The Inorganic Chemistry of Carbon Difluoride

Sir:

The organic chemistry of divalent carbon has received much attention and has been proportionately rewarding. We now wish to describe some inorganic reactions of CF_2 at moderate temperatures; to this purpose we have prepared a new class of CF_2 transfer reagents, the trifluoromethyl fluorophosphoranes.

The new compound $(CF_3)_3PF_2$ (b.p. 20°, m.p. $-102°$, infrared absorption at 1240, 1195, and 855 cm.$^{-1}$) is made by the action of SF_4[1] on $(CF_3)_3P$[2] at 25°. $(CF_3)_2PF_3$ (b.p. $-5°$, m.p. $-74°$, infrared absorption at 1240, 1195, 952, 890, and 790 cm.$^{-1}$) can be made by SbF_3 fluorination of $(CF_3)_2PCl_3$,[3] or more directly by the vigorous attack of SF_4 on $(CF_3)_2PI$[2] below room temperature. CF_3PF_4 (b.p. $-35°$, m.p. $-117°$, infrared absorption at 1240, 1190, 1018, 990, 915, and 900 cm.$^{-1}$) is formed in the reaction of CF_3PCl_4[4] with SbF_3.

The trifluoromethyl fluorophosphoranes are convenient sources of CF_2. Elision of CF_2 occurs stepwise and reversibly

$$(CF_3)_3PF_2 \rightleftharpoons (CF_3)_2PF_3 + CF_2$$

$$(CF_3)_2PF_3 \rightleftharpoons CF_3PF_4 + CF_2$$

$$CF_3PF_4 \rightleftharpoons PF_5 + CF_2$$

The reversibility is demonstrated by the reorganization of $(CF_3)_2PF_3$ (10% per day at 25°) to give $(CF_3)_3PF_2$ and CF_3PF_4. CF_3PF_4 disproportionates (5% per month at 25°) to give $(CF_3)_3PF_2$, $(CF_3)_2PF_3$, and PF_5, and the reaction of excess PF_5 with $(CF_3)_3PF_2$ (100°, 4 hr.) is a good synthesis method for CF_3PF_4.

In the absence of other reagents the CF_2 disappears irreversibly by forming dimer (tetrafluoroethylene), trimer (hexafluorocyclopropane), and high polymer. Trimer is favored by slow decomposition ($(CF_3)_3PF_2$ at 120° for 24 hr. gave 10% $(CF_2)_2$, 80% $(CF_2)_3$, and 10% $(CF_2)_x$), while dimer is the major product when CF_2 is generated rapidly ($(CF_3)_3PF_2$ at 200° for 10 min. gave 80% $(CF_2)_2$, 10% $(CF_2)_3$, and 10% $(CF_2)_x$).

$(CF_3)_3PF_2$ decomposes at 25° in the gas phase at 0.5 atm. at the rate of 0.5% per month and at the same rate in the pure liquid. At 100° in the gas phase, CF_3 groups are destroyed to the same extent (40% in 17 hr.) in experiments with 4 and 0.25 atm. of starting material. This pressure and phase independence argues for a monomolecular elision process which suggests that the CF_2 is a true intermediate.

When $(CF_3)_3PF_2$ is decomposed in the presence of other reagents (120° for 24 hr. are convenient conditions) the CF_2 may be intercepted. For example with iodine, CF_2I_2 is formed in 30% yield in addition to ICF_2CF_2I,[5] $ICF_2CF_2CF_2I$,[6] and $(CF_2)_3$. The new compound CF_2I_2 (*Anal.* Calcd.: I, 83.55; mol. wt., 304. Found: I, 83.40; mol. wt. (gas density), 298) is a yellow liquid: m.p. $-72°$; 0° vapor tension 14 mm. the ultraviolet absorption maximum is at 2980 Å. in the gas phase; infrared absorption of the gas is strong at 1120, 1070, and 745 cm.$^{-1}$. F^{19} magnetic resonance shows a single line, 100 p.p.m. downfield from CF_3COOH. CF_2I_2 reacts with mercury at room temperature to give tetrafluoroethylene.

CF_2 generated at 100° adds to HCl to give HCF_2Cl, which is of interest because it is probably the reverse of the reaction whereby C_2F_4 is formed from the pyrolysis of HCF_2Cl above 650°.[7] CF_2 generated in the presence of oxygen gives carbonyl fluoride, but hydrogen does not react with CF_2 at 100°. CF_2 is a reducing agent in its reaction with UF_6 or MoF_6, giving CF_4 and reduced metal fluorides.

The reaction with chlorine is complicated by a competing attack directly on $(CF_3)_3PF_2$. The products are CF_2Cl_2 (70%), CF_3Cl (20%), and $CFCl_3$ (10%). The elision of CF_2 accounts for the formation of CF_2Cl_2 and the direct cleavage of a C–P bond by chlorine gives rise to CF_3Cl. These events could account for the observed $CFCl_3$

$$(X = CF_3 \text{ or } F)$$

$CF_3PX_4 \longrightarrow FPX_4 + CF_2$	elision of CF_2
$CF_3PX_4 + Cl_2 \longrightarrow CF_3Cl + ClPX_4$	C–P cleavage
$CF_2 + ClPX_4 \longrightarrow ClCF_2PX_4$	insertion of CF_2
$ClCF_2PX_4 \longrightarrow FCCl + FPX_4$	elision of FCCl
$FCCl + Cl_2 \longrightarrow FCCl_3$	

No reaction with CF_2 was observed when $(CF_3)_3PF_2$ was pyrolyzed at 120° in the presence of BF_3, CO, NF_3, N_2O, PF_3, CS_2, SO_2, or CF_3I. The CF_2 appeared as dimer, trimer, and high polymer and the reagents were recovered unchanged.

Our surmise that the CF_2 here described is a free molecule is supported by the constancy of reaction conditions for various reagents, the kinetics, and the nature of the products (especially CF_2I_2). We are seeking conclusive evidence by physical methods.

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