individual measurements do not follow a temperature-dependent trend and, therefore, should be considered as experimental errors and not significant in terms of a change in a configurational equilibrium.

In conclusion, the constant value of the dipole moments measured in solution over the given temperature range in addition to published[4] infrared and Raman spectra and high-temperature nmr studies seem to provide strong evidence for a *cis–cis* (II) configurational equilibrium in solution.

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Chlorine Pentafluoride. Preparation and Properties

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Three communications reporting the synthesis of ClF_5 have appeared.[1–3] This halogen fluoride has been under independent investigation in the Rocketdyne laboratories, and we wish now to report on some of our work in this area. Chlorine pentafluoride was first prepared in low yields in our laboratories by reactions of F_2 with chlorine and chlorine-containing compounds in a glow discharge at −196°. Despite the very small quantities of ClF_5 isolated, we established the fact that Cl_2 and F_2 were sufficient for its formation and inferred its structure from the infrared spectrum subsequently published by Begun, *et al.*[4] Molecular weights determined from vapor density measurements of impure ClF_5 also inferred the composition.

What we believe to be the most useful laboratory preparation of ClF_5 involves the fluorination of an alkali metal chlorotetrafluoride, $MClF_4$. Those examined include $KClF_4$, $RbClF_4$, and $CsClF_4$. Although all salts yielded ClF_5 upon fluorination, the cesium and potassium salts were investigated more extensively in this study. The general reaction for the salt fluorination is

$$MClF_4 + F_2 \longrightarrow MF + ClF_5 \qquad (1)$$

From the above equation it is seen that only one condensable gaseous product should be obtained. This was confirmed repeatedly by experiment; *i.e.*, pure ClF_5 was obtained in these reactions.

The conversions of $MClF_4$ to ClF_5 were variable. Using $KClF_4$, conversions from 1 to 25% have been observed. The lowest conversion was observed at 80°, while at 150° a consistent conversion of 10% was noted. Higher conversions were obtained with $CsClF_4$ and ranged from 25 to 90%. With both salts, however, pure ClF_5 was the only condensable gaseous product.

Chlorine pentafluoride is a typical interhalogen fluoride in that it is a corrosive, highly oxidizing substance. It is colorless in the gas phase, water white in the liquid phase, and freezes to a white solid. Vapor pressures were measured on the range −79.0 to +25° and are fitted to the equation $\log P_{mm} = 7.2683 - 1137.16/T(°K)$. Measured vapor pressures at the noted temperatures are [T (°C), P (mm)]: −79.2, 16.5; −63.2, 55.0; −50.0, 128.0; −45.3, 166.0; −35, 290.0; −26.2, 453.5; −23.7, 507; −17.9, 634.5; −14.5, 734.5; −0.2, 1293; +24.8, 2855. The normal boiling point is −14.0° and the melting point is −103 ± 4°. The derived Trouton constant of 21.8 shows ClF_5 to be a nonassociated liquid. The density of ClF_5 was measured in the range of −80 to −23°. The density–temperature relationship of d (g/ml) $= 2.696 - (3.08 \times 10^{-3}T(°K))$ is derived from the measured values (°C, g/ml): −80, 2.100; −57, 2.0361; −23, 1.922.

The thermal stability of ClF_5 is somewhat less than that of ClF_3. The equilibrium

$$ClF_5 \rightleftharpoons ClF_3 + F_2$$

was found to be established fairly readily above 165° and has been studied in detail.[5]

Chlorine pentafluoride was smoothly reduced by burning with ammonia to give a mixture of NH_4Cl and NH_4F. Multiple analyses of the combustion products gave an F/Cl ratio of 4.92. These agreed closely with chromatographic assays, using the technique of Lysyj and Newton,[6] which showed the presence of small quantities of Cl_2. The molecular weight was determined from the vapor density and was found to be 128 (calcd, 130.5).

The high-resolution F^{19} nmr spectrum for ClF_5 has been recorded using a Varian DP-60 spectrometer operating at 56.4 Mc. The spectrum was obtained on a 50 mole % solution of ClF_5 in $CFCl_3$. Two band structures were noted in the nmr spectrum. A strong doublet was recorded at −247 ppm (relative to $CFCl_3$) and a weak quintet at −412 ppm. The coupling constant for the band structures is $J = 130$ cps. The seven-component F^{19} spectrum recorded confirms the C_{4v} symmetry deduced from infrared and Raman studies.[3]

A stable mass-cracking pattern for ClF_5 has been obtained with a CEC 21-103 C mass spectrometer. Observed ions, excluding Cl^{37} isotopes, with the relative abundance were [m/e, ion, abundance (%)]: 111, ClF_4^+, 82.0; 92, ClF_3^+, 18.6; 73, ClF_2^+, 100.0; 54, ClF^+, 21.0; 46, ClF_3^{2+}, 3.5; 37.5, ClF_2^{2+}, 0.5; 35, Cl^+,

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[1] D. F. Smith, *Science*, **140**, 889 (1963).

[2] E. Gatti, R. L. Krieger, J. E. Sicre, and H. J. Schumacher, *J. Inorg. Nucl. Chem.*, **28**, 655 (1965).

[3] F. P. Gortsens and R. H. Toeniskoetter, *Inorg. Chem.*, **5**, 1925 (1966).

[4] G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

[5] H. F. Bauer and D. F. Sheehan, *Inorg. Chem.*, **6**, 1736 (1967).

[6] I. Lysyj and P. R. Newton, *Anal. Chem.*, **35**, 90 (1963).

11.4. The base peak corresponding to the ion ClF_2^+ was most unexpected inasmuch as under the same conditions in our instrument no m/e 73 was observed from ClF_3 except those for chlorine.[7]

Chlorine pentafluoride appears to be less corrosive to metals than ClF_3. A large sample has been stored in a Hoke 304 stainless steel cylinder for over 4 years without detectable decomposition. Contrary to the initial report on ClF_5[1] we have found ClF_5 to be extremely reactive toward water and water vapor. The hydrolysis of ClF_5 was carefully studied in Kel-F and the experimentally established stoichiometry is indicated as

$$ClF_5 + 2H_2O \longrightarrow FClO_2 + 4HF$$

Subsequent decomposition of $FClO_2$ (in metal systems) no doubt accounts for the presence of Cl_2, ClO_2, and $FClO_3$ frequently encountered in contaminated ClF_5. These same products are encountered whenever ClF_5 comes into contact with a hydroxylic function in any form.

When ClF_5 was handled in Kel-F or Teflon apparatus above its boiling point, it was found to be appreciably and rapidly soluble in the polymer. After the ClF_5 had been in contact with the polymer at room temperature for 1 day, it was found that neither evacuation under high vacuum nor washing with water removed all of the ClF_5 from the polymer; only after pumping for days in a vacuum system were the last traces of ClF_5 removed.

As predicted, ClF_5 is a vigorous fluorinating agent. With the possible exception of carbon, the first-row nonmetals did not react with ClF_5 at 150° in 16 hr. In contrast, second- and third-row nonmetals except chlorine were reactive even at ambient temperature. Carbon reactivity varied with its form. Activated charcoal reacted vigorously at ambient temperature to form Cl_2, CF_4, CF_3Cl, and C_2F_6. Lampblack with 1% volatile impurities reacted only partially at 150°. Graphite powder and pressed graphite rod took up ClF_5 corresponding to 10 wt % of the graphite but only ClF_5 was found in the volatiles recovered. Basic hydrolysis of such graphitic material was accompanied by a deflagration and yielded products similar to those of ClF_5 hydrolyses. The graphite rod crumbled on prolonged exposure to ClF_5. The above results suggest an intercalation compound between graphite and ClF_5.

Among the products of reaction between ClF_5 and basic, neutral, and acidic hydroxides were HF, O_2, chlorine, and chlorine dioxide. ClF_5 attacked CO, PO, and SO multiple bonds but not NO or ClO multiple bonds. Of particular interest was the scant amount of toxic, noxious, or otherwise hazardous gas products in the reactions of ClF_5 with $Na_2B_4O_7 \cdot Na_2S_2O_3 \cdot 9H_2O$ and $NaHCO_3$. Metal fluoride hydrates reacted with ClF_5 at ambient temperature with the exception of $MgF_2 \cdot xH_2O$ which had to be warmed for complete reaction.

Experimental Details

Materials.—Chlorine trifluoride was obtained from the Matheson Co. The reactors used for the pressure fluorinations were either Monel or 304 stainless steel and equipped with Hoke M343 valves. The discharge apparatus used for the synthesis of ClF_5 was similar to that described elsewhere.[8]

Preparation by Electrical Discharge.—A 60-l. stainless steel tank was filled to 1 atm with a mixture of 10 parts of fluorine and 1 part of chlorine (by volume). The gas was pumped through an electrical discharge cell cooled in a solid CO_2 and trichloroethylene mixture, a U trap at −196°, and a manostat of the bubbler type filled with Fluorolube oil that maintained a pressure in the train of 30 mm; the pump was protected by a fluorine absorber made of NaCl and soda lime and a liquid nitrogen trap. The contents of the −196° trap adjacent to the discharge apparatus was fractionated in a metal vacuum line through traps cooled to −112, −126, and −196°. The middle trap contained ClF_5, and the other traps contained ClF_3 and ClF, respectively. The yield was of the order of 1 cc of ClF_5/4000 cc of gas mixture used.

Synthesis of ClF_5 from Alkali Metal Chlorotetrafluorides.—A previously passivated 500-ml stainless steel Hoke cylinder was loaded with 76.0 g (0.5 mole) of anhydrous cesium fluoride in a drybox, and 50 g (0.55 mole) of ClF_3 was condensed therein from a metal vacuum line. The reactor was heated for 4 hr at 80°. Most of the ClF_3 was found to have reacted after this treatment. Fifteen liters (0.67 mole) of fluorine was then condensed into the reactor which was then heated for 22 hr at 150°. After removal of the excess fluorine, 26 g (0.2 mole) of pure ClF_5, representing a 40% conversion, was distilled out of the reactor. Essentially the same procedure was employed with RbF and KF; the conversions with KF were not as high and ranged between 10 and 25%.

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[7] B. L. Tuffly, V. E. Bedwell, and E. F. C. Cain, "Proceedings of Ninth Annual Meeting of ASTM Committee E-14 on Mass Spectrometry," Chicago, Ill., 1961.

[8] W. Maya, *Inorg. Chem.*, **3**, 1063 (1964).

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Complexes of Sulfur Dioxide with Ionic Azides

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Numerous reactions between sulfur dioxide and inorganic salts have been reported. For example, potassium cyanide,[1] potassium iodide,[2] and alkali metal fluorides[3] are known to combine with sulfur dioxide, and in many cases the products undergo irreversible reactions. However, the reaction of an azide salt with sulfur dioxide has not been described.

During the course of a study of azides, it was observed that the alkali metal azides reversibly absorb sulfur dioxide at room temperature. The apparent ease of

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[1] F. Seel and E. Muller, *Ber.*, **88**, 1747 (1955); J. M. Ross and W. C. Smith, *J. Am. Chem. Soc.*, **86**, 2861 (1964).

[2] J. Jander and G. Turk, *Angew. Chem.*, **75**, 792 (1963).

[3] F. Seel and L. Riehl, *Z. Anorg. Allgem. Chem.*, **282**, 293 (1955).