monofluoride, ClF, did not react with NH_4F under similar conditions.

In all these experiments only occasional traces of NF_3 and N_2F_2 were found.

Experimental

Materials.—Reagent grade NH_4F and NH_4HF_2 were used as received from the J. T. Baker Chemical Co.

The ClF_3 was supplied by Harshaw Chemicals Corp., and, following distillation, analysis indicated a purity of better than 99%.

The ClF was prepared by a flow reaction between equimolar amounts of Cl_2 and ClF_3 in a monel tube at 340–350° using a residence time of 3.5 min. The ClF was purified by fractional condensation techniques and stored in a stainless steel cylinder previously passivated by treatment with gaseous fluorine.

Nitrogen gas (HP grade) was supplied by the Linde Corporation and further dried by passing through a phosphorus pentoxide drying column.

Apparatus.—All experiments were conducted in flow and vacuum systems constructed of copper tubing, stainless steel pipe, and 0.25 in. stainless steel Hoke needle valves equipped with Teflon packing. Traps were fabricated from unplasticized Kel-F polymer. Pressure measurements were made with stainless steel Acco Helicoid gages, 0–1500 mm. range (accuracy ±0.25%).

Reaction of Liquid ClF_3 with Solid NH_4F.—Slight excesses of the stoichiometric amounts of ClF_3 (according to eq. 2) were condensed and frozen on samples of NH_4F at liquid nitrogen temperatures. During each experiment, the system was evacuated, the $-196°$ bath was removed, and the ClF_3 was allowed to melt. The container warmed slowly in air and gases were evolved at a slow rate beginning at about $-50°$, the rate increasing with increasing temperature. The evolved gases were intermittently tapped from the system to maintain an arbitrary pressure of 0.5 atm. These gases were expanded into an evacuated system separated from the reactant system by a valve. As the temperature of the reactant mixtures reached -5 to 0°, the mixtures exploded violently. The evolved gases were identified as mixtures of varying ratios of N_2, Cl_2, and NF_2Cl.

In one experiment the reactant mixture did not explode and residual multicolored (red, yellow, white) solids were isolated which blanched and slowly decomposed on exposure to atmospheric air. The partly decomposed solids liberated oxygen from water and the aqueous solutions contained chloride and fluoride ions.

Reaction of Gaseous ClF_3 with Solid NH_4F.—From 1.0 to 7.5 g. of NH_4F was charged to a copper boat and inserted in a reactor fabricated from a 30 mm. (o.d.) tube of Kel-F plastic for visual observation of the reaction. ClF_3, pure or diluted with nitrogen, was passed over the salt. At total gas flow rates of from 85 to 160 ml./min. concentrations of ClF_3 equal to, or, greater than, 30% by volume with N_2 caused the NH_4F to burn, liberating sufficient heat to melt the Kel-F reactor and occasionally to ignite the copper boat. The only condensable products observed under these conditions were HF and Cl_2. At ClF_3 concentrations of less than 30% and flow rates of 140–160 ml./min., the reaction was characterized by the formation of a liquid zone which traveled slowly downstream the length of the boat as the reaction progressed and consumed NH_4F. At the conclusion of a run the copper boat either was empty or contained small amounts of a liquid solution of NH_4F in HF (molar ratios: 1:2–2.5). Condensable gases were trapped and the NF_2Cl was purified by fractional condensation from a $-125°$ to a $-196°$ trap.

Apparent induction times, from 5 to 20 min., were observed in many runs; however, the best yields of NF_2Cl were obtained in those runs having apparent induction times of from 0 to 2 min.

Typically, 7.696 g. of ClF_3 (13% by volume in N_2) was passed over an excess of NH_4F to provide 0.38 g. of NF_2Cl. The ClF_3 recovered was 1.886 g. The conversion of ClF_3 was 75.4% and the yield of NF_2Cl, based on ClF_3 consumed, was 11.5%.

Reaction of Gaseous ClF_3 with Solid NH_4HF_2.—The experiments were carried out analogously to those described above using NH_4F and the results and yields were similar.

Gaseous ClF with Solid NH_4F.—A number of runs were conducted using gaseous ClF (10% by volume in N_2) as a substitute for the ClF_3 in the above experiments and in each case the ClF was recovered unchanged.

Reaction of Gaseous ClF_3 with Fluorocarbon Oil Suspensions of NH_4F.—It was indicated that improved yields of NF_2Cl might be obtained providing temperature could be controlled more precisely in the over-all reaction zone. Therefore, runs were carried out using rapidly stirred suspensions of NH_4F in a non-volatile fluorocarbon oil which functioned as a heat sink. A special reactor was constructed of 60 mm. (o.d.) Kel-F tubing compression sealed at both ends with 0.25 in. thick Teflon plates. The gas inlet was a threaded 3/8 in. (o.d.) Kel-F tube led through a drilled and tapped hole in the top Teflon plate and extending below the surface of the suspension. The gas exit was a 0.25 in. copper pipe-to-flare fitting threaded through the Teflon cap. Stirring was by a Teflon-coated magnetic bar. The complete reactor was enclosed in an air bath capable of being maintained within ±1° at temperatures up to 100°. The reactor was charged with up to 5 g. of NH_4F in 40 ml. of oil.

Best yields (22% average) were obtained using mixtures of 11.7% ClF_3 in N_2 at a total gas flow rate of 178 ml./min. (STP) and an initial suspension temperature of 60 to 73°. At temperatures lower than 50° the NH_4F is not readily attacked by ClF_3 since the reaction rate is extremely slow. Above 73°, exhaustive fluorination of the NH_4F (eq. 4) increases concomitant with a rapid decrease in the yield of NF_2Cl.

The mass cracking pattern and infrared spectrum of NF_2Cl as observed by us are in agreement with the data reported by Petry.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
OF THE UNIVERSITY OF CALIFORNIA,
LOS ANGELES 24, CALIFORNIA

Aquation of *trans*-Dichlorobis-(ethylenediamine)-chromium(III) Ion in Aqueous Perchloric Acid[1]

BY DONALD C. OLSON AND CLIFFORD S. GARNER

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The products and kinetics of aquation of *trans*-dichlorobis-(ethylenediamine)-chromium(III) cation in nitric acid solution have been extensively studied by MacDonald and Garner.[2-4] We report here an ex-

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(2) D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem.*, **18**, 219 (1961).

(3) C. S. Garner and D. J. MacDonald in "Advances in the Chemistry of the Coördination Compounds," S. Kirschner, Ed., the Macmillan Co., New York, N. Y., 1961, pp. 266–275.

(4) D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.*, **83**, 4152 (1961).

(5) K. R. A. Fehrmann and C. S. Garner, *ibid.*, **83**, 1276 (1961).

tension of this study to aquation of this complex in perchloric acid solution, with the purpose of determining whether the weakly basic nitrate anion affects the products or kinetics of the aquation. It is known that the presence of nitrate ion may affect aquation reactions of chromium(III) complexes of this type from an investigation[5] of the aquation of *cis*-difluorobis-(ethylenediamine)-chromium(III) cation, for which the rate constant at 40.5° is twice as great in nitric acid as in perchloric acid of the same pH (1.04) under the same concentration conditions.

Experimental

trans-$[Cr(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ was prepared as described earlier[2] and dried at 105° for several hours. Fifty g. was dissolved in 250 ml. of 0.1 *F* $HClO_4$ (reagent grade) and 50 g. of recrystallized $NaClO_4$ was added; the mixture was stirred for 2–3 m.n. and filtered. The gray-green solid was washed with ethanol, then with diethyl ether, and dried at 105°; yield, 90%. Its visible absorption spectrum in water was essentially identical with the spectrum of *trans*-$[Cr(en)_2Cl_2]NO_3$ observed[3,4] in 0.1 *F* HNO_3. *Anal.* Calcd. for *trans*-$[Cr(en)_2ClCl_2]O_4$: Cr, 15.2; Cl (ligand), 20.7; C, 14.03; N, 16.36; H, 4.71. Found: Cr, 15.2; Cl (ligand), 20.7; C, 13.86; N, 16.41; H, 4.74.

The *trans* nitrate salt was precipitated from a 0.1 *F* HNO_3 solution of the chloride salt by addition of a tenfold excess of $NaNO_3$, and the solid was washed with ethanol and then with diethyl ether. The visible absorption spectrum in 0.1 *F* HNO_3 was the same as observed with earlier preparations.[3,4] *Anal.* Calcd. for *trans*-$[Cr(en)_2Cl_2]NO_3$: Cr, 17.0; Cl, 23.2; C, 15.75; N, 22.95; H, 5.29. Found: Cr, 16.6; Cl, 23.1; C, 15.59; N, 23.07; H, 5.16.

Two kinetic runs were made in 0.125 *F* $HClO_4$ with the perchlorate salt (initially 4.4 m*F*) and one, for comparison purposes, in 0.1 *F* HNO_3 with the nitrate salt (initially 8.8 m*F*), all in the dark at 35.00 ± 0.05° with the chromatographic separation technique developed earlier.[3,4] The Dowex AG50W-X8 (H^+ form, 100–200 mesh) cation-exchange column was operated at 5°, using $HClO_4$ eluting agents in the perchlorate runs and HNO_3 eluting agents in the nitrate run. Each chromatographic fraction was analyzed for Cr spectrophotometrically[4] and also titrimetrically[6]; the former method usually gave results 1–2% low relative to the EDTA titrimetric method.

Results and Discussion

Rate plots of ln *c vs. t*, where *c* is the molar concentration of unreacted *trans*-$[Cr(en)_2Cl_2]^+$ at time *t* determined from the *trans*-dichloro elution fraction, were linear over 3–4 half-times. Table I gives the first-order rate constants,[7] together with the value found earlier[3,4] in 0.1 *F* HNO_3. Within experimental error, the rates in $HClO_4$ and HNO_3 are the same; the rate constant found in the single HNO_3 run made in this investigation is 8% greater than the average value obtained earlier[3,4] in several runs with a different preparation of *trans*-$[Cr(en)_2Cl_2]NO_3$.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF *trans*-$[Cr(en)_2Cl_2]^+$ AT 35.00°

Medium	10^5k, sec.$^{-1}$
0.125 *F* $HClO_4$	9.7 ± 0.5[a]
	9.0 ± 0.4[a]
0.10 *F* HNO_3	9.5 ± 0.1[a,b]
	8.75 ± 0.05[c]

[a] This research. [b] Standard deviation of the four experimental points from linearity was only ±0.02; error given is an estimate of the over-all error. [c] MacDonald and Garner, ref. 3 and 4.

The same reaction products, namely, *trans*-$[Cr(en)_2(OH_2)Cl]^+$, *cis*-$[Cr(en)_2(OH_2)Cl]^+$, and the species tentatively characterized[3,4] as *trans*-$[Cr(en)(OH_2)_2Cl_2]^+$, were found chromatographically in the $HClO_4$ and HNO_3 runs. The percentages of each of these products formed at 1, 2, 3, 4, 6, 8, and 12 hr. were essentially the same in $HClO_4$ as in HNO_3 and as in the previous investigations[3,4] in HNO_3.

Thus, within experimental error the kinetics and products of aquation of *trans*-$[Cr(en)_2Cl_2]^+$ are not affected by the substitution of a nitrate medium for a perchlorate medium, despite the fact that nitrate ion can affect the rates and presumably the products of certain related reactions. The greater rate of aquation of *cis*-$[Cr(en)_2F_2]^+$ in 0.1 *F* HNO_3 than in 0.1 *F* $HClO_4$ over the range 10–40° is associated with a decrease in Arrhenius activation energy from 23 ± 1 in $HClO_4$ to 14 ± 2 kcal. mole^{-1} in HNO_3.[5] The source of this difference in E_a is not definitely known, but since the aquation of the dichloro complex is not acid-catalyzed, the nitrate effect in the former may be due to a more ready reaction of nitrate ion with the presumed reactive protonated intermediate, *cis*-$[Cr(en)_2F_2H]^{+2}$.

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[6] J. Kinnunen and B. Wennerstrand, *Chemist-Analyst*, **44**, 33 (1955); method modified by omission of the ascorbic acid.

[7] Equivalent to $k_{12} + k_{13} + k_{14} + k_{12}'$ in the notation of ref. 3 and 4.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES 24, CALIFORNIA

The *cis–trans* Isomerization of Dihydroxobis-(ethylenediamine)-chromium(III) Cations[1]

BY DONALD C. OLSON AND CLIFFORD S. GARNER

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In connection with a study of the hydrolysis of *cis*- and *trans*-$Cr(en)_2Cl_2^+$ ions in basic solution presently underway in this Laboratory a need arose to investigate the kinetics of *cis–trans* isomerization of $Cr(en)_2(OH)_2^+$. Woldbye[2] has made a thorough investigation of acid–base and *cis–trans* equilibria of the diaquo, hydroxoaquo, and dihydroxo complexes, but he reports only two semiquantitative data from which the approximate rate of isomerization of the dihydroxo ions might be deduced.

We report here a kinetic study of this isomerization, together with further observations on the *cis–trans* equilibrium.

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[1] Work partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University of California.

[2] F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958).