A Simplified Synthesis of Sulphur Chloride Pentafluoride

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Summary Sulphur chloride pentafluoride is formed rapidly and in high yield by the ambient-temperature reaction of SF_4 and ClF in the presence of CsF.

THE best reported methods for the synthesis of sulphur chloride pentafluoride, SF_5Cl, utilize reactions of SF_4 and ClF[1] or SF_4 with Cl_2 and CsF.[2] These reactions require elevated temperature conditions which must be controlled closely to obtain good conversions. An improved, simplified synthesis of SF_5Cl has been found which employs the ambient-temperature reaction of SF_4 and ClF in the presence of CsF.

$$SF_4 + ClF \xrightarrow{CsF} SF_5Cl$$

The formation of SF_5Cl occurs quickly and in very high yield. By-product formation is minimal, allowing easy separation of pure SF_5Cl. The amount of CsF used can vary. Successful preparations have been achieved with considerably less than stoicheiometric quantities of CsF. Since the CsF is not consumed, it can be re-used indefinitely.

The caesium fluoride used in this reaction was fused and rapidly transferred to a dry-nitrogen-filled glovebox upon solidification, but while still hot. After cooling, it was finely ground. This procedure, while basically intended to furnish anhydrous CsF, also appears to enhance its ability to react as a Lewis base with fluorine compounds that possess Lewis-acid character, for example, ClF_3.[3] The increased reactivity of CsF treated in this manner is comparable to that attained by the decomposition of the caesium fluoride hexafluoroacetone adduct.[4]

In a typical example, a 300 ml. Monel cylinder was loaded with CsF (5·0 g, 33 mmoles). The evacuated cylinder was charged with commercial SF_4 (209 cm^3, 9·33 mmoles) and ClF (216 cm^3, 9·65 mmoles) by successively condensing them into the cylinder at $-196°$. The vessel was then allowed to warm to ambient temperature and stored for 1 hr. Vacuum fractionation of the cylinder contents at this time revealed that a nearly quantitative conversion into SF_5Cl (200 cm^3, 8·92 mmoles) had occurred. The pure product was obtained by condensation in a U-tube cooled to $-126°$. The identity of the product was confirmed by vapour-pressure measurements[1] and its i.r. spectrum.[5] Using the above conditions with only a slightly longer reaction time, the same 5 g. of CsF was employed to convert 82·5 mmoles of SF_4 and 82·0 mmoles of ClF into 75·6 mmoles of SF_5Cl (92% yield).

The catalytic effect of CsF in this reaction probably occurs through polarization of the SF_4, which makes it readily susceptible to oxidation by the ClF. The formation of $CsSF_5$ can also occur, which salt is then oxidized with ClF. However, the reaction of CsF and SF_4 has been reported[2] to begin only at about 110° and even CsF, prepared as described, showed only a slow absorption of SF_4 at room temperature. Thus the oxidative chlorofluorination is much faster than the CsF–SF_4 complexing reaction.

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