Proc. Indian natn. Sci. Acad., Part A, Phys. Sci., **46**, No. 1, 1980, pp. 68–71.

Chemistry

COMPLEXES OF XENON HEXAFLUORIDE WITH FLUORIDES OF CALCIUM, STRONTIUM AND BARIUM

SUDHINDRA N. MISRA
Chemical Laboratories University, of Jodhpur, Jodhpur

(*Received 4 May 1979*)

Alkaline earth fluorides form sufficiently stable complexes with the stoichiometry $MF_2.XeF_6$ or M $[XeF_8]$ with xenon hexafluoride. These 1 : 1 complexes lose xenon hexafluoride slowly at $\sim$ 278 °K, the rate increasing with temperature. However, the decomposition pattern showed the existence of complexes of the type $2MF_2\ XeF_6$ and $3MF_2.XeF_6$. The final decomposition product was found to be corresponding metal fluoride. The plots of loss in weight (*dw*) against temperature (°K) have given the value for co-efficient of correlation, slope of the line and value of intercept.

Xenon hexafluoride has been known to form complexes with metals and non metals (Peacock *et al.*, 1964, 1966; Gard & Cady, 1964; Selig, 1964; Pullen & Cady, 1966; and Moody & Selig, 1966). In the present communication, the reactions of xenon hexafluoride with the fluorides of calcium, strontium and barium are being reported.

EXPERIMENTAL

XENON hexafluoride was prepared from the method described by Malm *et al.*, (1963), by taking xenon and fluorine (1:20) and heating to 300 °K and at 70 ATP. It was purified by standing over sodium fluoride in a monel reactor and was stored at liquid oxygen temperature. Calcium, strontium and barium fluorides have been prepared by decomposition of corresponding metal carbonate by 48 per cent hydrofluoric acid with subsequent dehydration and dehydrofluorination in a platinum cruicible.

The reaction vessel was made up of nickel with Hooke brass valves, while xenon hexafluoride storage can was provided 20,000 kg/cm^2 monel value. The metal vacuum line used was provided with monel bourdon gauges, monel tees and crosses. The extent of conversion of metal fluoride to xenon hexafluoride adduct was then determined from the increase in the weight of the starting material.

The samples of the compounds were dissolved very cautiously in water in nickel reactor and aliquots were analysed for fluoride and metal.

Reaction of Calcium Fluoride and Xenon Hexafluoride — The reaction vessel was a narrow nickel reactor (0.6 cm o.d.) which could be detatched from the vacuum line during the experiment, so that the changes taking place in the composition of solid samples could easily be followed. The vacuum line was evacuated and a small amount of fluorine was introduced in the line in order to complete the 'Pickling' of the line. A known amount of calcium fluoride was introduced in the reaction vessel and was heated at 100 °C for three hours. The transfer of fluoride to the reaction vessel was carried out in the dry box under stringently controlled anhydrous and inert atmosphere. The reaction vessel was then connected to the line. Some fluorine was condensed to calcium fluoride and the vessel was heated in a reactor at 100 °C for 4 hours. It was then attached to the line and the whole assembly was flamed while pumping.

This step was necessary as xenon hexafluoride explodes with a trace of moisture. Xenon hexafluoride was now condensed in a well seasoned fluoride. The reaction vessel was detatched from the line and was placed in a reactor at 110°C for 6 hours. Afterwards the reaction vessel was cooled to −15 °C and then attached to the line. Excess xenon hexafluoride was pumped out at −15 ° C till a constant weight of reaction vessel was observed. These hexafluoride metal fluoride complexes were pumped at different temperatures for 30 minutes each and at reduced pressure (0.01 mm).

TABLE I

Complexes of alkaline earth fluoride with xenon hexafluoride

Starting material	Initial weight	Final Wt.	Wt. of XeF_6	MF_2/XeF_6	%M	%F
CaF_2	0.0860	0.3638	0.2778	1.02	12.52 (12.38)	47.14 (46.94)
SrF_2	0.1239	0.3800	0.2511	0.99	23.75 (23.59)	41.30 (40.91)
BaF_2	0.1680	0.4043	0.2363	1.0039	32.90 (32.62)	36.40 (36.08)

Data in parentheses represent the calculated values.

RESULTS AND DISCUSSION

Xenon hexafluoride reacts with a number of fluorides of metals and metalloids. Caesium and rubidium octafluoroxenates are amongst the most stable solid compounds of xenon known so far.

Fluoride of alkaline earth metals absorb xenon hexafluoride and complexes with the stoichiometry : $MF_2.XeF_6$ have been formed.

These complexes are pale yellow solids extremely reactive substances. However, these complexes are much less stable than similar complexes with rubidium and caesium. These complexes are stable up to 278 °K and beyond it, these decompose slowly lose XeF_6 as shown below :

$$\underset{\text{I}}{CaXeF_8} \xrightarrow{278\ ^\circ K} \underset{\text{II}}{Ca_2XeF_{10}} \xrightarrow{313\ ^\circ K} \underset{\text{III}}{Ca_3XeF_{12}} \longrightarrow CaF_2$$

Calcium octafluoroxenate (I) starts decomposition even at 278 °K to yield dicalcium decafluoroxenate (II) by losing xenon hexafluoride. The plot Fig. 1 of the loss of weight (dw) against temperature (T) indicates two plateau corresponding to the stoichiometry (II) and (III) respectively. These products however could not be isolated. The decomposition pattern of these three species has led to the calculation of the value for coefficient of correlation, slope as well as the value of intercept which are given in the Table II.

Strontium octafluoroxenate also starts losing xenon hexafluoride on heating

TABLE II

Thermal decomposition of alkaline earth fluoride-xenon hexafluoride complexes

Complex Species (°K)	Coefficient of correlation	Slope	Intercept
CaF_2 XeF_6 (278–311)	0.9811	0.0105	0.02
$2CaF_2$ XeF_6 (313–338)	0.971	0.0083	0.657
$3CaF_2$ XeF_6 (343–393)	0.995	0.0330	—7.94
SrF_2 XeF_6 (278–309)	0.873	0.0065	1.16
$2SrF_2$ XeF_6 (313–330)	0.970	0.0078	0.808
$3SrF_2$ XeF_6 (335–393)	0.938	0.0833	—25.70
BaF_2 XeF_6 (278–309)	0.939	0.0076	0.833
$2BaF_2$ XeF_6 (311–330)	0.974	0.00947	0.304
$3BaF_2$ XeF_6 (335–398)	0.961	0.0258	—5.574

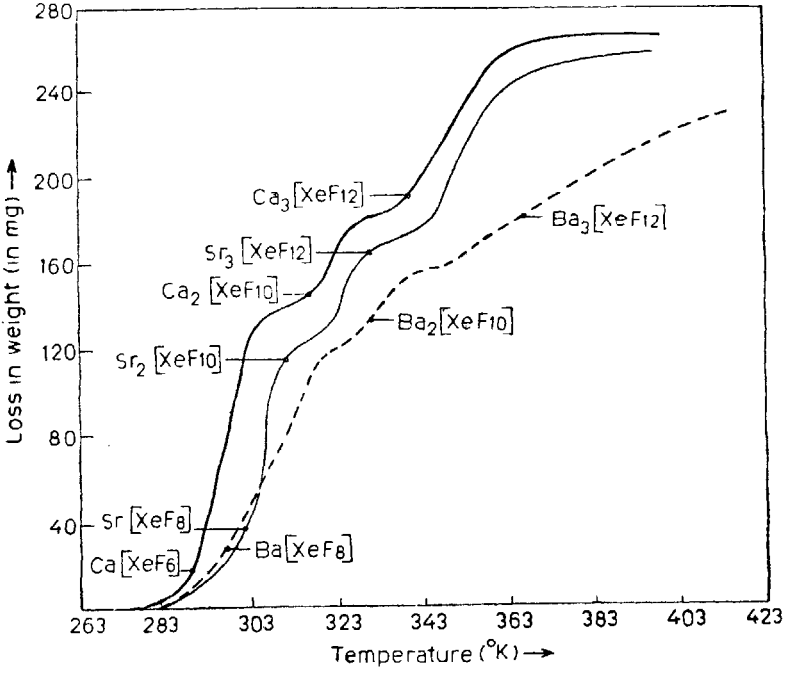

FIG. 1

A PLOT OF LOSS IN WEIGHT (dw) OF COMPLEX

(1) Ca F_2XeF_6 against temperature ——————

(2) Ba F_2XeF_6 against temperature - - - - -

(3) Sr F_2XeF_6 against temperature ——————

Note : Above 283 on *x*-axis Ca [X_6F_6] may be read as Ca [X_6F_8]

beyond 278 °K, but barium analogue is stable up to 283 °K and beyond it loses xenon hexafluoride. These follow the following decomposition pattern :

$$SrXeF_8 \xrightarrow{278\ ^\circ K} Sr_2XeF_{10} \xrightarrow{318\ ^\circ K} Sr_3XeF_{12} \xrightarrow{343\ ^\circ K} SrF_2 + XeF_6$$

$$BaXeF_8 \xrightarrow{283\ ^\circ K} Ba_2XeF_{10} \xrightarrow{321\ ^\circ K} Ba_3XeF_{12} \xrightarrow{343\ ^\circ K} BaF_2 + XeF_6$$

These 1:1 species have been characterized by elemental analyses, however, 2:1 and 3:1 could not be isolated.

Acknowledgements

The author thankfully acknowledges the kind permission of Professor G. H. Cady to work in the Fluorine Laboratories, University of Washington and to U. S. Naval Research for providing a Senior Research Fellowship.

References

Gard, G. L. C., and Cady, G. H. (1964) Reactions of xenon hexafluoride with antimony pentafluoride, hydrogen chloride, ammonia and perfluorocyclopentene. *Inorg. Chem.* **3,** 1745.

Moody, G. J., Selig, H. (1966) *J. inorg. nucl. Chem., Lett.*, **2,** 319.

Peacock, R. D., Selig, H., and Sheft, I. (1964) Complex compounds of xenon hexafluoride with the alkali fluorides. *Proc. Chem. Soc.*, **285**; (1966) Complex compounds of xenon hexafluoride with the alkali metal fluorides. *J. inorg. nucl. Chem.*, **28,** 2561.

Pullen, K. E., and Cady, G. H. (1966) The reaction of xenon hexafluoride with stannic fluoride. *Inorg. chem.*, **5,** 2057.

Selig, H. (1964) *Science,* **144,** 537.