TABLE I

$\mathrm{Ni}^{2+} + \mathrm{Cl}^- \rightleftarrows \mathrm{NiCl}^+$ Total Ni concn. = 0.0447 *M*

$[\mathrm{Cl}^-]$, *M*	395 mμ			400 mμ		
	Optical density	$\frac{\bar{\epsilon}\,[\mathrm{Cl}^-]}{(\bar{\epsilon} - \epsilon_0)}$	$\frac{[\mathrm{Cl}^-]}{(\bar{\epsilon} - \epsilon_0)}$	Optical density	$\frac{\bar{\epsilon}\,[\mathrm{Cl}^-]}{(\bar{\epsilon} - \epsilon_0)}$	$\frac{[\mathrm{Cl}^-]}{(\bar{\epsilon} - \epsilon_0)}$
0.000	0.223	..	...	0.212	..	...
0.545	.231	14	2.7	.226	9	1.7
1.089	.233	23	4.4	.231	13	2.6
2.178	.240	29	5.4	.241	18	3.4
3.267	.244	36	6.6	.247	23	4.2
4.356	.247	43	7.8	.251	28	5.0
5.446	.246	56	10.0	.251	35	6.2

$\mathrm{Ni}^{2+} + \mathrm{Br}^- \rightleftarrows \mathrm{NiBr}^+$ Total Ni concn. = 0.0447 *M*

$[\mathrm{Br}^-]$, *M*	395 mμ			400 mμ		
	Optical density	$\frac{\bar{\epsilon}\,[\mathrm{Br}^-]}{(\bar{\epsilon} - \epsilon_0)}$	$\frac{[\mathrm{Br}^-]}{(\bar{\epsilon} - \epsilon_0)}$	Optical density	$\frac{\bar{\epsilon}\,[\mathrm{Br}^-]}{(\bar{\epsilon} - \epsilon_0)}$	$\frac{[\mathrm{Br}^-]}{(\bar{\epsilon} - \epsilon_0)}$
0.000	0.223	..	...	0.212	..	...
0.544	.227	25	4.9	.219	17	3.5
1.088	.233	23	4.4	.226	18	3.5
2.176	.239	31	5.7	.234	23	4.4
3.264	.242	39	7.3	.240	28	5.2
4.352	.243	50	9.3	.241	36	6.7
5.440	.246	56	10.0	.245	40	7.4

in which the volume % of 6 *M* HX was varied from 0 to 100. The separate 6 *M* HX and 6 *M* $\mathrm{HClO_4}$ solutions had been standardized previously by titration against 1 *N* NaOH. Just prior to a spectrophotometric measurement, each sample was made by adding 5.00 ml. of the standard nickel solution to 50.00 ml. of the appropriate HX–$\mathrm{HClO_4}$ solution. The ionic strength of each sample was 5.7 *M*. The halide ion concentrations listed in Table I were calculated from the known molarities of the 6 *M* acids and on the assumption that no volume change attended either the preparation of the mixed HX–$\mathrm{HClO_4}$ solutions or the addition of standard nickel solution to each of the mixed HX–$\mathrm{HClO_4}$ solutions.

Measurements.—A Beckman Model DU spectrophotometer, fitted with a constant-temperature cell compartment, was used. Constant temperature was maintained at 25 ± 0.1° by circulating water through the cell compartment from a water bath which was maintained at 25 ± 0.01°. All data were obtained with matched 1-cm. cells. A blank was prepared for each sample. The blank solutions contained 5 ml. of 2 *M* $\mathrm{HClO_4}$ added to 50 ml. of the same HX–$\mathrm{HClO_4}$ solution as for the corresponding samples. The reproducibility of the measurements was determined by taking readings on two separate occasions for each sample. The reproducibility obtained was ± 0.75%.

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Reaction of Chlorine Trifluoride with Ammonium Fluoride. Preparation of Chlorodifluoramine

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Prior studies at this Laboratory involving attempts to moderate the reaction of $\mathrm{ClF_3}$ with $\mathrm{NH_3}$ by dilution of the reactants with inert gas, high gas flow rates, and the use of a special jet reactor[1] resulted in complete oxidation of the $\mathrm{NH_3}$ and often ignition as reported by Ruff and Krug.[2] The reaction is best represented by eq. 1.

$$2\mathrm{NH_3} + 2\mathrm{ClF_3} \longrightarrow \mathrm{N_2} + 6\mathrm{HF} + \mathrm{Cl_2} \qquad (1)$$

During this work it was found that $\mathrm{NH_3}$ in the form of the simple salts, $\mathrm{NH_4F}$ and $\mathrm{NH_4HF_2}$, reacts under certain conditions with $\mathrm{ClF_3}$ to yield chlorodifluoramine, $\mathrm{NF_2Cl}$. This compound was first prepared by Petry[3] by the reaction of difluoramine with boron trichloride. Liquid $\mathrm{ClF_3}$ reacts with $\mathrm{NH_4F}$ from −50 to about −5° to yield $\mathrm{NF_2Cl}$; however, the reacting mixture nearly always explodes on warming to temperatures of −5 to 0°. Gaseous $\mathrm{ClF_3}$ reacts smoothly with $\mathrm{NH_4F}$ and $\mathrm{NH_4HF_2}$ under controlled temperature and flow conditions to yield $\mathrm{NF_2Cl}$ according to eq. 2 and 3.

$$3\mathrm{NH_4F} + 5\mathrm{ClF_3} \longrightarrow 3\mathrm{NF_2Cl} + 12\mathrm{HF} + \mathrm{Cl_2} \qquad (2)$$

$$3\mathrm{NH_4HF_2} + 5\mathrm{ClF_3} \longrightarrow 3\mathrm{NF_2Cl} + 15\mathrm{HF} + \mathrm{Cl_2} \qquad (3)$$

The reaction expressed by either eq. 2 or 3 is always simultaneous with that given by eq. 4.

$$2\mathrm{NH_4F} + 2\mathrm{ClF_3} \longrightarrow \mathrm{N_2} + 8\mathrm{HF} + \mathrm{Cl_2} \qquad (4)$$

The latter reaction predominates whenever localized overheating of the reactants occurs. Consequently, the gaseous $\mathrm{ClF_3}$ was diluted with $\mathrm{N_2}$ and the flow rate of the gas mixture was regulated to eliminate hot spots in the solid ammonium fluoride reactant bed. It was later found that this is most easily accomplished by employing a suspension of solid ammonium fluoride in a fluorocarbon oil. The oil functions to dissipate localized heat and thus maintains a more uniform reaction temperature.

In contrast with the behavior of $\mathrm{ClF_3}$, chlorine

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[1] E. A. Tyczkowski and L. A. Bigelow, *J. Am. Chem. Soc.*, **77**, 3007 (1955).

[2] O. Ruff and H. Krug, *Z. anorg. allgem. Chem.*, **190**, 270 (1930).

[3] R. C. Petry, *J. Am. Chem. Soc.*, **82**, 2400 (1960).

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

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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).