THE REACTION OF KRYPTON DIFLUORIDE WITH XENON HEXAFLUORIDE IN NONAQUEOUS SOLVENTS

V. D. Klimov, V. N. Prusakov, and V. B. Sokolov

UDC 546;535.33/34:539.19

Krypton difluoride reacts with Lewis fluoro acids to form complexes with different compositions: $KrF_2 \cdot MF_5$, $KrF_2 \cdot 2MF_5$, $2KrF_2 \cdot MF_4$, $KrF_2 \cdot MF_3$ (M = As, Sb, Ta, Nb, Ti, Sn, B) [1, 2]. Infrared and Raman data [3, 4] indicate that, like the pseudoisoelectronic XeF_2 which reacts with the formation of the XeF^+ cation [5], krypton difluoride forms compounds containing the KrF^+ cation. These compounds can be considered to be ionic: $KrF^+MF_6^-$, $KrF^+M_2F_{11}^-$, $[(KrF^+)_2][MF_6]^{2-}$, $KrF^+MF_4^-$ [1, 4]. Xenon hexafluoride enters into complex-forming reactions with similar fluoro acids, forming compounds containing XeF_5^+ and $Xe_2F_{11}^+$ cations [6, 7]. Moreover, XeF_6 displays amphoteric properties by acting as a fluoride-ion acceptor, forming the complex anions XeF_7^- and XeF_8^{2-} [9].

The present paper reports the preparation of a third type of complex, the molecular compound $KrF_2 \cdot XeF_6$, and considers the question of the relative tendency of KrF_2 to give up a fluoride ion. The krypton difluoride was synthesized in an electric discharge [1], and the xenon hexafluoride was prepared by heating a mixture of xenon and fluorine in a molar ratio of 1:10 at 300°C and a pressure of 30 atm [10]. $KrF_2 \cdot XeF_6$ was synthesized by dissolving KrF_2 and XeF_6 in bromine pentafluoride or anhydrous hydrogen fluoride. The solubility of KrF_2 in BrF_5 at 20° is 16.5 moles per 1000 g of BrF_5 [11], while the solubility of xenon hexafluoride is about 11 moles. The solubilities of the two fluorides in HF are close to those in BrF_5.

Solutions of KrF_2 and XeF_6 in a molar ratio of 2:1 were light yellow in color. The excess solvent and KrF_2 were evaporated under vacuum at −25° to constant weight. This left a solid with the stoichiometric composition (as indicated by gravimetric analysis and measurement of the decomposition products). The product was a colorless crystalline material with a saturated vapor pressure of about 1 mm Hg at −10° and 11 mm Hg at 20°. It distilled under vacuum in a molar ratio of 1:1. Through the use of a NaF column we were able to separate the components of the gas mixture and to confirm the assumption that KrF_2 has only basic properties:

$$(KrF_2 \cdot XeF_6)_s \rightarrow KrF_{2(g)} + XeF_{6(g)} \xrightarrow{n\text{NaF}} XeF_6 \cdot n\text{NaF} + KrF_2 (Kr + F_2).$$

The melting point of the complex was determined in a quartz capillary and was found to be 40 ± 2°. Melting was accompanied by considerable evolution of gas, but the material was stable below 0°. $KrF_2 \cdot XeF_6$ decomposes slowly at room temperature in accordance with the following equation (krypton difluoride decomposes to the elements at room temperature, and the rate constant for decomposition of $KrF_{2(g)}$ at 20° is $3.1 \cdot 10^{-5}$ sec^{-1} in a nickel reactor with S/V = 0.95 [1]):

$$KrF_2 \cdot XeF_6 \rightarrow KrF_2 + XeF_6 \rightarrow Kr + F_2 + XeF_6.$$

The IR spectrum of the complex was recorded at 77°K. The window of the cell was cooled with liquid nitrogen, and the components of the gas phase over $KrF_2 \cdot XeF_6$ at 20° were condensed on the window inside the cell. The low-temperature spectra of KrF_2 and XeF_6 were first recorded (Fig. 1).

(Presented by Academician I. V. Tananaev, March 18, 1974.) Translated from Doklady Akademii Nauk SSSR, Vol. 217, No. 5, pp. 1077-1079, August, 1974. Original article submitted February 20, 1974.

© 1975 Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for $15.00.

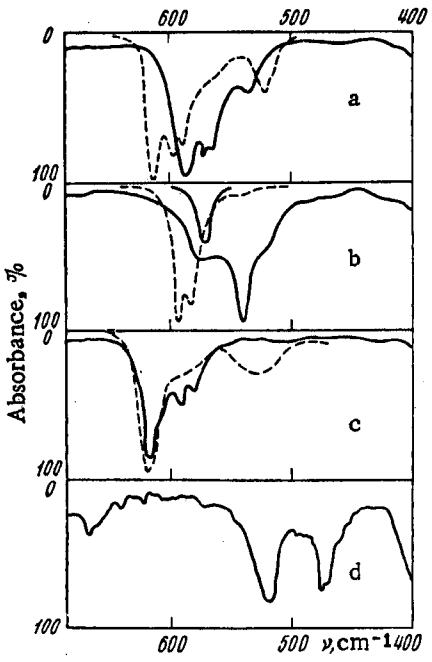

Fig. 1. Low-temperature IR spectra: a) $KrF_2 \cdot XeF_6$; b) KrF_2; c) XeF_6, all at 77°K, and d) $CsF \cdot XeF_6$ ($Cs^+XeF_7^-$) at 20°C. Broken lines are for the gaseous material at 20°C.

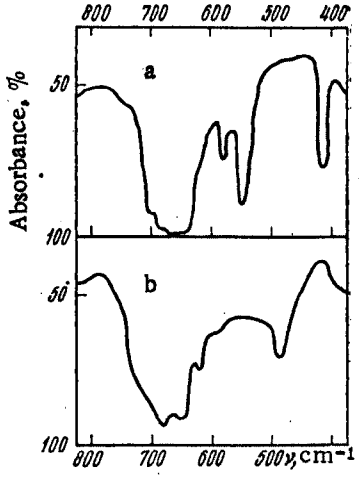

Fig. 2. IR spectra of $XeF_6 \cdot SbF_5$(s) (a) and $KrF_2 \cdot SbF_5$(s) (b).

The spectrum of solid krypton difluoride shows well-defined maxima at 520, 536, and 573 cm^{-1}. The intensities of the bands changed with an increase in temperature, which we attribute to polymerization of KrF_2 at 77°K. The band at 573 cm^{-1} is assigned to Kr—F stretching in the monomer molecule, and the bands at 520 and 536 cm^{-1} are assigned to polymeric forms of KrF_2.

The low-temperature spectrum of xenon hexafluoride contained bands of average intensity at 583 and 568 cm^{-1} and a strong band at 616 cm^{-1}. This spectrum of XeF_6 agrees satisfactorily with the spectrum of XeF_6 in an argon matrix at 4°K [12]. On the basis of the IR spectra, which are shown in Fig. 1. we can exclude the ionic form of the complex $KrF^+XeF_7^-$ (Kr—F stretching in the diatomic cation KrF^+ in complexes of KrF_2 appear as bands in the region from 590 to 630 cm^{-1} [1, 4]).* The spectroscopic and physicochemical data obtained in the present work indicate weak association of KrF_2 and XeF_6, which suggests formation of a molecular compound. Similar complexes of inert gases are known [13]: $XeF_2 \cdot XeF_4$, $XeF_2 \cdot IF_5$, $XeF_2 \cdot XeOF_4$, $XeF_2 \cdot (XeF_5 + AsF_6^-)$, etc. Linking of the components is via weak electrostatic interaction of the positively charged inert gas atom with the fluorine-containing ligands, which have a negative charge.

Since formation of the molecular compound $KrF_2 \cdot XeF_6$ was established, it seemed of interest to determine the location of krypton difluoride in the xenon fluoride electron-donor series. With this aim, we synthesized complexes of KrF_2 with antimony pentafluoride. Figure 2 shows the IR spectra of the resulting compounds, $Kr_2 \cdot SbF_5$ and $XeF_6 \cdot SbF_5$.

The spectrum of $XeF_6 \cdot SbF_5$ exhibits strong absorption in the 600-700 cm^{-1} region and narrow bands of average intensity at 420, 550, and 582 cm^{-1}. When the compound is described on the basis of an ionic model, the bands in the 600-700 cm^{-1} region are assigned to Sb—F stretching in the distorted octahedral anion S — F, and the narrow bands are assigned to Xe—F stretching in the pseudooctahedral cation XeF_5^+ of C_{4v}. Similarly, the krypton difluoride compound can be assumed to be $XeF_5^+SbF_6^-$ (violation of the selection rules for anions of octahedral symmetry in solids cannot be accepted as proof of the absence of an ionic structure and can be attributed to a decrease in symmetry of the anion in the crystal [14]).

A solid of the composition $XeF_6 \cdot SbF_5$ was separated from a solution of KrF_2, XeF_6, and SbF_5 (1 : 1 : 1) in BrF_5, which indicates that XeF_6 has stronger donor properties than KrF_2, and this is confirmed by the fact that XeF_6 replaces KrF_2 in its complexes.

It is known that krypton difluoride fluorinates xenon and the lower xenon fluorides to the hexafluoride [1]. Therefore, it is not possible to determine experimentally the place of KrF_2 with respect to XeF_2 and XeF_4, as it is in the case of XeF_6. However, published data [4, 15] and our data permit the conclusion that compounds of xenon difluoride with AsF_5, BF_3, and GeF_4 are stable at higher temperatures than are the corresponding compounds of krypton difluoride.

* The band at 687 cm^{-1} in the $KrF^+Sb_2F_{11}^-$ spectrum was assigned to the Kr—F vibration on the assumption that stretching frequencies are the same in the isoelectronic KrF+ and BrF [1].

Taking into account enthalpies of ionization of KrF_2 (232 kcal/mole), XeF_2 (211), XeF_4 (219), and XeF_6 (206) (calculated by the Born—Haber cycle), the lattice energies of the compounds formed by these fluorides with antimony pentafluoride (estimated by the Kapustinskii method), and certain experimental data [16] on the complex-forming reactions of xenon tetrafluoride, it can be concluded that the relative tendency of inert gas fluorides to give up fluoride ions decreases in the following series:

$$XeF_6(XeF_5^+,\ Xe_2F_{11}^+) > XeF_2(XeF^+,\ Xe_2F_3^+) > KrF_2(KrF^+) > XeF_4(XeF_3^+).$$

LITERATURE CITED

1. V. N. Prusakov and V. B. Sokolov, At. Energ., 31, 259 (1971).
2. H. Selig and R. D. Peacock, J. Am. Chem. Soc., 86, 3895 (1964).
3. B. Liu and H. F. Schaefer, J. Chem. Phys., 55, 2369 (1971).
4. B. Frlec and J. H. Holloway, J. Chem. Soc., Chem. Commun., 1973, 370.
5. F. O. Sladky, P. A. Bulliner, and N. Bartlett, J. Chem. Soc., A, 1969, 2179.
6. N. Bartlett, Endeavour, 31, 107 (1972).
7. K. Leary and N. Bartlett, J. Chem. Soc., Chem. Commun., 1973, 131.
8. R. D. Peacock, H. Selig, and J. Sheft, Proc. Chem. Soc., 1964, 285.
9. G. D. Moody and H. Selig, J. Inorg. and Nucl. Chem., 28, 2429 (1966).
10. J. G. Malm and E. H. Appelman, Atomic Energy Rev., 7, 3 (1969).
11. V. N. Prusakov and V. B. Sokolov, Zh. Fiz. Khim., 45, 2950 (1971).
12. H. Kim, Bull. Am. Phys. Soc., 13, 425 (1968).
13. N. Bartlett and M. Veschberg, Zs. Anorg. u. Allgem. Chem., 385, 5 (1971).
14. K. O. Christe and C. J. Schack, Inorg. Chem., 9, 2296 (1970).
15. N. Bartlett and F. O. Sladky, J. Am. Chem. Soc., 90, 5316 (1968).
16. R. J. Gillespie and B. Landa, J. Chem. Soc., Chem. Commun., 1971, 1543.