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REACTIONS IN THE SYSTEM VANADIUM PENTAFLUORIDE–XENON HEXAFLUORIDE

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SUMMARY

In the system XeF_6–VF_5 two new compounds $XeF_6 . VF_5$ and $XeF_6 . 2VF_5$ have been synthesized, in addition to the already known $2XeF_6 . VF_5$ (1). The Raman spectra indicate that ionic character decreases in the series $2XeF_6 . VF_5$, $XeF_6 . VF_5$ and $XeF_6 . 2VF_5$. The compound $2XeF_6 . VF_5$ can be described as an ionic compound $Xe_2F_{11}^+VF_6^-$, while $XeF_6 . 2VF_5$ can be formulated as a molecular adduct, with $XeF_6 . VF_5$ being intermediate in character. The melting points of $2XeF_6 . VF_5$ and $XeF_6 . 2VF_5$ are 97° and 39°, respectively, while $XeF_6 . VF_5$ decomposes below its melting point to $2XeF_6 . VF_5$ and VF_5.

INTRODUCTION

The system vanadium pentafluoride – xenon fluorides has been extensively investigated in the past (1,2,3,4). Moody and Selig (1) isolated the first compound in this system, $2XeF_6 . VF_5$, but no evidence was found for the formation of compounds with a $XeF_6 : VF_5$ mole ratio lower than two. Although vanadium pentafluoride is a weak Lewis acid, taking into account the existence of $XeF_2 . VF_5$ (3) or $KrF_2 . VF_5$ (5) and the much better fluoride ion donor ability of XeF_6 in comparison to XeF_2 or even KrF_2, it was expected that compounds such as $XeF_6 . VF_5$ and $XeF_6 . 2VF_5$ should also exist.

RESULTS AND DISCUSSION

To favour the formation of VF_5–rich complexes, we set out by treating XeF_6 with a large excess of VF_5 at room temperature so that all the xenon hexafluoride dissolved in vanadium pentafluoride. Then the reactor was cooled down to

$-35^\circ C$ and excess of vanadium pentafluoride was pumped away. The only volatiles detected in the vapour phase during the pumping at $-35^\circ C$ were excess of vanadium pentafluoride and traces of VOF_3. Xenon hexafluoride was not evident in the vapour phase as was shown by infrared spectroscopy. When practically constant weight was reached, the 1 : 2 compound was obtained.

$XeF_6 . 2VF_5$ is a colourless crystalline material with a vapour pressure of about 700 Pa at room temperature. It is stable under its own vapour pressure without decomposition at least to its melting point ($39 \pm 1^\circ C$). It melts to a colourless liquid. Under dynamic vacuum it decomposes very slowly at $-35^\circ C$ with a rate of decomposition of about 0.1 to 0.2 %/h. At higher temperatures the rate of decomposition is much greater, and the end product is the 2 : 1 compound which is also stable in dynamic vacuum.

The 1 : 1 compound was prepared from the 1 : 2 adduct by pumping it at $-25^\circ C$ to practically constant weight. The compound also has some vapour pressure at $-25^\circ C$, and its rate of the decomposition in a dynamic vacuum is 0.2 to 0.4 %/h. The only volatile detected in the vapour phase during the isolation was vanadium pentafluoride. The 1 : 1 compound has a vapour pressure at room temperature of about 700 Pa. It is stable under its own vapour pressure up to $+35^\circ C$, when it decomposes to the 2 : 1 compound and vanadium pentafluoride.

The compound $2XeF_6 . VF_5$ was prepared as described by Moody and Selig (1); by treating excess of xenon hexafluoride with vanadium pentafluoride and then pumping excess xenon hexafluoride away at $-25^\circ C$. The compound is a white crystalline material. It is the most stable compound in the system VF_5/XeF_6 and it melts without decomposition at $97 \pm 1^\circ C$.

In the Raman spectra of all three compounds, the V–F and Xe–F bands are easily discernible in the stretching modes region. An increasing number of bands attributable to ν (V–F) is observed in the series $2XeF_6 VF_5$, $XeF_6 VF_5$ and $XeF_6 . 2VF_5$ ($2XeF_6 . VF_5$, 715 cm^{-1} (vs), 702 cm^{-1} (sh); $XeF_6 . VF_5$, 722 cm^{-1} (vs), 694 cm^{-1} (w); $XeF_6 . 2VF_5$, 768 cm^{-1} (vs), 739 cm^{-1} (s), 728 cm^{-1} (s) (Fig. 1)). In the stretching region one should observe one strong Raman band, ν_1 (A_{1g}), and usually a weak one, ν_2 (Eg) (6), for fluorometalates with coordination number 6 and O_h symmetry, while for the coordination number 5, lower symmetries with more Raman bands, shifted to higher frequencies, would be expected, (trigonal bipyramid, D_{3h}, three bands, $2A_1'$ and E', tetragonal pyramid, C_{4v}, four bands, $2A_1$, B_1 and E and more if the polyhedron is deformed). The solid state effects should cause splittings and increased activity, but the Raman bands resulting from infrared allowed fundamentals of the free ion are likely to be weak (7). Because of their great intensity, the three Raman ν(V–F) bands of $XeF_6 . 2VF_5$ should not be understood as originating from an octahedral fluorovanadate ion under the influence of the solid state. They indicate a geometry different from octahedral.

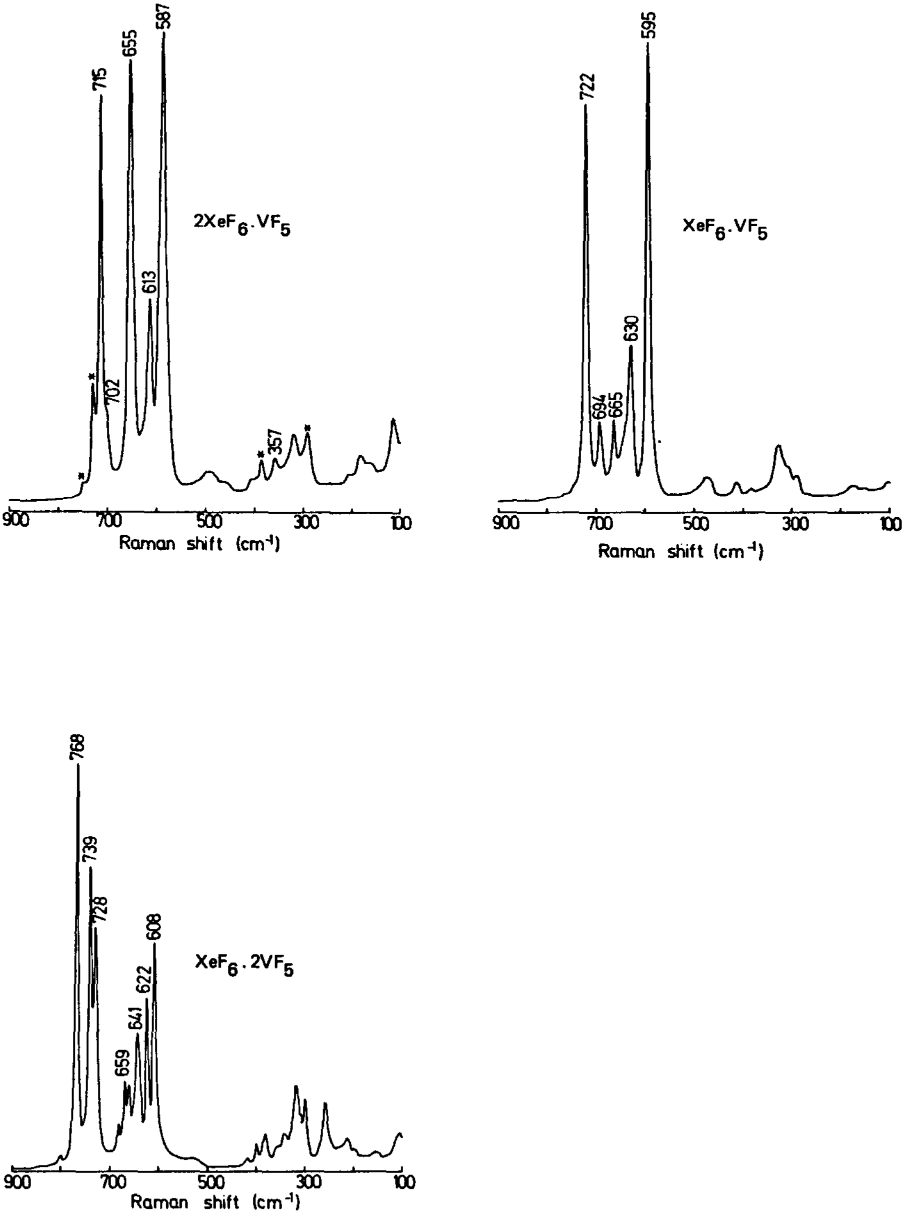

Fig. 1. Raman spectra of $2XeF_6.VF_5$, $XeF_6.VF_5$ and $XeF_6.2VF_5$ Asterisks denote lines arising from the FEP sample tube.

Therefore, the spectra suggest the possible existence of the octahedral VF_6^- ion in $2XeF_6.VF_5$, and presumably fluorine bridged VF_5 units in $XeF_6.2VF_5$. The compoun $2XeF_6.VF_5$ can be reasonably well described as the ionic compound $Xe_2F_{11}^+VF_6^-$ with relatively weak covalent bridging interactions between the ions. The band at 357 cm^{-1} can be attributed to the fluorine bridging of two XeF_5^+ units in $Xe_2F_{11}^+$ (8). The compound $XeF_6.2VF_5$ appears to have more a covalent character, and it can be described as a molecular adduct. Hence, it can be concluded that the ionic character decreases from $2XeF_6.VF_5$ toward $XeF_6.2VF_5$, with $XeF_6.VF_5$ having an intermediate character.

To ascertain the existence of new adducts, the melting point temperatures of different mixtures of vanadium pentafluoride and xenon hexafluoride were determined in FEP ampoules. The reading of the melting point temperature was taken when the last solid particle disappeared in the liquid phase. With these data the melting point — composition diagram (Fig. 2) was constructed.

The form of the curve is not of the simple eutectic type, but definitively confirms the formation of the compounds $XeF_6.2VF_5$ and $2XeF_6.VF_5$. The 1 : 2 compound melts at + 39°C, while the 2 : 1 compound melts at 97°C. The 1 : 1 compound decomposes at approximately 35°C to the 2 : 1 compound and vanadium pentafluoride, as was shown by recording the Raman spectrum of the compound as a function of temperature. From the shape of the peaks and the melting points, it can be concluded that the 2 : 1 compound is the most stable compound in this system.

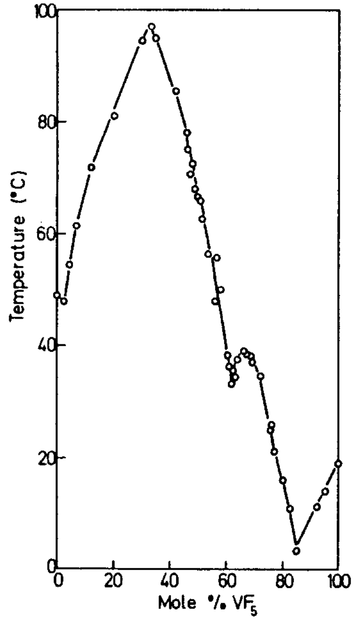

Fig. 2. Melting point — composition diagram

EXPERIMENTAL

General apparatus and techniques

The reactions were carried out in argon arc welded nickel pressure and weighing vessels equipped with Teflon packed nickel valves. The volume of the reaction vessels was about 100 ml. The reactions between xenon hexafluoride and vanadium pentafluoride were also carried out in FEP tubes (ϕ 8 mm) equipped with Teflon packed Kel-F valves.

Raman spectra were recorded using a Spex 1401 double monochromator. As exciting radiation the 514.5 nm line of an Ar^+ laser (Coherent Radiation) was used. The samples for recording Raman spectra were prepared directly in FEP tubes.

IR spectra were recorded using a Zeiss UR–20 spectrometer over the range 400 – 4000 cm^{-1} and a gas infrared cell equipped with AgCl windows.

Reagents

Vanadium pentafluoride was prepared by fluorination of pure vanadium metal, first at room temperature and at the end with excess of fluorine at 300°C (9). The vanadium pentafluoride obtained was pure with only traces of VOF_3, as shown by IR spectroscopy.

Xenon hexafluoride was prepared by the reaction between xenon and fluorine in the presence of nickel difluoride at 120°C (10). The last traces of XeF_4 were oxidized to XeF_6 by KrF_2 at 60°C.

Preparations

The 1 : 2 compound was prepared by introducing xenon hexafluoride to the reaction vessel by sublimation. Excess of vanadium pentafluoride was also added by sublimation and the mixture was warmed to room temperature so that all the xenon hexafluoride dissolved in the vanadium pentafluoride. The excess of vanadium pentafluoride was then pumped away at – 35°C.

The 1 : 1 compound was prepared from the 1 : 2 or directly from the reactants by pumping away excess of vanadium pentafluoride at – 25°C.

The 2 : 1 compound was prepared as described elsewhere (1).

The stoichiometry of the reactants was also followed by weighing the reactants and products with an accuracy of ± 1 mg throughout the experiments.

All the compounds were also prepared just by fusing together both reactants in the appropriate mole ratio.

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