The Chemical Properties of Chlorodifluoramine[1]

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Abstract: The thermal and photochemical reactions of chlorodifluoramine and aliphatic olefins produce β-chlorodifluoramines, bis(difluoramines), and dichlorides. A study of the equilibrium between chlorodifluoramine and tetrafluorohydrazine–chlorine is reported. Alkyldifluoramines are formed from aliphatic mercurials and chlorodifluoramine.

During an investigation of the interaction of difluoramine and Lewis acids, it was discovered that difluoramine and boron trichloride react to yield a new fluoronitrogen, chlorodifluoramine, $ClNF_2$.[3] Some additional methods of preparation have since appeared.[4–7]

Three reactions of this new material have been investigated in some detail: (1) its photochemical decomposition, (2) its reaction with olefins, and (3) its reaction with mercurials. In addition, some observations have been made on its reactions with nucleophilic reagents.

The Chlorodifluoramine–Tetrafluorohydrazine–Chlorine Equilibrium

The absorption spectrum of chlorodifluoramine (Figure 1) shows it to be ultraviolet active in the near-visible region. The following equilibrium was demonstrated by irradiating both a pure sample of chlorodifluoramine and a mixture of tetrafluorohydrazine and chlorine (1:5 mole ratio). This reaction is endothermic as written, but at elevated temperatures it

$$N_2F_4 + Cl_2 \overset{\text{ultraviolet}}{\rightleftarrows} 2NF_2Cl \qquad (1)$$

might be a practical route to chlorodifluoramine. Equilibrium constants obtained with four different mixtures of different temperatures are listed in Table I. The experimental procedure involved preparation of a known mixture of two of the three components in a 50-cc Pyrex bulb, thermostating the bulb in a constant-temperature water bath, and irradiating for 10–15 min with a Hanovia EH-4 light source. The lamp was turned off, the bulb removed from the water bath, and the equilibrium mixture expanded into a short path length infrared cell. Duplicate infrared spectra were obtained from which the equilibrium concentrations of $ClNF_2$ and N_2F_4 were determined. No change in the equilibrium concentrations was observed during the sampling period. The sample was then condensed back into the sample bulb and the procedure repeated at the same or different temperatures. For the first measurements at 49.90°, the mean deviation from the average value of the equilibrium constant was ±5% which was considered adequate in view of the limitations of quantitative infrared analysis. However, as successive measurements at different temperatures were made, the mean deviation increased, indicating deterioration of samples and/or losses due to repeated sampling. Additional data for mixture 4 is presented in Table IV in the Experimental Section.

Table I. Equilibrium Constants for the Reaction $N_2F_4 + Cl_2 \rightleftarrows 2ClNF_2$

Mixture no.	Initial pressure, mm[a]			Temp, °C	K
	N_2F_4	Cl_2	NF_2Cl		
1	55.2	190	. . .	49.90	0.0057
2	55.2	116	. . .		0.0054
3	55.2	520	. . .		0.0052
4	. . .	406	100		0.0050
1				69.70	0.0161
2					0.0158
3					0.0128
4					0.0130
1				83.10	0.0343
2					0.0374
3					0.0234
4					0.0275
1				41.25	0.0028
2					0.0040
3					0.0024
4					0.0031

[a] The same mixtures were used for all experiments. Experiments were made over a 2-week period in the order shown.

A plot of log K *vs.* $1/T$ for mixture 4 is shown in Figure 2. The triangles represent the average value of K for the four different mixtures in Table I. The temperature dependence of the equilibrium constant as determined from the data is

$$\log K = -(2640/T) + 5.77$$

giving a $\Delta H = \sim 12$ kcal for reaction 1. Sufficient accuracy was not obtained in these measurements to justify correction of the data for the N_2F_4 dissociation. Recalculation of the equilibrium constant at 83.10° (Table I) by correcting the equilibrium N_2F_4 pressure by the amount dissociated into NF_2 radicals gave a value of 0.0310. The corresponding correction at 29° was negligible.[8]

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[1] This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract No. DA-01-021 ORD-5135.

[2] Deceased. Correspondence regarding this article should be sent to Dr. T. E. Stevens of these laboratories.

[3] Preliminary accounts of the physical and chemical properties of $ClNF_2$ have appeared: R. C. Petry, *J. Am. Chem. Soc.*, **82**, 2400 (1960); R. C. Petry, Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, p 22M.

[4] D. M. Gardner, W. W. Knipe, and C. J. Mackley, *Inorg. Chem.*, **2**, 413 (1963).

[5] T. A. Austin and R. W. Mason, *ibid.*, **2**, 646 (1963).

[6] E. A. Lawton and J. Q. Weber, *J. Am. Chem. Soc.*, **85**, 3595 (1963).

[7] W. C. Firth, Jr., *Inorg. Chem.*, **4**, 254 (1965).

[8] The effect of change in light intensity and wavelength distribu-

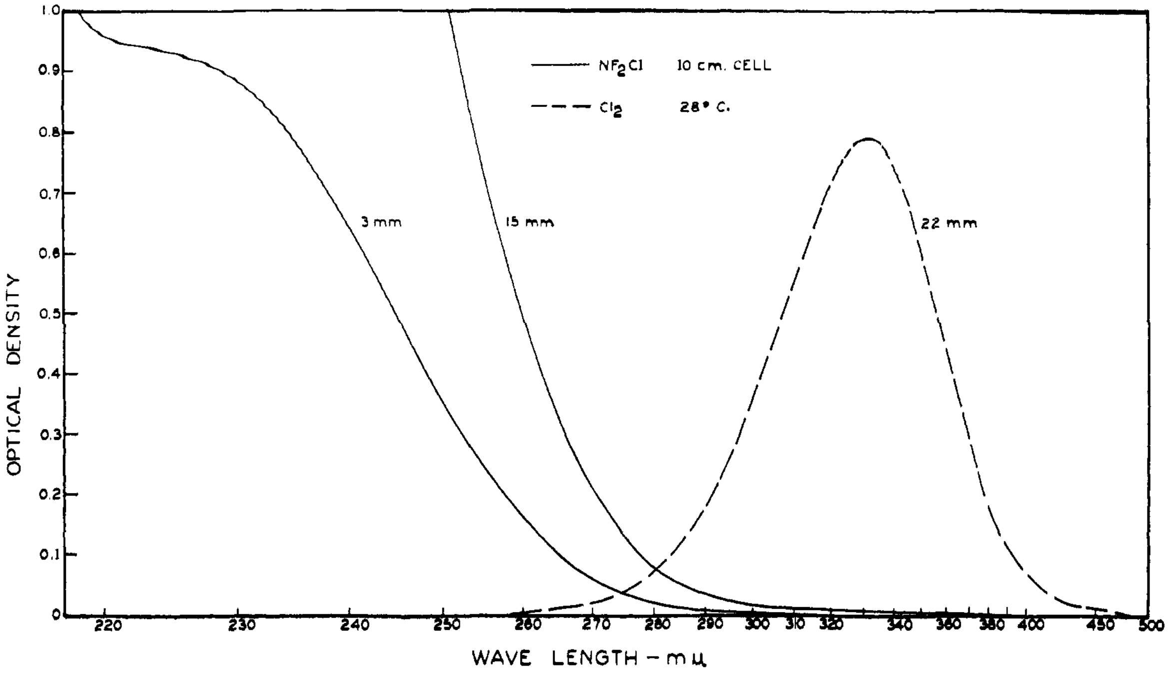

Figure 1. Ultraviolet absorption spectrum of chlorodifluoramine.

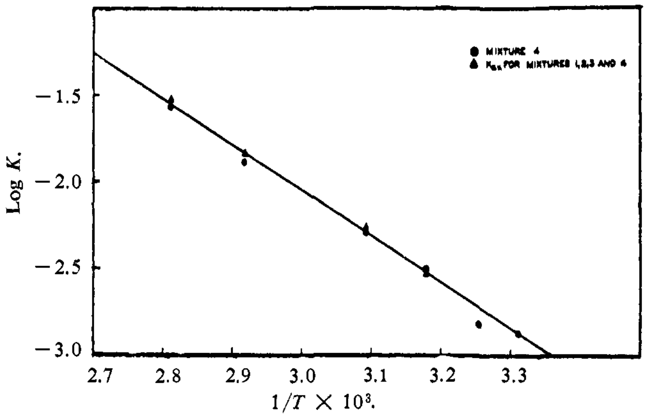

Figure 2. Log K as a function of $1/T$ for the equilibrium $N_2F_4 + Cl_2 \rightleftharpoons 2ClNF_2$.

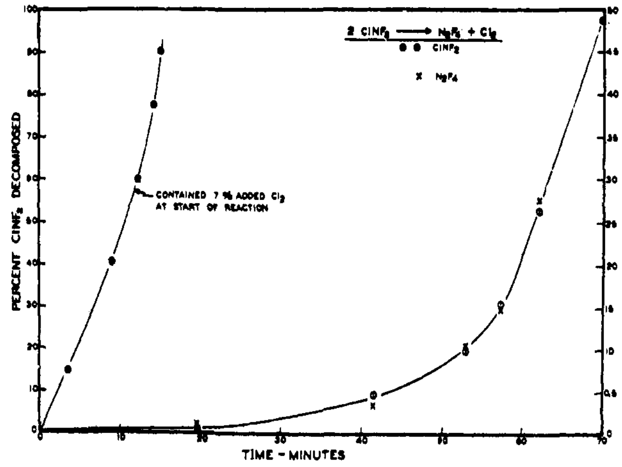

Figure 3. Photochemical decomposition of $ClNF_2$.

From the heat of formation of N_2F_4 (−2 kcal)[9] and the assumption that the temperature dependence of the photochemical equilibrium is a valid measure of ΔH for reaction 1, a heat of formation of approximately 5 kcal was obtained for $ClNF_2$.

The rate of photochemical decomposition of $ClNF_2$ was examined briefly (Figure 3). Chlorodifluoramine at 36 mm pressure in a Pyrex infrared cell (NaCl windows) was irradiated with a Hanovia EH-4 lamp at 27° for 70 min. Both the disappearance of NF_2Cl and the formation of N_2F_4 were followed by quantitative infrared analysis. The decomposition proceeded smoothly and exhibited marked autocatalysis. The decomposition curve with 7% added chlorine is also shown. The catalytic effect of chlorine is clearly demonstrated. The proposed mechanism is given in eq 2–5. The fact that $ClNF_2$ does not decompose in

$$NF_2Cl \overset{h\nu}{\rightleftharpoons} \cdot NF_2 + \cdot Cl \qquad (2)$$

$$\cdot Cl + NF_2Cl \longrightarrow Cl_2 + \cdot NF_2 \qquad (3)$$

$$Cl_2 \overset{h\nu}{\rightleftharpoons} 2 \cdot Cl \qquad (4)$$

$$2 \cdot NF_2 \rightleftharpoons N_2F_4 \qquad (5)$$

the presence of N_2F_4 (and hence NF_2 radicals) at ambient temperature in the absence of ultraviolet activation indicates that reaction 6 is not involved.

$$\cdot NF_2 + NF_2Cl \longrightarrow N_2F_4 + \cdot Cl \qquad (6)$$

Reaction of Chlorodifluoramine with Olefins

Chlorodifluoramine reacted with aliphatic olefins at elevated temperature (70–130°) to produce a mixture of the bis(difluoramine), the dichloride, and the β-chlorodifluoramine. The results are summarized in Table II.

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tion on the equilibrium have not been studied and it is possible that the observed equilibrium constants may represent a photochemical steady state and not true equilibrium constants for the system.

[9] G. T. Armstrong, S. Marantz, and C. F. Coyle, National Bureau of Standards Report No. 6584, U. S. Government Printing Office, Washington, D. C., 1959.

Table II. Reaction of Chlorodifluoramine and Olefins

	Reaction conditions					Calcd, %			Found, %			
Olefin	Initial pressure, mm	Temp, °C	Time, hr	Products	Yield[a]	C	H	N	C	H	N	F^{19} resonance
Ethylene	100	70	4	$ClCH_2CH_2Cl$	17							
Ethylene	400	130	12	$ClCH_2CH_2NF_2$	91[b]	20.79	3.49	12.13	21.77	3.75	12.91	−52.8φ
				$NF_2CH_2CH_2NF_2$[c,f]								
Propylene	407	130	6	$CH_3CHClCH_2Cl$	96[d]							
				$CH_3CHClCH_2NF_2$		27.81	4.67	10.81	27.42	4.64	10.62	−54.4φ
				$CH_3CH(NF_2)CH_2Cl$		27.81	4.67	10.81	27.86	4.74	11.25	−38.6φ
				$CH_3CH(NF_2)CH_2NF$[c]								
trans-Butene-2[e]	500	120	7	$CH_3CHClCHClCH_3$ (*dl* and *meso*)	95							
				$CH_3CH(NF_2)CHClCH_3$ (*erythro* and *threo*)								
				$CH_3CH(NF_2)CH(NF_2)CH_3$ (*dl* and *meso*)								

[a] Combined adduct yield based on recovered $ClNF_2$ and olefin. [b] By glpc analysis, the ratio of products was 1.3:2.5:1.0, respectively. [c] Reference 12. [d] By glpc analysis, the ratio of product was 1.2:0.4:1.1:1.0, respectively. [e] Because of the complexity of this mixture, no complete resolution of the mixtures was attained. [f] This product was not obtained in the 70° reaction.

$$NF_2Cl + CH_2{=}CH_2 \longrightarrow ClCH_2CH_2Cl + ClCH_2CH_2NF_2 + NF_2CH_2CH_2NF$$

Under the influence of ultraviolet light at room temperature, the reaction took a different course entirely. The photochemical reaction of ethylene with $ClNF_2$ at ambient temperatures proceeds according to the stoichiometry

$$2NF_2Cl + H_2C{=}CH_2 \longrightarrow ClCH_2CH_2Cl + N_2F_4$$

No C–NF_2 products are observed, and relatively long irradiation periods resulted in low conversion to products without decomposition of the unreacted $ClNF_2$. A plausible mechanism for this reaction is shown in eq 7–10.

$$NF_2Cl \overset{h\nu}{\rightleftharpoons} \cdot NF_2 + \cdot Cl \qquad (7)$$

$$\cdot Cl + CH_2{=}CH_2 \longrightarrow ClCH_2CH_2\cdot \qquad (8)$$

$$ClCH_2CH_2\cdot + ClNF_2 \longrightarrow ClCH_2CH_2Cl + \cdot NF_2 \qquad (9)$$

$$2\cdot NF_2 \rightleftharpoons N_2F_4 \qquad (10)$$

Since reaction 11 has an activation energy of about 14 kcal,[10] it would not be expected

$$\cdot NF_2 + CH_2{=}CH_2 \longrightarrow F_2NCH_2{-}CH_2\cdot \qquad (11)$$

to occur in the system under consideration. Reactions 12 and 13 would also lead to C–NF_2 products.

$$ClCH_2CH_2\cdot + \cdot NF_2 \longrightarrow ClCH_2CH_2NF_2 \qquad (12)$$

$$ClCH_2CH_2\cdot + N_2F_4 \longrightarrow ClCH_2CH_2NF_2 + \cdot NF_2 \qquad (13)$$

No estimate is available concerning the activation energy for reaction 13 while that for (12) can be assumed to be very small. The value of K_p for the N_2F_4 dissociation and the experimental conditions employed in the photochlorination experiment with ethylene and $ClNF_2$ allow an estimation of the mean values of the ratios $[\cdot NF_2]/[NF_2Cl]$ and $[N_2F_4]/[NF_2Cl]$ during the reaction. With the assumption that C–NF_2 products would be detectable at the 5% level in the product fraction, the following equations can be set up.

$$\frac{k_9[ClCH_2CH_2\cdot][NF_2Cl]}{k_{12}[ClCH_2CH_2\cdot][\cdot NF_2]} \geqq 20$$

$$\frac{A_1e^{-E_9/RT}}{A_2e^{-E_{12}/RT}}\frac{[NF_2Cl]}{[\cdot NF_2]} \geqq 20$$

Assuming $A_1 = A_2$

$$e^{(E_{12}-E_9)/RT}\frac{[NF_2Cl]}{[\cdot NF_2]} \geqq 20$$

In similar manner

$$e^{(E_{13}-E_9)/RT}\frac{[NF_2Cl]}{[N_2F_4]} \geqq 20$$

Using these values it is found that the activation energy differences, $E_9 - E_{12} \geqq 1.6$ kcal and $E_9 - E_{13} \geqq 1$ kcal, would account for the absence of $ClCH_2CH_2NF_2$ in the product.

It is apparent in the thermal reactions that there is more product derived from initiation of the reaction by addition of chlorine atoms to the olefin than from addition of the difluoramino radicals. This reflects the difference in activation energy of the two processes.[11] The difference between the thermal and photochemical reactions can be understood in terms of the comparative concentrations of difluoramino and chlorine radicals. In the presence of ultraviolet light at room temperature the chlorine atom concentration is high and the difluoramino radical low since tetrafluorohydrazine is not affected by light of these long wavelengths. Thermally the equilibrium between N_2F_4–Cl_2 and NF_2Cl can be established and at these temperatures the N_2F_4 is partially dissociated but the chlorine is not. These studies of chlorodifluoramine–olefin reactions complement very nicely those of the tetrafluorohydrazine–olefin reaction.[10,12]

Chlorodifluoramine and Mercurials

Chlorodifluoramine reacts with dimethyl-, diethyl- and di-*n*-butylmercury to produce a mixture of alkyl halide and alkyldifluoramine. However, from divinyl- and diphenylmercury only the organic halide was obtained. These reactions were conducted by stirring the liquid mercurial in an atmosphere of chlorodifluoramine for 5 to 48 hr. The halide–difluoramine mixture could be separated by gas chromatography. The alkyl

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(10) A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc., Sect. A*, 582 (1966).

(11) The activation energy for the process $Cl\cdot + CH_2{=}CH_2 \rightarrow ClCH_2CH_2\cdot$ is estimated to be no greater than 1.4 kcal/mole: E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, p 416.

(12) R. C. Petry and J. P. Freeman, *J. Org. Chem.*, in press.

chloride and alkyldifluoramine were produced in approximately equal amounts in all experiments, based on relative peak areas in the gas chromatogram of the combined fractions and the NF_2 balance for the experiments. The gas chromatogram of the *n*-butyl chloride–*n*-butyldifluoramine fraction from the di-*n*-butylmercury experiment showed a relative area ratio of 1:1.07 as compared to a relative ratio of 1:1.02 for a 1:1 mixture of the two compounds chromatographed under the same conditions. The data obtained for the aliphatic mercurials will be found in Table III in the Experimental Section.

Based on that data, the stoichiometry of these reactions closely approach that shown in eq 14. The relative reactivity of the mercurials toward $ClNF_2$ appears to be *n*-butyl > ethyl >> methyl. In an experiment not reported in Table III, a mixture of $ClNF_2$ and excess dimethylmercury heated for 3 hr at 50° resulted in less than 10% reaction. Chromatography of the CH_3Cl–CH_3NF_2 fraction indicated approximately equal amounts of each were formed.

$$3ClNF_2 + 2R_2Hg \longrightarrow N_2F_4 + RCl + RNF_2 + 2RHgCl \quad (14)$$

The mechanism of these reactions remains obscure. They apparently do not proceed by a free-radical path. In one experiment with diethylmercury, a 2:1 ratio of N_2F_4 to $ClNF_2$ was present at the start of the reaction. Although the stoichiometry was not measured in this case, the $C_2H_5NF_2/C_2H_5Cl$ ratio (determined by gas chromatography) was not significantly different from that observed in the experiment reported in Table III. The result is not consistent with the formation of these products by the following competing reactions if one assumes equal solubility for N_2F_4 and $ClNF_2$ in the liquid mercurial. Also it is not known why no difluoramine was produced from divinyl- or diphenylmercury.

$$R\cdot + NF_2Cl \longrightarrow RCl + \cdot NF_2$$

$$R\cdot + \cdot NF_2 \longrightarrow RNF_2$$

$$R\cdot + N_2F_4 \longrightarrow RNF_2$$

Reactions with Nucleophiles

A brief investigation of the reaction of chlorodifluoramine with some nucleophiles was made to determine if this reagent would function as a source of the difluoramino group. The principal reactions observed were of the redox type producing tetrafluorohydrazine and no particularly new chemistry was discovered.

Chlorodifluoramine is not attacked rapidly by aqueous base but is destroyed by ethanolic sodium ethoxide rapidly even at −80°. Tetrafluorohydrazine was recovered quantitatively. It is presumed that ethanol is oxidized during this process but no effort was made to isolate an organic product. The sodium salt of 2-nitropropane was oxidized to 2,3-dinitro-2,3-dimethylbutane. Sodium in liquid ammonia reduced NF_2Cl completely; all the fluorine was recovered as fluoride ion. Mercury reacts with chlorodifluoramine to produce N_2F_4 and mercurous chloride. These reactions may be generalized as

$$X^- + NF_2Cl \longrightarrow X\cdot + NF_2\cdot + Cl^-$$

Aniline and chlorodifluoramine reacted in the presence of β-naphthol to yield 1-benzeneazo-2-naphthol in fair yield. Although it is tempting to formulate this reaction as occurring through an N-difluoramino derivative which is dehydrofluorinated to the diazonium salt, there is actually no evidence aside from the product bearing on the mechanism of the reaction.

Summary

Chlorodifluoramine behaves as a source of chlorine and difluoramino radicals under the influence of heat and light. The product distribution from its thermal and photochemical reactions with olefins is fully consistent with previous studies involving difluoramino radicals alone. In addition $ClNF_2$ reacts with aliphatic mercurials to yield alkyldifluoramines. Toward strong nucleophiles $ClNF_2$ acts as an oxidizing agent and may be thought of as a source of positive halogen.

Experimental Section

Preparation of Chlorodifluoramine. A 1-l. Pyrex reagent bulb equipped with stopcock and condensing arm was charged *in vacuo* with 1.40×10^{-2} mole each of boron trichloride and difluoramine. The reactants were distilled into the reaction bulb with the condensing arm maintained at approximately −130° (methylcyclohexane slush bath temperature). The cooling bath was removed and the reaction mixture allowed to warm to ambient temperature. Reaction occurred below room temperature during the warm-up period and the bulb became coated with a white solid. The pressure in the reaction bulb corresponded to 2.0×10^{-2} mole of gaseous material at the completion of the reaction. Mass spectra and infrared analysis of the gaseous material showed the presence of NF_2Cl, HCl, and Cl_2, with small amounts of BCl_3 and BF_3. The solid nonvolatile reaction product was not identified, but appeared to contain the fluoroborate ion. The gaseous reaction mixture was separated by low-temperature vacuum fractionation through traps maintained at −130 and −196°. The −196° fraction contained the NF_2Cl contaminated with HCl and small amounts of Cl_2 and BF_3. Purification was accomplished by passage of this fraction through an Ascarite-packed tower at 0° and low pressure, followed by fractionation through a trap maintained at −130° to remove water. The passed fraction collected at −196° amounted to 6.96×10^{-3} mole (49.8% yield) and was essentially pure NF_2Cl.

An alternate purification method consisted of exposing the NF_2Cl fraction to 3 *N* sodium hydroxide solution (at room temperature) with stirring for 30 min, followed by fractionation through a trap at −130° to remove water. The physical properties, analysis, and characterization of chlorodifluoramine have been described.[3]

Olefin Addition Reaction. The conditions employed are found in Table II The reactions were conducted on a millimole scale in Pyrex bulbs by condensing in equimolar quantities of the olefin and NF_2Cl and heating the mixture in an oil bath at the temperature listed. The contents were then distilled on a vacuum line through traps at −80 and −196°. The contents of the −80° trap were then chromatographed on a dinonyl phthalate–chromosorb column to separate the components.

In the photochemical experiments the bulb was irradiated with a Hanovia EH-4 lamp at room temperature. The work-up was the same.

Reaction of $ClNF_2$ and Di-*n*-butylmercury. A 500-cc Pyrex reaction bulb equipped with stopcock and magnetic stirring bar was charged *in vacuo* with 2.2 g (0.0070 mole) of freshly distilled di-*n*-butylmercury and 0.0073 mole of pure $ClNF_2$. The reaction mixture was stirred at ambient temperature for 18 hr, during which time the pressure decreased from 228 to 170 mm and the formation of a white solid phase was observed. The reaction mixture was worked up by low-temperature vacuum fractionation through traps maintained at −24, −118, and −196°. There was no noncondensable fraction. The −196° fraction amounted to 0.0028 mole; quantitative infrared analysis showed 90% N_2F_4 and 10% $ClNF_2$. The −118° fraction weighed 0.46 g. Gas chromatography of the −118° fraction on a dinonyl phthalate column at 60° showed two components present in approximately equal amounts. These

Table III. Reaction of $ClNF_2$ with Dialkylmercury Compounds

Reactants, mmoles		Reaction conditions		Products, mmoles			Recovered reactants, mmoles	
$ClNF_2$	R_2Hg	Time, hr	Temp, °C	N_2F_4	$RCl + RNF_2$	RHgCl	$ClNF_2$	R_2Hg
R = n-C_4H_9								
7.3	7.0	18	25	2.5	4.6	4.2	0.3	...[a]
5.1	~10	24	25	1.7	...[a]	...[a]	0.0	...[a]
R = C_2H_5								
7.1	7.1	4	25	2.2	4.0	(3.5)[b]	0.7	2.4
14.3	14.3	48	25	4.8	8.3	(5.3)[b]	0.0	...[a]
R = CH_3								
2.0	~3	5	80	0.71	1.4	...[a]	0.0	...[a]

[a] Size of fraction not measured. [b] Appreciable mechanical losses were sustained.

Table IV. N_2F_4–NF_2Cl–Cl_2 Equilibrium. Experimental Data for Mixture 4,[a] Table I

Equilibrium pressure, mm N_2F_4	Cl_2	$ClNF_2$	K	Temp, °C
45.1	451.1	9.86	0.00478	49.90
(44.9)	(450.9)	(10.18)	(0.00512)	
Repeat irradiation				
44.7	450.7	10.55	0.00552	
(45.1)	(451.1)	(9.86)	(0.00478)	
42.2	448.2	15.56	0.0128	69.70
(42.1)	(448.1)	(15.80)	(0.0132)	
Repeat irradiation				
42.4	448.4	15.32	0.0123	
(42.0)	(448.0)	(15.95)	(0.0135)	
39.1	445.6	21.75	0.0271	83.10
(39.0)	(445.0)	(22.00)	(0.0279)	
47.3	453.3	5.50	0.00141	29.00
(47.4)	(453.4)	(5.19)	(0.00125)	
45.9	451.9	8.15	0.00320	41.25
(46.1)	(452.1)	(7.90)	(0.00300)	
47.3	453.3	5.40	0.00136	33.25
(47.2)	(453.2)	(5.49)	(0.00141)	
Repeat irradiation				
47.1	453.1	5.81	0.00158	
(47.1)	(453.1)	(5.82)	(0.00158)	
Repeat irradiation				
47.1	453.1	5.80	0.00158	
(47.3)	(453.3)	(5.50)	(0.00140)	

[a] Mixture 4 initially contained 406 mm of Cl_2 and 100 mm of $ClNF_2$. Experiment made in order listed. The figures in parentheses indicate duplicate analyses.

were separated and trapped by gas chromatography and identified as n-butyl chloride (0.0025 mole) and n-butyldifluoramine (0.002 mole). The −24° fraction was found to be unreacted di-n-butylmercury. The nonvolatile white solid remaining in the reaction bulb was washed with pentane and filtered. There was thus obtained 1.22 g (0.0042 mole) of n-butylmercuric chloride, mp 127–128° (lit.[13] mp 130°). Elemental analysis showed no fluorine.

The n-butyldifluoramine, bp 72°, was characterized by mass, infrared, and nmr spectra (F^{19} resonance, −54.6 ϕ) and molecular weight determination (calcd, 109; found, 107.2). The yield was 28% based on $ClNF_2$ consumed.

Anal. Calcd for $C_4H_9NF_2$: C, 44.00; H, 8.25; N, 12.85. Found: C, 44.47; H, 8.44; N, 12.67.

Dimethyl- and diethylmercury similarly yielded methyl- and ethyldifluoramine which was identified by comparison of their physical and spectral properties with those of authentic samples.[14] Data on these reactions are compiled in Table III.

Reaction of Aniline and Chlorodifluoramine in the Presence of β-Naphthol. Into an evacuated U-tube containing 0.43 g (0.003 mole) of β-naphthol, 0.81 g (0.01 mole) of aniline, and 5 ml of benzene was condensed 67 ml (0.003 mole) of NF_2Cl. The contents were warmed to room temperature and darkened after stirring for 2 hr at room temperature. A mass spectrum showed that the vapor above the solution contained 2.6% N_2O, 6.4% NO, 0.8% SiF_4, and 2.6% N_2F_4; the rest was benzene. After removing the volatile components, the dark residue was taken up in benzene, washed with 10% sulfuric acid and water, and dried. The red solution was chromatographed through silica gel and concentrated to yield a red solid which was identified as 1-phenylazo-2-naphthol, mp 133–135° (lit.[15] mp 135°).

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(13) K. H. Slotta and K. R. Jacobi, *J. Prakt. Chem.*, **120**, 249 (1929).

(14) J. W. Fraser, *J. Inorg. Nucl. Chem.*, **16**, 23 (1960).

(15) E. Bamberger, *Ber.*, **53**, 2319 (1920).