.

Exchange of $H_2{}^{18}O$ with Coordinated Water Molecules in $[CrNO]^{2+}$.—The complex $[CrNO]^{2+}$ was first prepared and isolated by Ardon and Herman.[19] They suggest this is a nitroso complex of Cr(III) with NO^-. There is no evidence to support this particular formulation and it could also be a nitrosyl containing Cr(I) and NO^+. There is evidence that the complex $[Cr(CN)_5NO]^{3-}$ is a nitrosyl of Cr(I).[20]

The spectrum of $[CrNO]^{2+}$ is unusual, being quite unlike the usual spectra of Cr(III) complexes. The details of the spectrum have been reported elsewhere.[8]

Although the composition of $[CrNO]^{2+}$ is not known, it was nevertheless of interest to study the lability of the coordinated water molecules in this complex for comparison with the results for $[CrI]^{2+}$ and to look for a possible *trans* effect of the NO group. The procedure was the same as that employed for the chloro complex. Runs were carried out for 15 and 60 min. and the results are collected in Table I (runs 7 and 8). The reaction is quite rapid and more than three water molecules exchange in 1 hr. A plot of log $(5 - x)$ against time gives a reasonable straight line passing through the point $x = 0$ at $t = 0$, from which we calculate a rate constant for the exchange of all five water molecules of *ca.* 2.9×10^{-4} sec.$^{-1}$.

It would appear that the water molecules are much more labile in this complex than in the halogeno complexes studied. Furthermore, it is not a simple *trans* effect since more than one water molecule exchanges. This behavior can be understood if this is a Cr(I) complex. Such a d^5 system might be expected to be more labile than the very stable d^3 system of Cr(III) complexes because of charge and crystal field effects.[21] However, it is also possible that this is a Cr(III) complex which in the activation process for water exchange undergoes electron transfer from the NO^- group to become effectively Cr(I).

Discussion

Ardon has shown[3] that hydrolysis in the presence of 1 *M* Cl^- or Br^- ions produces, by the acid-independent path, more than 10% of the respective complex $[CrX]^{2+}$ $(X^- = Cl^-, Br^-)^2$ in addition to $[Cr(H_2O)_6]^{3+}$. Since anation of $[Cr(H_2O)_6]^{3+}$ is known to be very slow,[22] Ardon suggests that $[CrX]^{2+}$ is formed by competition of X^- with H_2O for a five-coordinate intermediate, $[Cr(H_2O)_5]^{3+}$, produced when $[CrI]^{2+}$ dissociates, *viz.*

$$[Cr(H_2O)_5I]^{2+} \xrightleftharpoons{k} [Cr(H_2O)_5]^{3+} + I^- \qquad (6)$$

$$[Cr(H_2O)_5]^{3+} + X^- \longrightarrow [Cr(H_2O)_5X]^{2+} \; (X^- = Cl^-, Br^-) \qquad (7)$$

$$[Cr(H_2O)_5]^{3+} + H_2O \longrightarrow [Cr(H_2O)_6]^{3+} \qquad (8)$$

We propose an alternative explanation with reactions 1–5 in which iodide exhibits a strong labilizing influence on a coordinate water molecule in $[CrI]^{2+}$. We have tested our proposals and compared them with those of Ardon by means of tracer studies described here in perchloric and hydrochloric acid solutions containing $H_2{}^{18}O$. For example, if only reactions 6–8 were operating, the product of hydrolysis of $[CrI]^{2+}$ in $H_2{}^{18}O$ would be $[Cr(H_2O)_5(H_2{}^*O)]^{3+}$ instead of the observed $[Cr(H_2O)_4(H_2{}^*O)_2]^{3+}$. The $[CrCl]^{2+}$ produced by hydrolysis of $[CrI]^{2+}$ in the presence of 1 *M* HCl in labeled water would contain only $5[C]/([B] + [C])$ molecules of labeled water, or 0.4 molecule compared to 1.7 observed.

The sequence of reactions, 6–8, cannot be entirely excluded, however. If we add to them the demonstrated exchange reaction (1), then it is possible to account for all of the tracer studies. In a previous paper[23] reasons were cited for believing that five-coordinate species such as $[Co(NH_3)_5]^{3+}$ and $[Cr(H_2O)_5]^{3+}$ do not exist long enough to discriminate in their reactions. In this paper we have shown that the formation of $[CrCl]^{2+}$ during the hydrolysis of $[CrI]^{2+}$ in hydrochloric acid is not compelling evidence for the existence of free $[Cr(H_2O)_5]^{3+}$. An alternative mechanism, based on the demonstrated *trans* effect of the iodo ligand, is presented.

Ardon observed[3] that aquation of $[CrI]^{2+}$ was some 15% faster in the presence of 1 *M* Br^- and Cl^- than in the presence of an equal amount of I^-. This was attributed to mass law retardation of reaction 6. It could equally well be explained by a catalysis of aquation in the presence of Br^- and Cl^- by the occurrence of reactions 3–5. Neither argument is strong since the changes in rates are very small and specific salt effects in these 1 *M* solutions should be considerable.

The value of k_1, the pseudo-first-order rate constant in the alternate reaction scheme above, should be equal to $k_{H_2O}K[Cl^-]f/(1 + K[Cl^-])$ where K is the association constant for the ion pair, $[Cl^-, CrI^{2+}]$, k_{H_2O} is the rate constant for water exchange (reaction 4, $X^- = Cl^-$), and f is the probability that water loss will lead to chloride ion interchange.[24] The values of $k_1 = 2.0 \times 10^{-5}$ sec.$^{-1}$ and $1.2 \times 10^{-3} > k_{H_2O} > 2.7 \times 10^{-4}$ sec.$^{-1}$ are not unreasonable. Values of K for ions such as $[CrCl]^{2+}$ and Cl^- are equal to about 10.[25] Hence, values of f are in the range of 0.02–0.10, which is less than unity. In the anation of $[Cr(H_2O)_6]^{3+}$ by Cl^-,[22]

---

[18] This rate constant was extrapolated to this temperature from the results of Hunt and Plane.[6] $[H^+] = 0.42$, $I = 2.97$.

[19] M. Ardon and J. I. Herman, *J. Chem. Soc.*, 507 (1962).

[20] W. P. Griffith, J. Lewis, and G. Wilkinson, *ibid.*, 872 (1959).

[21] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 109.

[22] R. J. Baltisberger and E. L. King, *J. Am. Chem. Soc.*, **86**, 795 (1964).

[23] R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **3**, 1334 (1964).

[24] C. H. Langford, *ibid.*, **4**, 265 (1965).

[25] D. W. Archer, D. A. East, and C. B. Monk, *J. Chem. Soc.*, 720 (1965).

and in the anation of $[Co(NH_3)_5H_2O]^{3+}$ by a series of univalent anions,[26] the values of f needed are all in the range 0.1–0.2.

Acknowledgments.—This work was supported by the U. S. Atomic Energy Commission, COO-1087-92. We wish to thank Drs. R. K. Murmann and J. Phillipson and Mr. R. M. Sherrill for assistance with mass spectrometer measurements.

[26] References 24, 25, and A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

Studies of Ligand Exchange Reactions between Zirconium and Hafnium Chelates by Nuclear Magnetic Resonance[1]

BY A. C. ADAMS[2] AND EDWIN M. LARSEN

Received July 16, 1965

The n.m.r. spectra of benzene solutions containing mixtures of the metal acetylacetonates, M(acac)$_4$, and trifluoroacetylacetonates, M(tfac)$_4$, of zirconium and hafnium show six resolved methyl–proton resonances, which have been assigned to the five species M(acac)$_n$(tfac)$_{4-n}$. The exchange deviates somewhat from random exchange with the intermediate species favored. Equilibrium quotients (33°) for the formation of M(acac)$_3$(tfac), M(acac)$_2$(tfac)$_2$, and M(acac)(tfac)$_3$ from the parent compounds are $K_1 = 24$ (19), $K_2 = 52$ (41), and $K_3 = 18$ (15), respectively, where the values for hafnium are in parentheses. The shape of the spectra change with solvent, with the methyl–proton resonances not completely resolved in carbon tetrachloride, pyridine, nitrobenzene, chlorobenzene, and bromobenzene owing to a decrease in the separation of the resonances. Also, the chemical shifts of the methyl–proton resonances in these solvents are inverted compared to benzene. At higher temperature the resonances merge because the rate of exchange increases. The zirconium complexes exchange faster than the hafnium compounds, but the rate of exchange of the trifluoroacetylacetone and acetylacetone ligands is the same.

Ligand exchange occurs in solutions containing metal acetylacetonates, M(acac)$_4$, and metal trifluoroacetylacetonates, M(tfac)$_4$, where the metal is zirconium or hafnium. The equilibrium mixtures contain the five compounds, M(acac)$_4$, M(acac)$_3$(tfac), M(acac)$_2$(tfac)$_2$, M(acac)(tfac)$_3$, and M(tfac)$_4$. These species have been detected by using proton n.m.r. techniques.[1] The present paper reports the results of a more detailed study of these equilibrium systems.

Since our original note several papers have appeared in which n.m.r. is used to study the complex equilibrium mixtures resulting from ligand-exchange reactions.[3–5] These papers deal with the exchange of unidentate ligands, while the present paper is concerned with the exchange of bidentate ligands. However, the same general methods are used in both cases, and the papers in ref. 3–5 should be consulted for a more detailed discussion of the use of n.m.r. in characterizing equilibrium mixtures.

Experimental Section

The n.m.r. spectra were obtained with a Varian Associates Model A-60 spectrometer using standard Varian accessories. The chemical shifts were measured in p.p.m. relative to tetramethylsilane as an internal standard. Negative values of the chemical shift refer to resonances downfield from the tetramethylsilane resonance. The resonance areas were measured by tracing the spectra on graph paper and "counting squares." The areas were measured by this method rather than by the integrator circuit on the spectrometer because the resonances are very close together. The average separation of the methyl resonances is only 0.042 p.p.m.

The complexes were prepared by a previously reported method.[6] The purity of the complexes was checked by metal analyses and melting points.[6] The solvents were distilled and stored over drying agents (sodium metal, calcium hydride, or anhydrous magnesium sulfate). The n.m.r. samples were prepared by accurately weighing the metal complexes, M(acac)$_4$ and M(tfac)$_4$, to give a total weight of about 0.1 g. The solids were dissolved in 1.0 ml. of solvent. The nitrobenzene and carbon tetrachloride solutions contained about 0.05 g. of the metal complexes in 1 ml. of solvent because of the low solubilities of the compounds.

Discussion

Exchange in Benzene Solutions.—The n.m.r. spectra of benzene solutions containing mixtures of the zirconium or hafnium compounds have six resolved methyl resonances. The resonances have been assigned by considering the variation in the area of a given resonance as the relative concentration of the acetylacetone and trifluoroacetylacetone ligands is changed.[1] The mole fractions[7] of the different species are calculated from the areas of the resonances. A plot of the mole

---

[1] Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964. For a preliminary communication see A. C. Adams and E. M. Larsen, *J. Am. Chem. Soc.*, **85**, 3508 (1963).

[2] National Science Foundation predoctoral fellow Sept. 1961–Jan. 1965.

[3] M. D. Rausch and J. R. Van Wazer, *Inorg. Chem.*, **3**, 761 (1964).

[4] K. Moedritzer and J. R. Van Wazer, *ibid.*, **3**, 268 (1964).

[5] K. Moedritzer and J. R. Van Wazer, *ibid.*, **3**, 139 (1964).

[6] E. M. Larsen, G. Terry, and J. Leddy, *J. Am. Chem. Soc.*, **75**, 5107 (1953).

[7] The mole fractions are calculated without considering the solvent; in this sense, mole fraction refers to the fraction of the metal which is in a specified species.