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SHORT COMMUNICATION

A New Method for the Preparation of Sulphuryl Chloro Fluoride

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It has been observed that a suspension of sodium fluoride in boiling acetonitrile could be used for the preparation of fluorine compounds such as silicon tetrafluoride [1], thiophosphoryl fluoride [2], sulphur tetrafluoride [3,4], and fluorocyclophosphazenes [5]. This method, when adopted for the fluorination of sulphuryl chloride [6], it is observed that a mixture of sulphuryl fluoride and sulphuryl chloro fluoride is obtained. On the other hand, when lead fluoride is substituted for sodium fluoride, pure sulphuryl chloro fluoride is evolved. Based on this observation, a new method has been standardised for the preparation of a pure sample of sulphuryl chlorofluoride by fluorinating sulphuryl chloride by lead fluoride in acetonitrile medium.

40g of leadfluoride is suspended in 100 ml of dry acetonitrile in a three necked flask fitted with a mechanical stirrer and an ice-cooled refluxcondenser. The preparation unit is well protected from moisture by connecting appropriate guard tubes or cold traps. All operations are carried out in a slow stream of dry nitrogen. To the gently refluxing acetonitrile

is added 10 ml of sulphuryl chloride dissolved in 30 ml. of acetonitrile over a period of one hour by means of a dropping funnel whose end dips in to the suspension.

Bubbles of gas (sulphuryl chlorofluoride) are evolved and are swept into two traps maintained at -40°C and at liquid nitrogen temperature respectively. Vapours of unreacted sulphuryl chloride and acetonitrile are condensed in the first trap, while sulphuryl chloro fluoride is collected in the second trap. The solvent is allowed to reflux for a further period of 1½ hours after addition. It has been observed that a relatively small quantity of hydrogen chloride (5 - 7%) is also evolved along with sulphuryl chloro fluoride.

The second trap containing sulphuryl chloro fluoride and hydrogen chloride is removed from the reaction line and connected to a previously evacuated trap cooled by liquid nitrogen. Condensed products are now warmed to -80°C to remove hydrogen chloride. Hydrogen chloride boils at - 85°C and is removed by fractional distillation. Hydrogen chloride gets condensed in the trap cooled by liquid nitrogen during an interval of 10 minutes. A colourless liquid (sulphuryl chlorofluoride) remains in the trap maintained at -80°C. The trap is allowed to warm up and the issuing gas is collected in a previously evacuated dry glass globe (2 litre capacity).

The purity of the sample is checked by infrared spectra and chemical analysis. The following bands are observed in the infrared spectrum :-

Observed : 475, 501, 630, 825, 1230, 1360, 1465, 1645cm^{-1}

Reported [7] : 474, 501, 629, 824, 1228, 1359, 1467, 1644cm^{-1}

No other species is found to be present along with this sample.

For chemical analysis, a known quantity of the gas is hydrolysed in 2N sodium hydroxide. The amounts of sulphate [8], chloride [9], and fluoride [10] are estimated by standard methods. The analytical results of a typical experiment are given below :

	Sulphur	Chlorine	Fluorine
Found	26.88%	29.59%	15.96%
Calculated	27.0%	29.95%	16.03%

From the results it could be inferred that the sample is at least 99.5% pure. It is necessary to emphasise that strictly anhydrous condition should be maintained throughout the experiment.

The yield of sulphuryl chloro fluoride is found to be 40%.

As has been already mentioned, one of the impurities associated with sulphuryl chloro fluoride when prepared by this method is observed to be hydrogen chloride. The presence of hydrogen chloride could be attributed to the possible reaction between sulphuryl chloride and acetonitrile. Acetonitrile is found to undergo reaction with sulphuryl chloride on prolonged boiling releasing hydrogen chloride as one of the products (5 - 7%). The nature of this reaction is, however, not clear and needs further investigation.

Unlike the earlier methods [11-15] described in the literature for the preparation of sulphuryl chloro fluoride, the present method does not require high pressure or temperature conditions. Further, the sample is free from sulphuryl fluoride. Lead fluoride is found to be a more suitable fluorinating reagent for this preparation than sodium fluoride. The residue after fluorination is found to contain lead chloride fluoride, indicating that only one of the fluorine atoms is replaced. The presence of lead chloride fluoride is confirmed by X-ray powder pattern [16] and far infrared spectra [17].

Sulphuryl chloro fluoride has been found to be a good fumigant for insect infestations in flour and grain in storage bins and could be used for confused flour beetle and black carpet larvae [18].

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