We obtained no nmr evidence for the analogous reaction with FSSF, although any higher fluorosulfanes that could have been formed may have decomposed instantaneously on contact with the glass apparatus. However, it is possible that the higher sulfanes constituting our reaction products were formed by the intermediate synthesis of fluorosulfanes, for example

$$2FSSF + H_2S \longrightarrow S_5F_2 + 2HF \qquad (8)$$

$$S_5F_2 + 2H_2S \longrightarrow H_2S_7 + 2HF \qquad (9)$$

Without a metal vacuum system we were unable to pursue this hypothesis. Similarly, while the mixture of FSSF, $SSF_2$, and $SF_4$ could be prepared in glass with no side formation of $SOF_2$ or $SiF_4$, attempts to isomerize the FSSF to the more stable[14] $SSF_2$ isomer were accompanied by considerable $SOF_2$ formation together with the production of some $SiF_4$.

Since Moissan and Lebeau[15] had described the reaction of $SOF_2$ with $H_2S$ upon heating, we treated $SOF_2$ with an equimolar amount of $H_2S$ at room temperature to determine whether the presence of $SOF_2$ would interfere with the reactions of sulfur fluorides with $H_2S$. After 16 hr at room temperature, there had been no detectable reaction between $SOF_2$ and $H_2S$. From this we conclude that $SOF_2$ impurities do not participate in the reaction of $SF_4$ with $H_2S$. We further verified this by adding $SOF_2$ to the $SF_4$ before reaction with $H_2S$.

Our work indicates that fluorosulfanes, $S_nF_2$ with $n > 3$, react very quickly with $H_2S$. We were unable to observe these species *via* fluorine nmr spectroscopy, in analogy to Seel.[14]

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# Chlorine Monofluoride Addition to Halo Imines. Magnetic Nonequivalence in Some Perfluoro Amines

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Chlorine monofluoride adds to $(CF_3)_2C{=}NCl$, $Cl_2C{=}NF$, $((CF_3)_2C{=}N)_2$, $F_2C{=}NF$, $(CF_3)_2C{=}NF$, and $ClFC{=}NF$ to give $(CF_3)_2FCNCl_2$, $Cl_2FCNFCl$, $(CF_3)_2CFN{=}NCCl(CF_3)_2$ and $((CF_3)_2CFN)_2$, $F_3CNFCl$, $(CF_3)_2FCNFCl$, and $ClF_2CNFCl$. The measurably slow nitrogen inversion process in the last two compounds is detected by $^{19}F$ nmr spectra which show magnetic nonequivalence of fluorines resulting from an asymmetric nitrogen. $ClF_2CNFCl$ gives spectra characteristic of slow inversion at temperatures in excess of 100°. Mercury easily dechlorinates $Cl_nF_{3-n}CNF_{2-x}Cl_x$ ($n$ = 1–3, $x$ = 1, 2) to corresponding imines.

Chlorine monofluoride is a useful reagent, acting as a fluorinating or chlorinating agent as well as a chlorofluorinating agent.(2),(3) Recent papers describe the addition of ClF to carbon–nitrogen multiple bonds giving $>NCl$(4) or $-NCl_2$(5) derivatives. We have found that ClF adds readily to $>C{=}NF$ imines when the carbon substituents are chlorine or fluorine. In some cases, where $CF_3$ is bonded to the imine carbon, cesium fluoride is required to catalyze the reaction. Each product which contains chlorine bonded to carbon will rapidly lose chlorine at room temperature in the presence of mercury to give $>C{=}NF$ imine. Two of the new compounds, $ClF_2CNFCl$ and $(CF_3)_2FCNFCl$, contain an asymmetric center. At 25° the carbon fluorines of $ClF_2CNFCl$ are magnetically nonequivalent as are the $CF_3$ groups in $(CF_3)_2CFNFCl$ as detected with $^{19}F$ nmr.(6) An nmr–temperature study shows hindered inversion about the nitrogen which can be overcome thermally in the case of $(CF_3)_2CFNFCl$ at 60° but is still observed for $ClF_2CNFCl$ at greater than 100°. Most acyclic amines known to invert slowly have a temperature of coalescence below 25°, although there are exceptions.(7),(8)

Dechlorofluorination of halodifluoraminomethanes with mercury provides a straighforward route to the formation of fluoro imines. Thus, with $NF_2CCl_2CN$,(9) the syn and anti isomers ($FN{=}CClCN$) are obtained, as are the imines *syn*- and *anti*-$FN{=}CClF$(10) and $-FN{=}CCl_2$ from $NF_2CCl_2F$ and $NF_2CCl_3$. Mercury does not react similarly with $NF_2CClF_2$ apparently because of the stronger carbon–chlorine bond due to the electron-withdrawing properties of the fluorine atoms bonded to carbon. Fluoroimines have been prepared previously from the fluorination of organic nitrogen compounds, the reductive defluorination of $>CFNF_2$ compounds,(11),(12) and the dehydrofluorination of $>CHNF_2$ compounds.(11)

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However, when compounds of the form $Cl_nF_{3-n}CNF_{2-x}Cl_x$ ($n = 1-3$, $x = 1, 2$) react with mercury, only dechlorination occurs.

## Experimental Section

**Materials.**—The imines $FN{=}CCl_2$ and $FN{=}CFCl$ were prepared by the reaction of $NF_2CCl_3$[9] and $NF_2CCl_2F$[9,13] respectively, with mercury. $(CF_3)_2C{=}NF$ and $((CF_3)_2C{=}N)_2$ were prepared by the method of Ruff,[14,15] and $(CF_3)_2C{=}NCl$ was obtained by treating $(CF_3)_2C{=}NH$ with ClF over CsF. Chlorine monofluoride (Ozark-Mahoning Co.) was used without further purification.

**General Procedures.**—Gases and volatile liquids were handled in a conventional Pyrex vacuum apparatus equipped with a Wallace and Tiernan or Heise Bourdon tube type pressure gauge. Gaseous starting materials and purified products were measured quantitatively by $PVT$ techniques. For gas chromatographic separations, the columns were constructed of 0.25-in. aluminum or copper tubing packed with 20% Kel-F polymer oil, 20% FC-43 (3M Co.), or FS-1265 (Analabs) on acid-washed Chromosorb P. In some cases, fractional condensation was used to effect crude separation. Molecular weight measurements were carried out by vapor density techniques with a Pyrex weighing vessel. Vapor pressure studies were made by using the method of Kellogg and Cady.[16]

Infrared spectra were recorded with a Perkin-Elmer 457 spectrophotometer using a 5-cm gas cell equipped with KBr windows. Fluorine-19 nmr spectra were obtained on a Varian HA-100 spectrometer using trichlorofluoromethane as an internal standard. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E mass spectrometer at an ionization potential of 70 eV.

**Reaction of $NF_2CCl_3$ with Mercury.**—$NF_2CCl_3$[9] (13 mmol) and excess mercury were stirred at room temperature for 31 hr. The volatile product was essentially pure $FN{=}CCl_2$ which was identified by its mass spectrum;[17] mol wt 116.5 (calcd 115.9); $^{19}F$ nmr: single broad peak at $\phi$ −57.3; and infrared spectrum[17] at 10 mm: 1560 (m, doublet), 1020 (s), 940 (s, triplet), 798 (vw), 650 $cm^{-1}$ (m).

**Reaction of $NF_2CF_2Cl$ with Mercury.**—$NF_2CF_2Cl$[9] (1 mmol) and excess mercury were stirred at 140° in a 125-$cm^3$ glass vessel for 42 hr. The volatile products consisted of $CF_4$, $SiF_4$, $N_2$, and unreacted $NF_2CF_2Cl$.

**Preparation of $(CF_3)_2C{=}NCl$.**—$(CF_3)_2C{=}NH$ (5 mmol) and ClF (8 mmol) were condensed into a 75-ml Hoke bomb containing 10 g of CsF and held at −78° for 0.5 hr. $(CF_3)_2C{=}NCl$ (57%) was obtained after fractionation at −98°. The $(CF_3)_2CFNCl_2$ (37%) was stopped at −63°.

**Preparation and Properties of $Cl_2FCNFCl$.**—ClF (2.2 mmol) and $FN{=}CCl_2$ (1.8 mmol) were condensed into a 50-ml Pyrex vessel fitted with a Teflon stopcock (Fischer-Porter Co.) and allowed to react for 3 hr at −20°. Pure $Cl_2FCNFCl$ was obtained in 60% yield after separation from the other volatile products *via* gas chromatography with a 25-ft FC-43 column at 0°.

Chlorofluoro(dichlorofluoromethyl)amine is a colorless liquid at 25° which slowly decomposes at 53° to $Cl_2$, $FN{=}CFCl$, and trace amounts of $FN{=}CF_2$. Reaction with mercury is rapid to give $FN{=}CFCl$ as the only volatile product. Because of its thermal instability, vapor pressure data for pure $Cl_2FCNFCl$ were obtained only up to 368 Torr at 46.2°. Between 273 and 319.2°K, vapor pressure may be calculated from the equation $\log P_{Torr} = 7.12 - 1454/T$. Vapor pressure data are as follows ($T$, °K; $P$, Torr): 273, 59.7; 287.8, 116.6; 295.5, 158.5; 312.0, 283.1; 319.2, 367.5. The experimental molecular weight was found to be 171.4 (calcd 170.4). Two resonances were observed in the $^{19}F$ nmr, a doublet (relative areas of 1:1) at $\phi$ 46.0 assigned to the CF fluorine and a broad overlapping doublet centered at $\phi$ −22.1 assigned to the NF fluorine. The ratio of the relative areas of the NF and CF resonances is 1.0:1.1 and $J_{F-F} = 28$ cps. The infrared spectrum (12 Torr) is as follows: 1135 (vs), 1007 (m), 927 (s), 906 (s), 880 (s), 785 (m), 756 (w), 719 (m), 688 (vw), 600 $cm^{-1}$ (w). The principal peaks in the mass spectrum correspond to the ions $CN^+$, $CF^+$, $NF^-$, $Cl^+$, $HCl^+$, $NCF^+$, $CCl^+$, $NCl^+$, $NCCl^+$, $FNCF^+$, $CFCl^+$, $NFCl^+$, $NCFCl^+$, $CF_2Cl^+$, $FNCFCl^+$ (100%), $CFCl_2^+$, $FNCCl_2^+$, $CCl_3^+$, and $FNCCl_2F^+$. All chlorine-containing fragments give the correct isotopic ratios. *Anal.* Calcd for $Cl_2FCNFCl$: C, 7.0; N, 8.2; F, 22.3; Cl, 62.4. Found: C, 6.68; N, 7.67; F, 21.1; Cl, 62.4.

**Preparation and Properties of $ClF_2CNFCl$.**—ClF (2.6 mmol) and $FN{=}CFCl$ (2.2 mmol) were condensed into a 50-ml bulb and allowed to react for 3 hr at −20°. Pure $ClF_2CNFCl$ was obtained in 67% yield after separation from the other volatile products (including $FN{=}CCl_2$) *via* gas chromatograph with a 25-ft Kel-F column.

Chlorofluoro(chlorodifluoromethyl)amine is a colorless gas at 25° which slowly decomposes to $Cl_2$ and $FN{=}CF_2$ but reacts rapidly with mercury giving the imine as the only volatile product. The boiling point is 16.5° from a Clausius–Clapeyron plot described by the equation $\log P_{Torr} = 7.64 - 1378/T°K$. Vapor pressure data are as follows ($T$, °K; $P$, Torr): 226.0, 37.1; 250.5, 142.6; 264.2, 268.7; 273.0, 393.4; 280.0, 525.5; 283.0, 595.2; 286.5, 673.8; 289.0, 737.2; 291.0, 794.7. The molar heat of vaporization is 6.3 kcal and the Trouton constant is 21.8. The experimental molecular weight is 153.3 (calcd 153.9). See Results and Discussion for details on $^{19}F$ nmr. The infrared spectrum (13 Torr) is as follows: 1220 (vs), 1210 (vs), 1162 (vs), 1107 (vw), 1060 (vs), 923 (s), 884 (m), 853 (m), 816 (s), 788 (m), 706 (m), 662 (m), 600 $cm^{-1}$ (m). The principal peaks in the mass spectrum correspond to the ions $CF^+$, $NF^+$, $Cl^+$, $HCl^+$, $NCF^+$, $CCl^+$, $NCl^-$, $CF_2^-$, $NCCl^+$, $NCF_2^+$, $CFCl^-$, $NFCl^+$, $CF_3^+$, $NCFCl^+$, $FNCF_2^+$, $ClCF_2^-$ (100%), $FNCFCl^+$, and $FNCF_2Cl^+$. *Anal.* Calcd for $ClF_2CNFCl$: Cl, 46.2. Found: Cl, 46.1.

**Preparation of $CF_3NFCl$.**—ClF (0.7 mmol) and $FN{=}CF_2$ (0.5 mmol) were condensed into a 10-ml bulb and allowed to react for 4 hr at −20°. $CF_3NFCl$ was obtained in about 75% yield and was identified by its infrared and $^{19}F$ nmr spectra.[18]

**Preparation and Properties of $(CF_3)_2CFNCl_2$.**—ClF (10 mmol) and $(CF_3)_2C{=}NCl$ (6.7 mmol) were condensed into a 75-ml Monel vessel containing roughly 10 g of finely powdered anhydrous CsF and several steel balls. The vessel was held at −78° for 1 hr followed by shaking for 17 hr at 25°. Pure $(CF_3)_2CFNCl_2$ was obtained in 80% yield by gas chromatography with a 6-ft FS-1265 column. No reaction occurs without CsF at either 27 or 80°. (See preparation of *N*-chlorohexafluoroisopropylimine.)

Dichloro(heptafluoroisopropyl)amine is a stable yellow liquid at 25°. The boiling point is 70.5° from the equation $\log P_{Torr} = 7.73 - 1667/T°K$. Vapor pressure data are as follows ($T$, °K; $P$, Torr): 299.0, 133; 304.3, 175; 307.5, 213; 312.3, 247; 316.8, 295; 321.5, 349; 326.0, 405; 329.5, 466; 330.8, 491; 332.5, 517; 334.8, 557; 336.3, 599; 337.3, 620; 340.0, 680; 341.8, 711; 343.8, 762. The molar heat of vaporization is 7.7 kcal and the Trouton constant is 22.4. The experimental molecular weight is 253.9 (calcd 254). Two resonances were observed in the $^{19}F$ nmr, a doublet (relative areas 1:1) at $\phi$ 72.2 assigned to the equivalent $CF_3$ groups and a broad, partially resolved multiplet centered at $\phi$ 139.8 assigned to the CF fluorine. The relative areas of the $CF_3$ and CF resonances were found to be 5.9:1.0 ($J_{CF_3-F} = 3$ cps). The infrared spectrum (8 Torr) is as follows: 1305 (s), 1288 (s), 1260 (vs), 1212 (w), 1190 (w), 1165 (m), 1128 (w), 1082 (s), 995 (s), 810 (w), 728 (m), 545 (w), 480 $cm^{-1}$ (w). The principal peaks in the mass spectrum correspond to the ions $CN^+$, $Cl^+$, $HCl^-$, $CF_2^+$, $CF_3^+$ (100%), $CF_2CN^+$, $CF_2Cl^+$, $CF_3CN^+$, $CF_3CF^+$, $CF_3FCN^+$, $CF_3CF_2^+$, $CF_3CNCl^+$, $CF_3FCNCl^+$, $(CF_3)_2CN^+$, $(CF_3)_2CF^+$, $C_3F_5NCl^+$, $C_2F_4NCl_2^+$, $(CF_3)_2CNCl^+$, and $(CF_3)_2CFNCl_2^+$. *Anal.* Calcd for $(CF_3)_2CFNCl_2$: C, 14.18; N, 5.51; F, 52.4; Cl, 27.65. Found: C, 14.31; N, 5.40; F, 52.4; Cl, 26.98.

**Preparation and Properties of $(CF_3)_2CFNFCl$.**—ClF (6.4 mmol) and $(CF_3)_2C{=}NF$ (3.8 mmol) were condensed into a 75-ml Monel vessel containing approximately 10 g of finely divided anhydrous CsF and several steel balls. The vessel was warmed to and held at −78° for 1 hr followed by shaking for 13 hr at 25°. Pure $(CF_3)_2CFNFCl$ was obtained in 71% yield by gas chromatography with a 24-ft Kel-F column. No reaction occurs without CsF.

Chlorofluoro(heptafluoroisopropyl)amine is a stable colorless

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liquid at room temperature. Vapor pressure data are as follows ($T$, °K; $P$, Torr): 240, 26; 251, 51; 263.3, 99.5; 273.3, 166; 282, 245; 291, 347; 298, 457; 303, 561; 305, 601; 308, 669; 311.3, 767. The equation $\log P_{\mathrm{Torr}} = 7.71 - 1503/T$°K gives a boiling point of 38.1°. The molar heat of vaporization is 7.05 kcal and the Trouton constant is 22.7. The experimental molecular weight is 238.8 (calcd 237.5). See Results and Discussion for details on the $^{19}$F nmr. The infrared spectrum (10 Torr) is as follows: 1305 (s), 1288 (s), 1260 (vs), 1187 (m), 1157 (m), 1080 (m), 1010 (m), 915 (w, sh), 892 (m), 800 (w), 749 (m), 724 (m), 582 cm$^{-1}$ (w). The principal peaks in the mass spectrum correspond to the ions $CN^+$, $Cl^+$, $HCl^+$, $CF_2^+$, $NCl^+$, $CF_3^+$ (100%), $C_2F_2N^+$, $FCNCl^+$, $CF_3CF^+$, $CF_3CFN^+$, $C_2F_5^+$, $CF_3CNCl^+$, $C_3F_6^+$, $CF_3CFNCl^+$, $CF_3CFNFCl^+$, $(CF_3)_2CF^+$, $(CF_3)_2CNF^+$, $(CF_3)_2CNCl^+$, and $(CF_3)_2CFNFCl^+$. *Anal.* Calcd for $(CF_3)_2CFNFCl$: Cl, 15.0. Found: Cl, 15.1.

**Preparation and Properties of $(CF_3)_2CFN{=}NCCl(CF_3)_2$ and $((CF_3)_2CFN)_2$.**—ClF (5 mmol) and $((CF_3)_2C{=}N)_2$[15] (2.5 mmol) were condensed into a Pyrex vessel and held at 25° for 25 min. Excess ClF was removed by pumping on the contents of the vessel at −78° and the reaction products were separated by gas chromatography using a 1.5-ft column packed with 20% Kel-F on Chromosorb P. Pure $(CF_3)_2CFN{=}NCCl(CF_3)_2$ is obtained in 54% yield.

$N$-(Heptafluoroisopropyl)-$N'$-(2-chlorohexafluoroisopropyl)-diazine is a stable light yellow liquid at 25°. Vapor pressure data are as follows ($T$, °K; $P$, Torr): 294.7, 70; 311.7, 150; 335.2, 362; 347.2, 552; 352, 650; 355, 712. An extrapolated boiling point of 83.4° is obtained from the equation $\log P_{\mathrm{Torr}} = 7.78 - 1750/T$°K. The molar heat of vaporization is 8.1 kcal and the Trouton constant is 22.7. Three resonances are found in the $^{19}$F nmr: a singlet at $\phi$ 71.8 assigned to the $CF_3$ groups bonded to CCl, a doublet at $\phi$ 76.8 ($J_{\mathrm{CF_3-CF}} = 4.9$ cps) assigned to the remaining $CF_3$ groups, and a septet at $\phi$ 163.3 ($J_{\mathrm{CF-CF_3}} = 4.9$ cps) assigned to CF. Peak areas were in the ratio 6:6:1. The infrared spectrum (7 Torr) is as follows: 1387 (w), 1338 (m), 1290 (s), 1268 (s), 1258 (s), 1215 (w), 1200 (m), 1180 (m), 1080 (m), 1015 (s), 845 (w), 770 (w), 740 (m), 630 (w), 540 (w), 480 cm$^{-1}$ (w). The principal peaks in the mass spectrum correspond to the ions $CF_2^+$, $CF_3^+$ (100%), $CF_2Cl^+$, $C_2F_4^+$, $C_3F_6N_2^+$, $C_3F_7^+$, $C_3F_6Cl^+$, and $C_6F_{13}N_2^+$. *Anal.* Calcd for $(CF_3)_2CFN{=}NCCl(CF_3)_2$: F, 64.55; C, 18.82; N, 7.32; Cl, 9.31. Found: F, 64.4; C, 18.55; N, 7.32; Cl, 8.62.

When the reactants are held in the presence of an excess of anhydrous CsF (5 g), both chlorofluorination and fluorination occur. For example, ClF (5 mmol) and $((CF_3)_2C{=}N)_2$ (2.5 mmol) on CsF (5 g) at 25° for approximately 2 hr followed by gas chromatographic separation give $(CF_3)_2CClNNCF(CF_3)_2$ (45%) and $((CF_3)_2CFN)_2$ (27%). None of the latter is formed without CsF.

Bis(heptafluoroisopropyl)diazine which was reported previously[15] is identified by mass, nmr, and infrared spectra and fluorine analysis. The $^{19}$F nmr is a complex multiplet centered at $\phi$ 161.5 which is assigned to the two CF fluorines which are split by the adjacent trifluoromethyl groups. A doublet at $\phi$ 76.6 ($J_{\mathrm{CF_3-F}} = 5$ cps) is assigned to the $CF_3$ groups. The relative areas of the resonances are 1:6. Principal peaks in the mass spectrum correspond to the ions $CF_2^+$, $CF_3^+$ (100%), $CF_3N_2^+$, $C_2F_4^+$, $C_2F_5^+$, $C_3F_5^+$, $C_3F_7^+$, $C_3F_6N_2^+$, $(M - 2F)^+$, and $(M - F)^+$. The infrared spectrum (8 Torr) is as follows: 1420 (w), 1380 (w), 1310 (vs), 1295 (vs), 1260 (vs), 1200 (s), 1170 (s), 1090 (s), 1020 (s), 770 (w), 740 cm$^{-1}$ (s). *Anal.* Calcd for $((CF_3)_2FCN)_2$: F, 72.7. Found: F, 73.0.

## Results and Discussion

Chlorine monofluoride readily adds across the double bond in $(CF_3)_2C{=}NF$ and $(CF_3)_2C{=}NCl$, in the presence of cesium fluoride, to give $(CF_3)_2FCNFCl$ and $(CF_3)_2CFNCl_2$ in yields greater than 70%. Although the latter reactions do not occur in the absence of CsF, ClF does add to $Cl_2C{=}NF$, $ClFC{=}NF$, $F_2C{=}NF$, and $((CF_3)_2C{=}N)_2$ without the metal fluoride. In the presence of anhydrous CsF, $((CF_3)_2C{=}N)_2$ reacts with an excess or deficit of ClF to give both the chlorofluorinated (I) and difluorinated (II) products. The relative amounts of the two products formed are unpredictable and cannot be correlated with any single factor, such as temperature, reaction time, or physical state of CsF. Both must be formed from reaction between the original reactants, for, once formed, neither product will react further with ClF either with or without CsF. No reaction occurs when the dimer is added to preformed $Cs^+ClF_2^-$ (CsF + ClF) at −20°; when warmed to 25° where the ClF equilibrium vapor pressure is negligible, reaction occurs but only trivial amounts of II are formed. On the other hand, when ClF is present neat, II does not form at all. While the addition of the components of ClF to the dimer apparently proceeds *via* a straightforward nucleophilic attack on the positive carbon by fluorine of the polar ClF molecule to form a carbanion which undergoes further reaction with the chloronium ion, formation of II must occur *via* a more complex mechanism not obvious from the results.

$FCl_2CNFCl$ and $F_2ClCNFCl$ are thermally unstable and lose chlorine to give $FClC{=}NF$ and $F_2C{=}NF$. Thus, starting with $Cl_2C{=}NF$ a series of imines and substituted perhalomethylchlorofluoramines results.

$$Cl_2C{=}NF + ClF \longrightarrow Cl_2FCNFCl \xrightarrow[\mathrm{Hg}]{\Delta\ \mathrm{or}} ClFC{=}NF + HgCl_2$$

$$ClFC{=}NF + ClF \longrightarrow ClF_2CNFCl \xrightarrow[\mathrm{Hg}]{\Delta\ \mathrm{or}} F_2C{=}NF + HgCl_2$$

$$F_2C{=}NF + ClF \longrightarrow F_3CNFCl \xrightarrow[\mathrm{Hg}]{\Delta\ \mathrm{or}} \text{no reaction}$$

The $^{19}$F nmr spectrum of $(CF_3)_2FCNFCl$ is reasonably well resolved at −40°. The $CF_3$ region consists of two multiplets of equal area. The multiplets are assigned to two magnetically nonequivalent $CF_3$ groups, $CF_3^a$ and $CF_3^b$. The nonequivalence is attributed to slow inversion about the asymmetric nitrogen.[6] At −40° the center of the $CF_3^a$ multiplet is at $\phi$ 72.4 and consists first of two separate quartets arising from interaction with the NF fluorine ($J_{\mathrm{CF_3^a-NF}} = 24.1$ cps) and $CF_3^b$ ($J_{\mathrm{CF_3^a-CF_3^b}} = 9.4$ cps). Each quartet is then split into two overlapping quartets from interaction with the CF fluorine ($J_{\mathrm{CF_3^a-CF}} = 2.8$ cps). The $CF_3^b$ multiplet appears as a pentet of doublets centered at $\phi$ 74.2. Since the spin–spin couplings of both $CF_3^a$ ($J_{\mathrm{CF_3^a-CF_3^b}} = 9.4$ cps) and the NF fluorine ($J_{\mathrm{CF_3^a-NF}} = 9.7$ cps) with $CF_3^b$ are approximately the same value, the overall effect is a splitting of $CF_3^b$ by four essentially equivalent fluorines to give the pentet which is then split by the CF fluorine ($J_{\mathrm{CF_3^b-CF}} = 3.8$ cps). The CF fluorine at $\phi$ 158.8 is a partially resolved multiplet which closely resembles a calculated 16-peak spectrum derived from the experimental coupling constants. The NF peak, found at $\phi$ −1.5, is broad and unresolved. No evidence for NF–CF spin–spin coupling is found although a weak interaction, *i.e.*, $J_{\mathrm{NF-CF}} < 2$ cps, could be masked by the broad CF and NF resonances. An integration of the total spectrum gives NF = 0.93, $CF_3^a = CF_3^b = 3.0$, and CF = 0.93. A temperature study of the $CF_3$ resonances shows that as the sample is heated, the two nonequivalent $CF_3$ groups become magnetically equivalent and the resonance bands coalesce at $T_c \approx 60°$. The broadness of the resulting resonance arises from a secondary quadrupole broadening from the nitrogen.

The $^{19}$F nmr of $ClF_2CNFCl$ is similar to that of $(CF_3)_2FCNFCl$ with the carbon fluorines $CF^a$ and $CF^b$ magnetically nonequivalent. At room temperature both $CF^a$ and $CF^b$ are well resolved and each is a doublet of doublets resulting from $CF^a$–$CF^b$ ($J_{\mathrm{CF^a-CF^b}} = 128$

cps) and CF–NF ($J_{CF^a-NF} = 24$ cps, $J_{CF^b-NF} = 13$ cps) coupling. The rather large magnitude of $J_{CF^a-CF^b}$ is not without precedent, for values as high as 270 cps have been observed for nonequivalent carbon fluorines adjacent to an asymmetric carbon[19] and, therefore, it is not unexpected in this case. In this ABX system the area ratio of the inner to outer doublets is 2.52:1 (theoretical 2.62:1).[20] Enhancement of the inner doublets is typical of spectra obtained when the chemical shift difference and spin–spin coupling values are similar; *i.e.*, for $ClF_2CNFCl$ $\Delta\phi_{CF^a-CF^b}$ (cps)/$J_{CF^a-CF^b}$ (cps) $\cong 2$. $CF^a$ is centered at $\phi$ 55.6 and $CF^b$ at $\phi$ 52.9 while the broad unresolved NF fluorine is found at $\phi$ −7.2. An integration of the total spectrum gives NF = 1.0 and $CF^a = CF^b = 0.98$.

An attempt to collapse the two CF multiplets proved unsuccessful. At −60° the centers of the two CF multiplets are separated by 330 cps but are shifted to about 237 cps at +60°. At 100° the peaks still do not coalesce. Higher temperatures were not attempted due to excessive pressure from the $ClF_2CNFCl-CCl_3F$ mixture in the nmr tube.

An interesting aspect of the temperature study of the magnetically nonequivalent nuclei in $(CF_3)_2FCNFCl$ and $ClF_2CNFCl$ is the rather high temperature of coalescence, especially for the latter compound in which the CF resonances are separated by 237 cps at 60°. Other workers have found that when highly electronegative substituents, particularly halogens, are bonded to the asymmetric nitrogen, there is a significant rise in the temperature of coalescence.[6,21,22] The collapse of the $CF_3$ groups in $(CF_3)_2FCNFCl$ at 60° can be rationalized in terms of the relatively bulky $CF_3$ groups which would increase the inversion rate because of greater steric interactions when the substituents are in a pyramidal position.[23]

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# Solubility Study of Calcium Hydrogen Phosphate. Ion-Pair Formation[1a]

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The solubility of $CaHPO_4$ has been determined in the ternary system $Ca(OH)_2-H_3PO_4-H_2O$, at 5, 15, 25, and 37°. The solubility product constant, $K_{sp} = (Ca^{2+})(HPO_4^{2-})$, varies with pH unless formation of ion pairs $CaHPO_4^0$ and $CaH_2PO_4^+$ is taken into consideration. Solubility product constants and their standard errors for $CaHPO_4$ are $(1.97 \pm 0.03) \times 10^{-7}$, $(1.64 \pm 0.01) \times 10^{-7}$, $(1.26 \pm 0.02) \times 10^{-7}$, and $(0.92 \pm 0.02) \times 10^{-7}$ at 5, 15, 25, and 37°, respectively. Association constants and standard errors are $(2.4 \pm 0.3) \times 10^2$, $(1.9 \pm 0.2) \times 10^2$, $(3.8 \pm 0.5) \times 10^2$, and $(3.9 \pm 0.9) \times 10^2$ for $CaHPO_4^0$ and $5 \pm 1$, $10 \pm 1$, $10 \pm 1$, and $11 \pm 1$ for $CaH_2PO_4^+$ at the same respective temperatures. Thermodynamic functions for the dissolution reaction for $CaHPO_4$ and the association reactions for $CaHPO_4^0$ and $CaH_2PO_4^+$ are also presented.

## Introduction

Anhydrous calcium hydrogen phosphate, $CaHPO_4$, is a stable phase in the system $Ca(OH)_2-H_3PO_4-H_2O$. Accurate information about the solubility of $CaHPO_4$ is of great value in establishing its stability range, in determining its thermodynamic properties, and in understanding interrelations among the calcium phosphates that precipitate from aqueous solutions.

Two values are given in the literature for the apparent solubility product of $CaHPO_4$ at 25°,[2,3] but these are not in good agreement. It is now known that the apparent solubility products for calcium phosphates vary with the equilibrium pH if they are calculated without taking into account ion-pair formation.[4] The neglect of ion-pair formation at relatively high concentrations accounts for much of the discrepancy in the reported values.

In this paper, we report the solubilities of $CaHPO_4$ at four temperatures in the dilute range of the phase diagram for this system. Three different experimental conditions were used to minimize effects due to metastability of $CaHPO_4$ with respect to other calcium phosphates and to ascertain that equilibrium was reached. Solubility products and standard heat and entropy of the dissolution reaction for $CaHPO_4$ and association constants and standard heats and entropies of association for the ion pairs $CaHPO_4^0$ and $CaH_2PO_4^+$ are reported for 5, 15, 25, and 37°. Equilibrations were made in the ternary system to avoid complications in the interpretation of data which might result from the presence of other ions.

[1] (a) This paper is based on a dissertation submitted by Hershel McDowell to the faculty of Howard University in partial fulfillment of the requirement for the Ph.D. degree. (b) Director, Research Associate Program of the American Dental Association at the National Bureau of Standards. (c) To whom reprint requests should be made at Howard University.

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