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REACTION OF SULPHURYL CHLOROFLUORIDE WITH A FEW METALS AND METAL OXIDES

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SUMMARY

Sulphuryl chlorofluoride has no observable reaction with metals and metal oxides at room temperature. Metals like copper, silver, iron, and zinc react with the chlorofluoride in the temperature range 200-400°C. Metal chlorides, metal fluorides and sulphur dioxide are the main products of these reactions. With the corresponding metal oxides, on the other hand, the respective metal sulphates are formed in addition to the metal chlorides and fluorides. In the case of lead and lead oxide, lead chlorofluoride is formed instead of lead chloride and lead fluoride. Sulphuryl fluoride is formed in small quantities in all these reactions by the decomposition of the chlorofluoride. Glass is not attacked by sulphuryl chlorofluoride below 500°C.

During the course of our investigations on the reactivity of sulphuryl chlorofluoride, it is observed that sulphuryl chlorofluoride does not react with glass upto 500°C. However, it reacts with metals and metal oxides between 200° and 400°C. The reaction products with metals are the corresponding metal chlorides, metal fluorides and sulphur dioxide. With the oxides, in addition to the metal chlorides and metal fluorides, metal sulphates are formed. The results of these investigations are presented in this communication.

EXPERIMENTAL

A pure sample of sulphuryl chlorofluoride is prepared by fluorination of sulphuryl chloride with lead fluoride in boiling acetonitrile [1]. The gas is stored in a dry, evacuated glass globe.

Powder samples of the following metals and the respective metal oxides are employed for the reactions: copper (45μ), silver (105μ), iron (63μ) zinc (63μ), lead (0.5 mm) and nickel (53μ).
(particle sizes are indicated in parenthesis)

About a gram of the metal powder is taken in a glass reaction tube (20 cm x 4 cm) fitted with vacuum stopcocks and ground glass joints. The reaction tube is evacuated and a known amount (150-200 mg) of sulphuryl chlorofluoride is frozen over it and then allowed to attain room temperature. The tube is introduced into a tubular furnace and heated at a slow rate attaining the desired temperature (200-400^{o}C) in about 2-3 hours. A change in colour and form of the powder indicates the occurrence of reaction. The reaction is allowed to proceed at this temperature for 10-12 hours. At the end of this period, the reaction tube is taken out of the furnace and cooled to room temperature. Infrared spectrum of the gaseous products is recorded in the range 400-4000 cm^{-1}. The solid products are identified by their X-ray powder diffraction patterns and qualitative analysis.

RESULTS

The IR spectra of the gaseous products indicate that sulphur dioxide and small quantities of silicon tetrafluoride (reaction of metal fluorides with glass) and sulphuryl fluoride are the only gaseous components in all the reactions. X-ray powder pattern and qualitative analyses of the solid components indicate the presence of metal chloride and metal fluoride in the case of copper, silver, iron and zinc and metal chlorofluoride in the case of lead as expected. However, nickel does not undergo any noticeable reaction even at 400^{o}C. The extent of reaction is about 95% (based on the amount of sulphur dioxide and

sulphuryl fluoride produced). A part of the sulphuryl chlorofluoride undergoes decomposition at the metal surface [2] to sulphuryl fluoride.

$$2\ SO_2ClF \longrightarrow SO_2F_2 + SO_2 + Cl_2$$

Sulphuryl fluoride is reported to undergo decomposition only at about 1000°C [3].

The reaction of sulphuryl chlorofluoride with metals could be represented by the following general equations:

$$2\ M + SO_2ClF \xrightarrow{200\text{-}400^\circ C} MCl + MF + SO_2$$

(M = univalent metal eg. Ag)

$$2\ M + 2\ SO_2ClF \xrightarrow{200\text{-}400^\circ C} MCl_2 + MF_2 + 2\ SO_2$$

(M = divalent metal eg: Zn, Cu, Fe)

$$Pb + SO_2ClF \xrightarrow{350^\circ C} PbClF + SO_2$$

When the respective metal oxides are used, instead of the above metals for reaction, metal chlorides, metal fluorides and metal sulphates are formed. The reactions may be represented by the following general equations:

$$MO + SO_2ClF \xrightarrow{200\text{-}400^\circ C} MF_2 + MCl_2 + MSO_4$$

(M = Cu, Ni)

$$M_2O + SO_2ClF \xrightarrow{200\text{-}400^\circ C} MF + MCl + M_2SO_4$$

(M = Ag)

Owing to the complexity of the reactions the products could not be accounted quantitatively in terms of the equations given. The interesting observations made are:

i) sulphuryl chlorofluoride does not react with zinc oxide even at 400°C.

ii) lead dioxide forms lead chlorofluoride as in the case of reaction with lead. Oxygen is liberated during the reaction.

iii) sulphur dioxide is one of the products of reaction with cuprous oxide. Cuprous chloride is found in the solid products.

iv) traces of sulphuryl fluoride is formed in most reactions.

DISCUSSION

The present investigation bears light to the fact that sulphuryl chlorofluoride is of intermediate reactivity as compared to sulphuryl chloride and sulphuryl fluoride. Sulphuryl chloride reacts with metals and metal oxides to give chlorides, sulphates or a mixture of the two [4] and sulphuryl fluoride does not react with metals under ordinary conditions.

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