

THE REACTION OF KRYPTON DIFLUORIDE WITH XENON
HEXAFLUORIDE IN NONAQUEOUS SOLVENTS

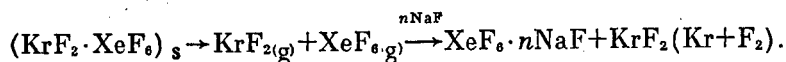
V. D. Klimov, V. N. Prusakov, and V. B. Sokolov

UDC 546;535.33/34:539.19

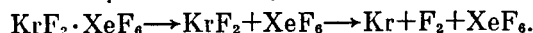
Krypton difluoride reacts with Lewis fluoro acids to form complexes with different compositions: $\text{KrF}_2 \cdot \text{MF}_5$, $\text{KrF}_2 \cdot 2\text{MF}_5$, $2\text{KrF}_2 \cdot \text{MF}_4$, $\text{KrF}_2 \cdot \text{MF}_3$ ($M = \text{As, Sb, Ta, Nb, Ti, Sn, B}$) [1, 2]. Infrared and Raman 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: $\text{KrF}^+\text{MF}_6^-$, $\text{KrF}^+\text{M}_2\text{F}_{11}^-$, $[(\text{KrF}^+)_2][\text{MF}_6]^{2-}$, $\text{KrF}^+\text{MF}_4^-$ [1, 4]. Xenon hexafluoride enters into complex-forming reactions with similar fluoro acids, forming compounds containing XeF_5^+ and $\text{Xe}_2\text{F}_{11}^+$ 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 $\text{KrF}_2 \cdot \text{XeF}_6$, 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]. $\text{KrF}_2 \cdot \text{XeF}_6$ 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:



The melting point of the complex was determined in a quartz capillary and was found to be $40 \pm 2^\circ$. Melting was accompanied by considerable evolution of gas, but the material was stable below 0°. $\text{KrF}_2 \cdot \text{XeF}_6$ 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 $\text{KrF}_2(\text{g})$ at 20° is $3.1 \cdot 10^{-5} \text{ sec}^{-1}$ in a nickel reactor with $S/V = 0.95$ [1]):



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 $\text{KrF}_2 \cdot \text{XeF}_6$ 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.

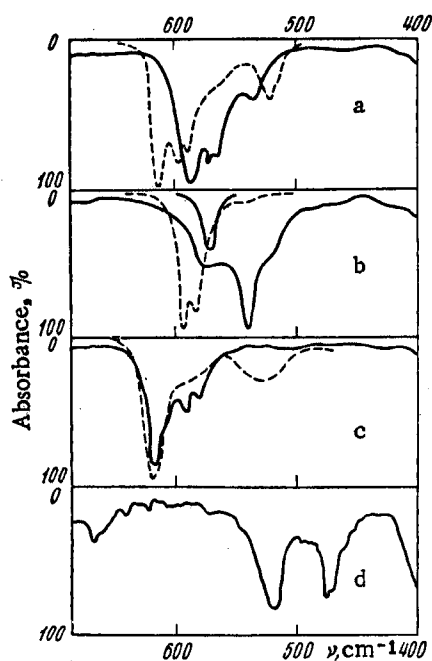


Fig. 1. Low-temperature IR spectra: a) $\text{KrF}_2 \cdot \text{XeF}_6$; b) KrF_2 ; c) XeF_6 , all at 77°K , and d) $\text{CsF} \cdot \text{XeF}_6$ ($\text{Cs}^+ \text{XeF}_6^-$) at 20°C . Broken lines are for the gaseous material at 20°C .

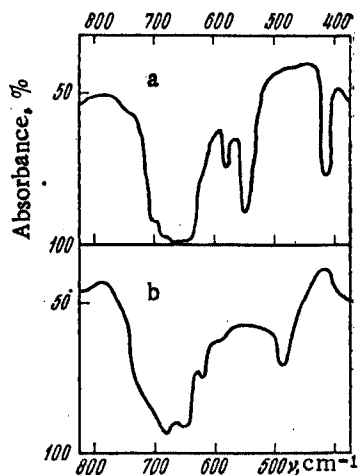


Fig. 2. IR spectra of $\text{XeF}_6 \cdot \text{SbF}_5(\text{s})$ (a) and $\text{KrF}_2 \cdot \text{SbF}_5(\text{s})$ (b).

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 $\text{KrF}^+ \text{Sb}_2\text{F}_{11}^-$ spectrum was assigned to the $\text{Kr}-\text{F}$ vibration on the assumption that stretching frequencies are the same in the isoelectronic KrF^+ and BrF [1].

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 $\text{Kr}-\text{F}$ 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 $\text{KrF}^+ \text{XeF}_6^-$ ($\text{Kr}-\text{F}$ 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]: $\text{XeF}_2 \cdot \text{XeF}_4$, $\text{XeF}_2 \cdot \text{IF}_5$, $\text{XeF}_2 \cdot \text{XeOF}_4$, $\text{XeF}_2 \cdot (\text{XeF}_5 + \text{AsF}_6^-)$, 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 $\text{KrF}_2 \cdot \text{XeF}_6$ 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, $\text{Kr}_2 \cdot \text{SbF}_5$ and $\text{XeF}_6 \cdot \text{SbF}_5$.

The spectrum of $\text{XeF}_6 \cdot \text{SbF}_5$ exhibits strong absorption in the $600\text{--}700 \text{ cm}^{-1}$ 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 $600\text{--}700 \text{ cm}^{-1}$ region are assigned to $\text{Sb}-\text{F}$ stretching in the distorted octahedral anion $\text{S}-\text{F}$, and the narrow bands are assigned to $\text{Xe}-\text{F}$ stretching in the pseudooctahedral cation XeF_5^+ of C_{4v} . Similarly, the krypton difluoride compound can be assumed to be $\text{XeF}_5^+ \text{SbF}_6^-$ (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 $\text{XeF}_6 \cdot \text{SbF}_5$ was separated from a solution of KrF_2 , XeF_6 , and SbF_5 (1:1:1) in BrF_5 , which

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:



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. Frllec 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.