Trifluoromethyliodine(v) Tetrafluoride

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Summary Trifluoromethyliodine(v) tetrafluoride has been prepared by the oxidation of trifluoromethyl iodide at −78° with chlorine trifluoride.

ALTHOUGH the oxidation of trifluoromethyl iodide by fluorine[1] or by chlorine trifluoride[2] has been described, the product, formulated as CF_3IF_2,[1] readily decomposes and is not well characterised. We now report the preparation of trifluoromethyliodine(v) tetrafluoride from CF_3I and ClF_3 (3:4 mole ratio), a route that has been used to prepare higher members of the series $C_nF_{2n+1}IF_4$.[2] The reaction is conveniently carried out at −78° in a monel metal, Kel-F vacuum system. Providing the addition of ClF_3 is slow and the CF_3I is diluted by perfluorohexane (1:3), little C–I bond cleavage occurs and the yield of CF_3IF_4 is essentially quantitative. Pentafluorophenyliodine(v) tetrafluoride† is prepared similarly.

CF_3IF_4 is a white, moisture-sensitive solid, which is readily volatile at 20° and soluble in CCl_3F. It is characterised by its n.m.r. spectrum, first-order A_3X_4, δ_A $-56{\cdot}1$, δ_X $-$ 32·4 p.p.m., J_{AX} 18 Hz (chemical shifts to high-field of CCl_3F). The spectroscopic equivalence of the IF_4 group indicates either that the CF_3 group is *trans* to the lone pair, or that a fast intramolecular exchange process occurs. The mass spectrum of CF_3IF_4 consists of peaks assigned to CF_3IF^+ (1), CF_3I^+ (34), IF_4^+ (16), IF_3^+ (13), IF_2^+ (70), IF^+ (21), I^+ (47), and CF_3^+ (100). For $C_6F_5IF_4$ a molecular-ion peak is observed.

Decomposition of CF_3IF_4 at 20° is detectable after one hour, the products being CF_4, CF_3I, IF_5, and I_2. The stability of R_fIF_4 compounds with respect to decomposition increases in the order $CF_3 < (CF_3)_2CF < C_6F_5$, and $C_6F_5IF_4$ is stable indefinitely at 20°.

Attempts to isolate CF_3IF_2 from CF_3I and ClF_3 were unsuccessful. Although n.m.r. evidence for the formation of CF_3IF_2 was obtained (first-order A_3X_2 spectrum, δ_A $-28{\cdot}8$, δ_X $-172{\cdot}7$ p.p.m. J_{AX} 8 Hz), the compound decomposed rapidly at 20°. It has been reported that $C_6F_5IF_2$, which is prepared from C_6F_5I and F_2 at $-78°$, decomposes above $-5°$.[3] It is clear that CF_3IF_4 and $C_6F_5IF_4$ are more stable than the analogous iodine(III) compounds, in contrast to previous work.[2]

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† This compound and $(CF_3)_2CFIF_4$ were characterised by analysis and by their n.m.r. and mass spectra.

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