

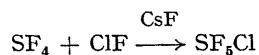
A Simplified Synthesis of Sulphur Chloride Pentafluoride

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Summary Sulphur chloride pentafluoride is formed rapidly and in high yield by the ambient-temperature reaction of SF₄ and ClF in the presence of CsF.

THE best reported methods for the synthesis of sulphur chloride pentafluoride, SF₅Cl, utilize reactions of SF₄ and ClF¹ or SF₄ with Cl₂ and CsF.² These reactions require elevated temperature conditions which must be controlled closely to obtain good conversions. An improved, simplified synthesis of SF₅Cl has been found which employs the ambient-temperature reaction of SF₄ and ClF in the presence of CsF.



The formation of SF₅Cl occurs quickly and in very high yield. By-product formation is minimal, allowing easy separation of pure SF₅Cl. The amount of CsF used can vary. Successful preparations have been achieved with considerably less than stoichiometric 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, ClF₃.³ 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 SF₄ (209 cm³, 9.33 mmoles) and ClF (216 cm³, 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 SF₅Cl (200 cm³, 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 measurements¹ 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 SF₄ and 82.0 mmoles of ClF into 75.6 mmoles of SF₅Cl (92% yield).

The catalytic effect of CsF in this reaction probably occurs through polarization of the SF₄, which makes it readily susceptible to oxidation by the ClF. The formation of CsSF₅ can also occur, which salt is then oxidized with ClF. However, the reaction of CsF and SF₄ has been reported² to begin only at about 110° and even CsF, prepared as described, showed only a slow absorption of SF₄ at room temperature. Thus the oxidative chlorofluorination is much faster than the CsF-SF₄ complexing reaction.

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