activation parameters are not available. If we choose $Cr(NH_3)_5Cl^{2+} + Cr^{2+}$ as a model reaction, it is possible to estimate values for the desired comparison. The reaction $Cr(NH_3)_5Cl^{2+} + Cr^{2+}$ has $\Delta H^* = 11$ kcal. mole^{-1} and $\Delta S^* = -23$ e.u.; its rate at 0° is *ca.* 700-fold lower than that of $Cr(OH_2)_5Cl^{2+} + Cr^{2+}$. If we assume that the rate factor resides exclusively in the entropy term,[26] ΔS^* for $Cr(OH_2)_5Cl^{2+} + Cr^{2+}$ becomes -10 e.u. Since the values of ΔS^* for $CrCl^{2+} + Cr^{2+}$ and $CrCl^{2+} + Hg^{2+}$ are essentially the same (-10 and -5 e.u.), the 5-kcal. difference in activation enthalpy provides the factor of $\sim 10^3$ by which the rate of $CrCl^{2+} + Cr^{2+}$ exceeds that of $CrCl^{2+} + Hg^{2+}$. It is also of interest to note that the $CrCl^{2+} + Cr^{2+}$ exchange reaction, with $\Delta G° = 0$, has a higher rate than does $CrCl^{2+} + Hg^{2+}$, with a substantially negative value of $\Delta G°_{298} = -7.6$ kcal. The electron-transfer aspect of the $CrCl^{2+} + Cr^{2+}$ reaction is the distinguishing factor between these two systems. The lack of correlation of the two systems with regard to k and $\Delta G°$ suggests that the transition states may not be as similar as we have suggested. The bridging in the substitution reaction may be of a different sort than in the electron-transfer case, or a chlorine atom transfer may be the central feature of the latter process.

Acknowledgment.—We appreciate helpful discussions with Drs. E. L. King and T. W. Swaddle and are grateful to them for access to their unpublished data on the kinetics of aquation of chlorochromium(III) ion. We are grateful to Dr. T. W. Newton for supplying us with the Los Alamos computer programs and for the aid he has given us in adapting these programs for kinetic data to our computer facilities.

[26] Activation parameters for $Cr(NH_3)_5F^{2+} + Cr^{2+}$ are $\Delta H^* = 13.4$ kcal./mole and $\Delta S^* = -30$ e.u. (ref. 21); and for $Cr(OH_2)_5F^{2+} + Cr^{2+}$, 13.7 kcal. mole^{-1} and -20 e.u. (ref. 20).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF COLORADO, BOULDER, COLORADO

The Rate of Aquation of Halopentaaquochromium(III) Ion in Acidic Aqueous Solution[1]

BY THOMAS W. SWADDLE AND EDWARD L. KING

Received December 22, 1964

The rates of aquation of fluorochromium(III) ion, chlorochromium(III) ion, and iodochromium(III) ion have been studied in acidic solution of unit ionic strength over a range of temperature. All observed reaction pathways are first order in chromium complex; the orders with respect to hydrogen ion for these pathways are +1 and 0 for fluorochromium(III) ion, and 0 and −1 for chlorochromium(III) ion and iodochromium(III) ion. Activation parameters were evaluated for each rate law term. For the rate law term $k_0[Cr(OH_2)_5F^{2+}]$, the value of ΔS^* is abnormally positive, which is interpreted to mean that the corresponding transition state yields hydrofluoric acid and hydroxochromium(III) ion, not fluoride ion and aquochromium(III) ion. Measurement of the equilibrium extent of aquation of fluorochromium(III) ion as a function of temperature allowed evaluation of ΔH and $\Delta S°$ for the reaction: $Cr(OH_2)_5F^{2+} + H^+ + H_2O = Cr(OH_2)_6^{3+} + HF$.

This paper presents studies of the rate of aquation of chloropentaaquochromium(III) ion and iodopentaaquochromium(III) ion

$$Cr(OH_2)_5X^{2+} + H_2O = Cr(OH_2)_6^{3+} + X^-$$

and of fluoropentaaquochromium(III) ion

$$Cr(OH_2)_5F^{2+} + H^+ + H_2O = Cr(OH_2)_6^{3+} + HF$$

in acidic aqueous solution with ionic strength $I = 1.00$ M over a range of temperature. With data from the analogous study involving bromopentaaquochromium(III) ion,[2] it is possible to compare for the four reactions the rate coefficients and activation parameters for corresponding terms of the rate law

$$-\frac{d \ln [Cr(OH_2)_5X^{2+}]}{dt} = \sum k_i[H^+]^i$$

which each reaction obeys (with the experimental acidity range disclosing $i = 0$ and -1 for $X^- = Cl^-$, Br^-, and I^-, and $i = 1$ and 0 for $X^- = F^-$).

Experimental Details

Reagents.—Reagent grade perchloric acid was used without further purification. Lithium perchlorate, used to maintain the ionic strength, was prepared from reagent grade lithium carbonate and perchloric acid; the salt was recrystallized several times from distilled and de-ionized water. Dowex 50W-X8 was used in the cation-exchange procedures.

Fluoropentaaquochromium(III) Ion.—An acidic solution containing fluorochromium(III) ion (as fluoropentaaquochromium(III) ion will be called) as the only chromium- and fluoride-containing species was prepared as follows. Equimolar amounts of chromium(III) perchlorate and potassium fluoride were brought together at relatively high concentrations (~ 2 M); the solution was boiled under reflux for 3 hr. and cooled to 0°, and the precipitated potassium perchlorate was removed. Fifteenfold dilution of this solution with water followed by cation-exchange separation allowed isolation of fluorochromium(III) ion from a small amount of difluorochromium(III) ion, which was eluted with 0.1 M perchloric acid, and larger amounts of

---

[1] This work was supported by the United States Atomic Energy Commission, Contract AT (11-1)-1286.

[2] F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964).

hexaaquochromium(III) ion and possibly hydrolytic dimers[3] which remained in the resin phase when fluorochromium(III) ion was eluted with 1.0 *M* perchloric acid. The composition of fluorochromium(III) ion was established by spectrophotometric determination of chromium as chromate ion after treatment with alkaline hydrogen peroxide ($a_{CrO_4^{2-}} = 4.82 \times 10^3$ l. mole^{-1} cm.$^{-1}$ at 372 mμ). The fluoride content was determined by titration with thorium(IV) after removal of chromium(III) by precipitation as the hydroxide with a very slight excess of sodium hydroxide, a procedure which liberates the bound fluoride ion. The titration was made at pH ~5 using alizarin red-S indicator. The ratio (fluoride)/(chromium) was 0.95, which is within experimental uncertainty of the expected value 1.00.

Chloropentaaquochromium(III) Ion.—The preparation of an acidic solution containing chlorochromium(III) ion as the only chromium- and chloride-containing species was accomplished in a procedure using cation-exchange resin very similar to that just described for preparation of fluorochromium(III) ion. The composition of this species was established by the chromium analysis already mentioned. The concentration of chloride ion in a sample after complete aquation of chlorochromium(III) ion was determined by a spectrophotometric procedure involving mercury(II) thiocyanate and iron(III) ion. Prior to analysis for chloride, aquochromium(III) ion formed in the aquation was removed by cation-exchange resin. The ratio (chloride)/(chromium) was found to be 0.99_6. The stock solution, approximately 0.2 *M* chlorochromium(III) ion and 0.8 *M* hydrogen ion, was stored at 0°, where aquation proceeds at a very low rate.

Iodopentaaquochromium(III) Ion.—Since the equilibrium concentration of iodochromium(III) ion in concentrated solutions of aquochromium(III) ion and iodide ion is extremely low, this complex ion could not be prepared by the methods used for preparation of fluoro and chloro species. Rather it was prepared by oxidation of chromium(II) ion with excess triiodide ion

$$2Cr^{2+} + I_3^- = 2CrI^{2+} + I^-$$

The excess triiodide ion was reduced with sulfite, and the cationic chromium(III) species, as well as zinc ion (present in the preparation from the use of zinc to produce chromium(II)), were absorbed into a cation-exchange resin phase. After neutral sulfur dioxide and anionic species iodide ion and sulfate ion were rinsed completely from the column with 0.1 *M* perchloric acid, the green chromium(III)–iodide species was eluted with 1.0 *M* perchloric acid. (Our preparation differed from Espenson's,[4] therefore, in certain respects, particularly our use of excess iodide and our separation of iodochromium(III) ion from the reaction mixture by an ion-exchange procedure.) The middle fractions of eluent, containing ~60% of the chromium, and essentially no zinc ion, were preserved as a frozen mass at ~−12°. A Volhard analysis for iodide on a completely aquated sample combined with the usual spectrophotometric analysis for chromium after conversion to chromate gave a ratio (iodide)/(chromium) of 1.00_4.

Spectrophotometric Measurements.—All spectrophotometric measurements were made using a Cary Model 15 spectrophotometer. Numerical values of absorbancy indices, where reported, are based on decadic logarithms. For the halochromium(III) species studied, the positions of maxima (in mμ) and the corresponding molar absorbancy indices (in l. mole^{-1} cm.$^{-1}$) in dilute perchloric acid are: fluorochromium(III) ion, (595, 12.2), (417, 11.9), and (268, 4.34), with a point of inflection ($a = 4.62$ l. mole^{-1} cm.$^{-1}$) at 666 mμ; chlorochromium(III) ion, (609, 16.4) and (428, 20.8), with strong absorption in the ultraviolet and a point of inflection ($a = 6.7$ l. mole^{-1} cm.$^{-1}$) at 675 mμ; and iodochromium(III) ion, (650, 36.1, an unsymmetric peak), (474, 32.6), and (260, 5740), with a point of inflection ($a = 2115$ l. mole^{-1} cm.$^{-1}$) at 306 mμ.

Experimental Results

Equilibrium in the Reaction: $Cr(OH_2)_5F^{2+} + H^+ + H_2O = Cr(OH_2)_6^{3+} + HF$.—Aquation of fluorochromium(III) ion does not go to completion under the conditions of the experiments reported here. From 9.6% (77°, 0.98 *M* H^+) to 37.4% (95°, 0.12 *M* H^+) of the fluorochromium(III) present initially remains at equilibrium. The concentration of fluorochromium(III) ion in portions of reaction mixture in which reaction had gone over 99% toward equilibrium was determined by an ion-exchange procedure. A diluted portion of reaction mixture was poured through a column of cation-exchange resin (Dowex 50W-X8, 50–100 mesh, hydrogen ion form), and the cationic chromium(III) species were taken into the resin phase. Fluorochromium(III) ion was then separated from the aquochromium(III) ion by elution with 1 *M* perchloric acid. Over 99% of the fluorochromium(III) ion was recovered in this procedure. Fluorochromium(III) ion was converted by alkaline hydrogen peroxide to chromate ion for the spectrophotometric analysis already mentioned. With the equilibrium concentration of fluorochromium(III) ion known, equilibrium concentrations of hydrogen ion, hydrofluoric acid, and aquochromium(III) ion were calculated from the initial concentrations and the reaction stoichiometry. Such measurements were made at 77.2, 86.0, and 94.7°; the time required for establishment of equilibrium at 68.0° was inconveniently long, and direct evaluation of the position of equilibrium at this temperature was not attempted. These experiments are summarized in Table I. Since the reaction was studied in Pyrex vessels, the possible consumption of hydrofluoric acid in reaction with silica was a matter of concern. However, the approximate constancy of values of the equilibrium quotient with variation of concentrations of hydrogen ion and hydrofluoric acid indicates the attack of hydrofluoric acid upon Pyrex under the conditions of these experiments to be negligible; this conclusion is supported by the close correspondence of results obtained in duplicate kinetic experiments run in Pyrex vessels and polyethylene vessels.

TABLE I

EQUILIBRIUM QUOTIENT VALUES FOR

$Cr(OH_2)_5F^{2+} + H^+ + H_2O = Cr(OH_2)_6^{3+} + HF$

$$Q = \frac{[HF][Cr(OH_2)_6^{3+}]}{[Cr(OH_2)_5F^{2+}][H^+]}$$

$I = 1.00\ M^a$ $[Cr(OH_2)_5F^{2+}]_0{}^b = 5.28 \times 10^{-3}\ M$

$[H^+]$, *M*	10^2Q		
	77.2°	86.0°	94.7°
0.0645	5.5		
0.1212	5.0	4.8	4.6
0.2188	4.8	4.6	4.4
0.412	4.6	4.5	4.3
0.605	4.8	4.5	4.1
0.798	4.6	4.4	4.4
0.979	4.6	4.4	4.4
0.979	4.7[c]	4.6[c]	
0.982	4.4[d]		
Av. value	4.8	4.5	4.4

[a] Ionic strength maintained with lithium perchlorate. [b] Here, and elsewhere, a zero subscript for a concentration means the value at zero time. [c] $[HF]_0 = 2.8 \times 10^{-3}$ *M;* in all other runs, $[HF]_0 = 0$. [d] $[Cr(OH_2)_5F^{2+}]_0 = 2.64 \times 10^{-3}$ *M.*

---

(3) J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).

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

Wilson and Taube evaluated this equilibrium quotient as 3.8×10^{-2} at 25° in solutions of 0.5 *M* ionic strength.[5] The agreement is quite adequate considering the differences of temperature and ionic strength.

Aquation of Fluorochromium(III) Ion.—Individual reaction mixtures in Pyrex reaction vessels were removed from the thermostat bath as a function of time; analysis for fluorochromium(III) ion was made using the procedure described in the preceding section.

The initial concentration of hydrogen ion was high enough (0.12–0.98 *M*, except for one experiment at 0.067 *M*) compared to that of fluorochromium(III) ion (5.3×10^{-3} *M*) that the change in the former quantity was very small in the course of an experiment. In each experiment, therefore, the data can be correlated with a rate law which does not involve the concentration of hydrogen ion. If the aquation is first order in fluorochromium(III) ion, the rate law governing each experiment will be

$$-\frac{\mathrm{d}[\mathrm{CrF}^{2+}]}{\mathrm{d}t} = k[\mathrm{CrF}^{2+}] - k'[\mathrm{Cr}^{3+}][\mathrm{HF}]$$

since the predominant form of fluoride at the acidity of these experiments is hydrofluoric acid. Integration of this rate law gives

$$k = \frac{2.303([\mathrm{CrF}^{2+}]_0 - [\mathrm{CrF}^{2+}]_\infty)}{t([\mathrm{CrF}^{2+}]_0 + [\mathrm{CrF}^{2+}]_\infty)} \times \log \frac{[\mathrm{CrF}^{2+}]_0{}^2 - [\mathrm{CrF}^{2+}][\mathrm{CrF}^{2+}]_\infty}{[\mathrm{CrF}^{2+}]_0([\mathrm{CrF}^{2+}] - [\mathrm{CrF}^{2+}]_\infty)}$$

which was used to evaluate *k*, the pseudo-first-order rate coefficient for the forward reaction. (Since the same power of the concentration appears in the numerator and the denominator of each quotient of this expression, absorbancy values of the processed portions of reaction mixture, which are directly proportional to the concentration of fluorochromium(III) ion, were used in this equation.[6]) In an experiment at 77.2°, $[\mathrm{H}^+] \cong 0.414$ *M*, reaction was followed for 95 hr.; at this time reaction had gone ~70% to completion with equilibrium corresponding to ~81% reaction. Values of $10^6k \times$ sec. for seven points at 10–15-hr. intervals in this experiment were 4.4_0, 4.4_0, 4.5_1, 4.5_9, 4.3_3, 4.3_5, and 4.24. This run was typical, being neither the best nor the worst. A summary of values of *k* is given in Table II.

TABLE II

VALUES OF THE PSEUDO-FIRST-ORDER RATE COEFFICIENT

$$-\frac{\mathrm{d}[\mathrm{CrF}^{2+}]}{\mathrm{d}t} = k[\mathrm{CrF}^{2+}]$$

$I = 1.00\ M^a$ $[\mathrm{CrF}^{2+}]_0 = 5.28 \times 10^{-3}\ M$

$[\mathrm{H}^+]$,[b] *M*	10^6k, sec.$^{-1}$ 68.0°[c]	77.2°	86.0°	94.7°
0.066		2.1		
0.123		2.29	6.14	15.6
0.221	1.06	2.94	7.64	19.3
0.414	1.55	4.40	10.9	26.8
0.607	2.11	5.56	14.2	34.5
0.801	2.54	7.29	17.7	42.9
0.982	3.07	8.35	21.5	50.9

[a] Ionic strength maintained with lithium perchlorate. [b] This is the average hydrogen ion concentration during the run. It is ~2% lower than the initial concentration at the lowest concentration and ~0.2% lower at the highest concentration. [c] Since reaction at 68.0° was not followed to completion, the concentration of fluorochromium(III) ion at equilibrium was extrapolated from values at the higher temperatures.

Aquation of Chlorochromium(III) Ion.—Light absorption by chlorochromium(III) ion in the ultraviolet region of the spectrum (values of a_λ (in l. mole^{-1} cm.$^{-1}$) are 144 at 245 mμ, 245 at 240 mμ, 426 at 235 mμ, and 730 at 230 mμ) is enormously greater than that by aquochromium(III) ion ($a \cong 1$ l. mole^{-1} cm.$^{-1}$ at 230 mμ). Measurement of absorbancy in this wave length range was an effective method of evaluation of the pseudo-first-order rate coefficient for aquation of chlorochromium(III) ion. It was verified that chlorochromium(III) ion obeyed Beer's law at each wave length and that the absorbancy was independent of slit width in the range employed. The wave length used in a particular run depended upon the initial concentration of chlorochromium(III) ion, which ranged from 1.7×10^{-3} to 9.2×10^{-3} *M*; in general, the absorbancy of the first sample from an experiment was ~1.5. Uncertainties due to nonreproducibility of wave length setting, which could be troublesome in a spectral region where the absorbancy is changing rapidly with wave length, were eliminated by measuring each of the eight samples from a particular run at the same time with the wave length setting unaltered during the measurements. Between removal of an aliquot and completion of an experiment, all samples were stored at temperatures <0° where they are effectively quenched. (In many cases, the samples froze.) First-order rate coefficients were evaluated from the slopes $\Delta \ln (A - A_\infty)/\Delta t$, both by consideration of each point relative to the initial point and by consideration of all points simultaneously using the method of averages. The generally good agreement of the rate coefficients calculated in these two ways (an average difference of ~0.9%) verifies the conformity of the data to the expectations of an irreversible first-order reaction. (At the highest initial concentration of chlorochromium(III) studied (~0.01 *M*), aquation proceeds 99.9% to completion.) In most experiments, reaction was followed 60–80% to completion. The pseudo-first-order rate coefficients for this reaction are presented in Table III.

Aquation of Iodochromium(III) Ion.—Iodochromium(III) ion has an absorption maximum at 260 mμ, $a = 5.47 \times 10^3$ l. mole^{-1} cm.$^{-1}$, which is convenient for following its concentration. Aquochromium(III) ion is relatively transparent at this wave length ($a \cong 5$ l. mole^{-1} cm.$^{-1}$). The rate of aquation of iodochromium-

---

(5) A. S. Wilson and H. Taube, *J. Am. Chem. Soc.*, **74**, 3509 (1952).

(6) The absorbancy data as a function of time for all experiments on fluorochromium(III) have been deposited as Document No. 8278 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

TABLE III

VALUES OF THE PSEUDO-FIRST-ORDER RATE COEFFICIENT

$$-\frac{d[CrCl^{2+}]}{dt} = k[CrCl^{2+}]$$

$I = 1.00\ M^a$ $[CrCl^{2+}]_0 = 1.65 \times 10^{-3}\ M$

35.0°		50.0°		60.0°	
[H⁺], *M*	10^6k, sec.⁻¹	[H⁺], *M*	10^6k, sec.⁻¹	[H⁺], *M*	10^6k, sec.⁻¹
0.0161	9.84	0.0161	94.3	0.0158^d	367.
0.0264	6.38	0.0203	76.5	0.0179^d	338.
0.0203	8.14	0.0264	60.3	0.0203	303.
0.0470	4.00	0.0323^b	51.1	0.0222^d	275.
0.114	2.375	0.0470	37.0	0.0264	226.
0.222	1.73	0.0716^b	27.0	0.0370^d	177.
0.428	1.47	0.1306^b	18.4	0.0470	141.2
0.990^b	1.28	0.222	13.55	0.079^c	96.7
		0.428	10.61	0.222	49.0
		0.990^b	8.78	0.440^d	36.5
				0.990	29.6,^{b} 29.2

[a] Ionic strength maintained with lithium perchlorate. [b] $[CrCl^{2+}]_0 = 3.3 \times 10^{-3}\ M$. [c] $[CrCl^{2+}]_0 = 9.2 \times 10^{-3}\ M$. [d] $[CrCl^{2+}]_0 = 1.84 \times 10^{-3}\ M$.

TABLE IV

VALUES OF THE PSEUDO-FIRST-ORDER RATE COEFFICIENT

$$-\frac{d[CrI^{2+}]}{dt} = k[CrI^{2+}]$$

$I = 1.00\ M^a$ $[CrI^{2+}]_0 = 4.75 \times 10^{-5}\ M$

t, °C.	[H⁺], *M*	10^4k, sec.⁻¹	*t*, °C.	[H⁺], *M*	10^4k, sec.⁻¹
20.18	1.00	0.586^b	31.96	1.000	3.10
20.18	0.856	0.589^b	32.07	0.856	3.34
20.18	0.787	0.634^b	31.97	0.595	3.84
20.18	0.404	0.811^b	31.97	0.438	4.44
20.18	0.2115	1.14^b	32.09	0.2115	7.19
20.22	0.058	2.99	31.71	0.0964	12.97
19.91	0.0196	7.67	31.98	0.0580	20.2
			31.88	0.0196	55.8
21.29	0.0964	2.29			
			39.30	1.007^c	8.46
24.97	1.00	1.138	39.26	1.000	8.37
24.95	0.856	1.19	39.29	0.856^c	9.04
24.97	0.438	1.581	39.18	0.595	10.36
25.07	0.0964	4.20	39.19	0.438^c	12.17
24.88	0.058	6.53	39.18	0.2884	15.84
25.00	0.0196	17.81	39.20	0.2115	19.66

[a] Ionic strength maintained with lithium perchlorate. [b] Corrected for photoaquation as described in text. [c] $[CrI^{2+}]_0 = 3.72 \times 10^{-5}\ M$.

(III) ion is much greater than that of chlorochromium(III) ion, and the aquation reaction mixture was kept in the thermostated 10-cm. cell during a run. In most experiments a jacketed thermostated cell was used; this remained in the cell compartment during a run. In such experiments, the temperature was checked by immersion of the thermometer bulb directly in the cell.

For the experiments at 20.18°, at which the reaction was relatively slow, an ordinary (*i.e.*, nonjacketed) 10-cm. cell containing the reaction mixture was kept immersed in a darkened thermostat bath. This cell was removed periodically for spectral measurement; this required so little time (1–1.5 min.) that a negligible temperature change occurred. (Room temperature was within a few degrees of 20°.) In these experiments, the short exposures to daylight when the cell was being transferred to the spectrophotometer from the thermostat appeared to cause a slight amount of photocatalyzed aquation. This conclusion was reached on the basis of a 4% difference in the first-order rate coefficients for otherwise identical runs in one of which the cell containing reaction mixture suffered twenty-three 30-sec. exposures to daylight and in the other of which there were nine such exposures. The reported values of *k* for these experiments were corrected (0.3% per 30-sec. exposure) for the slight photoaquation.

Reaction was followed 75–90% toward completion and plots of log $(A - A_\infty)$ *vs.* time were very nicely linear. The pseudo-first-order rate coefficients were obtained from the slopes of such plots. Consideration of the excellent linearity as well as the general reproducibility suggests that these rate coefficients, which are given in Table IV, are known to 1%.

Interpretation of Results

The pseudo-first-order rate coefficient for each reaction studied varied with the concentration of hydrogen ion. In the acidity range covered by these experiments,

TABLE V

VALUES OF ΔH^* and ΔS^* ASSOCIATED WITH RATE LAW TERMS

$$-\frac{\mathrm{d}\ln[\mathrm{Cr(OH_2)_5X^{2+}}]}{\mathrm{d}t} = k_i[\mathrm{H^+}]^i$$

Rate law term	$k(298.2)^a$	ΔH^*, kcal. mole^{-1}	ΔS^*, cal. mole^{-1} deg.$^{-1}$
$k_1[\mathrm{CrF^{2+}}][\mathrm{H^+}]$	1.36×10^{-8}	24.5 ± 0.3	-12.4 ± 0.8
$k_0[\mathrm{CrF^{2+}}]$	6.22×10^{-10}	28.7 ± 0.6	-3.9 ± 1.8
$k_0[\mathrm{CrCl^{2+}}]$	2.77×10^{-7}	24.3 ± 0.2	-7.1 ± 0.5
$k_{-1}[\mathrm{CrCl^{2+}}][\mathrm{H^+}]^{-1}$	2.84×10^{-8}	29.4 ± 0.1	$+5.5 \pm 0.3$
$k_0[\mathrm{CrI^{2+}}]$	8.41×10^{-5}	23.0 ± 0.3	-0.2 ± 0.9
$k_{-1}[\mathrm{CrI^{2+}}][\mathrm{H^+}]^{-1}$	3.43×10^{-5}	28.9 ± 0.2	$+17.9 \pm 0.8$

[a] Calculated using the listed values of ΔH^* and ΔS^*. Dimensions: jth order rate coefficients (moles l.$^{-1}$)$^{1-j}$ sec.$^{-1}$.

the rate of aquation of fluorochromium(III) ion increases with increasing concentration of hydrogen ion, as does that of azidochromium(III) ion,[7] and the rates for chlorochromium(III) ion and iodochromium(III) ion decrease with increasing acidity, as does that of bromochromium(III) ion.[2] The rate coefficients given in Tables II–IV were treated using a high-speed computer by a nonlinear least-square program[8] to obtain the enthalpy and entropy of activation corresponding to the important terms in each of the rate laws

$$k = \left(\frac{kT}{h}\right)\sum_i [\mathrm{H^+}]^i e^{\Delta S_i^*/R} e^{-\Delta H_i^*/RT}$$

The data for all temperatures were treated simultaneously to obtain the best values of ΔH_i^* and ΔS_i^*; the data from experiments at a particular temperature were not treated separately to obtain best values of k_i for that temperature. These values are summarized in Table V.

In arriving at activation parameters for aquation of fluorochromium(III) ion, all twenty-four data of Table II were used with each point weighted according to the inverse of the square of the estimated experimental uncertainty. The values of k calculated using the derived activation parameters agree with the experimental values with an average deviation of 1.5%. There is a very faint suggestion in the data of a rate law term with an inverse first-power hydrogen ion dependence, and it is reasonable that such a rate law term would become important at low concentrations of hydrogen ion. Incorporation of such a term in the rate law does not, however, improve the quality of the fit sufficiently to justify its inclusion. Over a much wider range of acidity (pH ~1–8), the rate of aquation of *trans*-difluorobis(ethylenediamine)cobalt(III) ion is governed by three terms with hydrogen ion dependences[9]: $i = 1, 0$, and -1.

In arriving at activation parameters for aquation of chlorochromium(III) ion, all thirty data of Table III were used with a weighting proportional to the inverse square of the magnitude of k. The values of k calculated using the derived activation parameters agree with the experimental values with an average deviation of 1.2%. (The data also were used to obtain activation parameters with the weighting of each value proportional to the inverse first power of the magnitude of k. The resultant activation parameters differ slightly from those given in Table V. They are $\Delta H^*_0 = 24.6 \pm 0.7$ kcal. mole^{-1}, $\Delta S^*_0 = -6.0 \pm 2.2$ cal. mole^{-1} deg.$^{-1}$, $\Delta H^*_{-1} = 29.0 \pm 0.2$ kcal. mole^{-1}, and $\Delta S^*_{-1} = +4.1 \pm 0.7$ cal. mole^{-1} deg.$^{-1}$. The values of k calculated using these activation parameters derived with inappropriate weighting agreed with the experimental values with an average deviation of 1.6%.)

In arriving at activation parameters for aquation of iodochromium(III) ion, all twenty-nine data of Table IV were used, with a weighting proportional to the inverse square of the magnitude of k. The average difference between values of k calculated using these parameters and the experimental values is 1.5%.

The activation parameters derived from our data for iodochromium(III) ion differ greatly from values reported in another study[4] conducted over a narrower range of acidity ($[\mathrm{H^+}] = 0.20$–0.95), a comparable range of temperature ($t = 15$–$32°$), and at a higher concentration of iodochromium(III) ion (~0.01 M). The reason for this discrepancy is unclear, but the difference arises largely from experiments run at lower acidities. Rate coefficients calculated using the parameters of Table V differ from those reported by Espenson[4] for 0.948 M hydrogen ion by only an average difference of 2.4%. The differences at 0.200 M hydrogen ion are much larger, being −51% (15°), −24% (20°), −13% (25°), and +8% (32°). Where large discrepancies (>8%) between such calculated and experimental values exist, the values calculated using the activation parameters given in Table V are smaller in every case (seven comparisons), where smaller discrepancies ($\leqslant$8%) exist, the calculated values are smaller in three additional comparisons. Since a major difference between the studies was the absence of a purification step in the preparation of iodochromium(III) ion for the earlier study, these comparisons may suggest the presence of a catalytic impurity in some of the reaction mixtures studied by Espenson.[10] Using the activation parameters of Table V, one calculates a pseudo-first-order

---

(7) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **3**, 234 (1964).

(8) Some calculations were made by T. W. Newton at Los Alamos Scientific Laboratory using the program by R. H. Moore. This program (described in Los Alamos report LA2367 (March 4, 1960) and Addenda (January 14, 1963)) also was used in some of the calculations which were made at the Computing Center of the University of Colorado. J. E. Lauer was of assistance in the latter calculations.

(9) F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Am. Chem. Soc.*, **78**, 4883 (1956).

(10) J. H. Espenson (private communication) has suggested that photochemical aquation may be an explanation since his solutions were exposed to fluorescent room lights, in which case the photochemical reaction would appear to be relatively more important the lower the acidity.

rate coefficient for aquation of iodochromium(III) ion in 1 M perchloric acid at 30° of 2.26×10^{-4} sec.$^{-1}$, which agrees reasonably well both with the value of 2.30×10^{-4} sec.$^{-1}$ observed by Ardon[11] and with that (2.28×10^{-4} sec.$^{-1}$) interpolated from Espenson's work.[4]

For the chloro, bromo,[2] and iodo species, values of ΔH^*_0 are 24.3 ± 0.2, 23.8 ± 0.3, and 23.0 ± 0.3 kcal. mole^{-1}, respectively, and values of ΔH^*_{-1} are 29.4 ± 0.1, 27.1 ± 0.2, and 28.9 ± 0.2 kcal. mole^{-1}, respectively. The corresponding values are similar to one another, as are corresponding values of enthalpy of activation for aquation of halopentaamminechromium(III) ions.[12] Values of ΔS^*_0 for chloro, bromo, and iodo species show a linear correlation with $\bar{S}°$ for the analogous halide ion, illustrated in Figure 1.[13] Such a relationship is reasonable if the entropy of solvation of the departing anion is relevant in establishing the partial molal entropy of the transition state.[14] That the slope of the line (approximately 0.5) is less than unity is reasonable since the halide ion has not gained complete freedom in the transition state. The value of ΔS^*_0 for aquation of fluorochromium(III) ion is not rationalized by this correlation, but is approximately 12 cal. mole^{-1} deg.$^{-1}$ too positive. Although no rigorous theory demands linear correlation of ΔS^* and $\bar{S}°$, the linear correlation involving the chloro, bromo, and iodo complexes is striking, *as is the deviation of the fluoro complex.* It seems reasonable, therefore, to conclude that the transition state of charge 2+ for aquation of fluorochromium(III) ion differs in important ways from corresponding transition states for species with less basic ligands, chloride, bromide, and iodide. The more positive value of ΔS^*_0 for aquation of azidochromium(III) ion[7] relative to that for the complex of the similar but less basic ligand thiocyanate ion was explained in terms of a transition state which yielded hydroxochromium(III) ion and hydrazoic acid. Applied to the present system, where it seems equally appropriate, the explanation suggests a transition state of charge 2+ which produces hydroxochromium(III) ion of charge 2+ and neutral hydrofluoric acid, not aquochromium(III) ion of charge 3+ and anionic halide ion. It is reasonable that the entropy of activation for such a pathway would be more positive than it would be for one in which additional charge is developing.

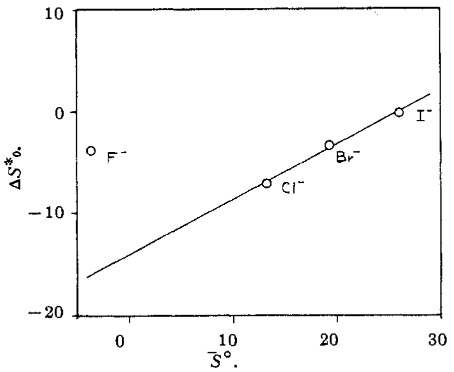

Figure 1.—The entropy of activation ΔS^*_0 (for the term zero-order in hydrogen ion) *vs.* $\bar{S}°_{X^-}$. Standard partial molal entropies for halide ions from W. M. Latimer ("The Oxidation States of the Elements and their Potentials in Aqueous Solution," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, pp. 54–63) except for fluoride ion, $\bar{S}°_{F^-} = -3.6 \pm 0.2$ cal. mole^{-1} deg.$^{-1}$ (C. C. Stephenson, H. P. Hopkins, and C. A. Wulff, *J. Phys. Chem.*, **68**, 1427 (1964)).

The relatively rapid aquation of fluoroiron(III) ion also proceeds by pathways involving first-order and zero-order dependences upon hydrogen ion concentration.[15] The activation parameters, which appear to be known less accurately than those of the present work, are qualitatively consistent with those of the present study. The entropy of activation for aquation of fluoroiron(III) ion *via* the pathway which is hydrogen ion independent is similar to that for fluorochromium(III) ion, and it seems reasonable that the immediate products formed from this transition state are hydrofluoric acid and hydroxoiron(III) ion.

The data of Table I give for the net aquation of fluorochromium(III) ion, $Cr(OH_2)_5F^{2+} + H^+ + H_2O = Cr(OH_2)_6{}^{3+} + HF$, in a solution of 1.00 M ionic strength the thermodynamic quantities: $\Delta H = -1.3 \pm 1$ kcal. mole^{-1} and $\Delta S° = -6.2 \pm 3$ cal. mole^{-1} deg.$^{-1}$. (The molar concentration scale is used.) For the analogous reaction of fluoroiron(III) ion in a solution of 0.50 M ionic strength, the thermodynamic parameters are[16] $\Delta H = +0.65$ kcal. mole^{-1} and $\Delta S° = -8.2$ cal. mole^{-1} deg.$^{-1}$. The temperature range from which the latter values were obtained was 15–35°. Although making a correction for the temperature dependence of ΔH hardly is justified considering the experimental error and the difference of ionic strength, a reasonable value of $\Delta C_p \cong -30$ cal. mole^{-1} deg.$^{-1}$ makes the thermodynamic parameters for the chromium(III) and iron(III) reactions in still closer agreement.[17] This similarity, like that observed for the monothiocyanate complexes of chromium(III)[18] and iron(III),[19] is reasonable. Since fluoride ion and water are adjacent in

---

(11) M. Ardon, *Proc. Chem. Soc.*, 333 (1964).

(12) M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Am. Chem. Soc.*, **83**, 2453 (1961).

(13) For ΔS^*_{-1} the correlation is less good, values for the chloro and bromo species being in the wrong order, +5.5 and 4.7 cal. mole^{-1} deg.$^{-1}$, respectively. If the values of ΔS^*_{-1} for chloro and iodo species are used to define a linear ΔS^*_{-1} *vs.* $\bar{S}°$ relationship, the interpolated value of ΔS^*_{-1} for bromochromium(III) ion would be 11 cal. mole^{-1} deg.$^{-1}$, which is 6 cal. mole^{-1} deg.$^{-1}$ more positive than the reported value (4.7 ± 0.7 cal. mole^{-1} deg.$^{-1}$).[2] The value of ΔH^*_{-1} for bromochromium(III) ion is also a little out of line, being ~2 kcal. mole^{-1} less than ΔH^*_{-1} for chloro- and iodochromium(III) ions. Since these deviations of ΔH^*_{-1} and ΔS^*_{-1} for bromochromium(III) ion are of opposite sign, appropriate changes of each might give values which are reasonably consistent with the data and yet which are correlated better with the corresponding parameters for chloro- and iodochromium(III) ions. With the values of ΔH^*_0 and ΔS^*_0 already reported[2] and $\Delta H^*_{-1} = 29.1$ kcal. mole^{-1} and $\Delta S_{-1} = 11$ cal. mole^{-1} deg.$^{-1}$, the calculated and observed values of the pseudo-first-order rate coefficient have an average difference of 7%.

(14) A. G. Evans and S. D. Hamann, *Trans. Faraday Soc.*, **47**, 25 (1951).

(15) D. Pouli and W. MacF. Smith, *Can. J. Chem.*, **38**, 567 (1960).

(16) R. E. Connick, L. G. Hepler, Z Z. Hugus, Jr., J. W. Kury, W. M. Latimer, and M-S. Tsao, *J. Am. Chem. Soc.*, **78**, 1827 (1956).

(17) L. G. Hepler (Thesis, University of California, Berkeley, (1953); University of California Radiation Laboratory Report, U.C.R.L. 2202) estimated ΔH for the chromium(III) reaction as +0.6 kcal. mole^{-1} on the basis of observed heats for the analogous reactions of other cations of charge 3+. The difference between this estimate and our experimental value also would be reduced if ΔC_p had a value of ~−30 cal. mole^{-1} deg.$^{-1}$.

(18) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

(19) G. S. Lawrence, *Trans. Faraday Soc.*, **52**, 236 (1956).

the spectrochemical series,[20] replacement of one of these ligands by the other is not influenced particularly by the magnitude of the crystal field stabilization energy, which is 12*Dq* for chromium(III) and 0 for high spin iron(III). (Thiocyanate ion is also adjacent to water in the spectrochemical series, being on the opposite side of water from fluoride.) Fluoride ion is adjacent to water also in the nephelauxetic series,[21] which seems related to the complex-forming tendencies of ligands.[22]

---

[20] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 44.

[21] C. E. Schaffer and C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **8**, 143 (1958).

[22] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, p. 222.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING,
THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS

The Phase Equilibria and Crystal Chemistry of the Rare Earth Group VI Systems. I. Erbium–Selenium[1]

BY D. J. HAASE, H. STEINFINK, AND E. J. WEISS

Received September 8, 1964

The phases occurring in the erbium–selenium system are: ErSe, f.c.c., a = 5.662 Å., m.p. 1630°; the solid solution series, Er_2Se_3–Er_3Se_4, orthorhombic, Fddd, a = 11.38 Å., b = 8.09 Å., c = 24.20 Å., m.p. 1400–1440°; α-$ErSe_2$, orthorhombic, Cmma, a = 16.22 Å., b = 15.80 Å., c = 11.88 Å., transition to β-$ErSe_2$ at 890°; β-$ErSe_2$, orthorhombic, Immm, a = 4.061 Å., b = 5.571 Å., c = 13.16 Å., peritectic at 1010°. Two eutectics were observed at approximately 3 atom % selenium and 1310° and approximately 55.5 atom % selenium and 1370°.

Introduction

The phase equilibrium relations in the binary system erbium–selenium were investigated as part of a program of research on compounds formed between rare earth and group VI elements.

Iandelli[2] has reported that ErSe is face-centered cubic; Muir[3] in his investigations of rare earth chalcogenides prepared a material which had a composition corresponding to $ErSe_{1.49}$, but it was not a single phase specimen. Miller, *et al.*,[4] report a phase Er_2Se_3 on which they made physical measurements, but no crystal data are given. The aim of this investigation is to study the binary phase diagram systematically and to characterize the intermediate phases which exist in this system.

Experimental

Elemental erbium (Lindsay, 99.9% purity) in the form of millings or ingots and selenium (American Smelting and Refining Co., 99.99% purity) in exactly weighed portions were prereacted in evacuated 9-mm. o.d. Vycor tubes at 600° for 48 hr. The reaction temperature of the prereaction cycle was limited to less than 700° because at temperatures in excess of 700° the erbium reacted with Vycor. The prereacted material having compositions greater than 40 mole % erbium was then sealed in tantalum tubes in an argon environment and the sealed tantalum tubes were heated in a vacuum induction furnace to temperatures of approximately 1800°. The surface of the tantalum tubing which had been in contact with the molten material showed no evidence of having been attacked during the reaction period. The material thus obtained was equilibrated and quenched at various temperatures. The samples containing less than 40 mole % erbium reacted completely in the Vycor tubing and did not require further reaction in tantalum at the high temperature. These two techniques were sufficient to produce all of the phases present in the systems.

The melting points of the congruent melting phases and the liquidus lines were determined by cycling small portions of the samples in an argon-filled resistance furnace in which a V-formed tantalum strip constituted the heating element. The samples were observed with a focused optical pyrometer. The pyrometer was calibrated against the melting point of platinum and also against an NBS standard Pt—Pt-10% Rh thermocouple. No emissivity corrections were made and the temperatures in Figure 1 are considered accurate to ±25°, although the precision of the measurements is ±5°. At the end of the cycling process, the samples were investigated by powder X-ray diffraction analysis and in all cases the patterns were identical with those obtained from the samples before they had been exposed to this treatment. The temperature of the incongruent melting phase was obtained by quenching compositions from various temperatures and determining the phases present by X-ray diffraction techniques and microscopic examination. The chemical composition of the specimens was determined by a chelometric titration of erbium, and selenium was determined by the sodium thiosulfate procedure. The densities of the materials were determined by the displacement method using acetone as the submersing liquid.

Results

The condensed phase diagram is shown in Figure 1. The solid lines represent that portion of the diagram which could be located accurately and the dashed lines represent those areas which are uncertain. The system has three eutectic points and one continuous solid solution region. The known eutectic points appear at approximately 3 atom % selenium and 1310° and at approximately 55.5 atom % selenium and 1370°, and an

---

[1] This work is being sponsored by a grant from the U. S. Air Force Office of Scientific Research.

[2] A. Iandelli, "Rare Earth Research," The Macmillan Company, New York, N. Y., 1961, p. 135.

[3] H. M. Muir, "Rare Earth Chalcogenides—Final Report," Research Chemical Division of Nuclear Corporation of America, June 1961.

[4] J. F. Miller, L. K. Matson, and R. C. Himes, Proceedings of the Third Rare Earth Conference, 1963.