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Note

Analytical and preparative-scale gas chromatography of xenon fluorides

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Xenon fluorides are of great interest in fluorine chemistry owing to their very reactive nature. The fluorination of xenon usually leads to the formation of an equilibrium mixture containing XeF_2, XeF_4, XeF_6 together with gaseous fluorine and xenon. Moreover, a small amount of hydrogen fluoride is usually present as an impurity as a result of hydrolysis of the xenon fluorides.

By means of known equilibrium constants for the xenon–fluorine system[1], it is possible to calculate the necessary composition of the original mixture for the maximum yield of a required xenon fluoride, but attempts to achieve a 100% yield of a particular xenon fluoride have hitherto been unsuccessful. Therefore, the analysis of xenon fluoride mixtures and the preparative-scale separation of these compounds is very important. It has been shown[2,3] that the first of these problems could be solved by gas chromatography (GC).

The aim of this work was to devise suitable methods for the quantitative analysis and preparative-scale separation of all three known xenon fluorides.

EXPERIMENTAL AND RESULTS

Materials

Xenon difluoride and xenon tetrafluoride were prepared from gaseous xenon and fluorine in a nickel chamber by previous methods[4] and purified by fractional sublimation and, later, by preparative-scale GC. Attempts to prepare xenon hexafluoride by the method described by Malm *et al.*[5] gave a mixture of xenon fluorides containing about 20% of XeF_6.

High-purity helium (*ca.* 99.9%) was used as a carrier gas. For additional purification, it was passed through a tube cooled with liquid nitrogen and through traps packed with phosphorus pentoxide on glass-wool, molecular sieve 5A and activated charcoal.

Apparatus

A Tswet 1-64 gas chromatograph was modified for the chromatography of reactive solid halides. All parts that came into contact with agressive compounds were made of monel, nickel and PTFE, and the thermal conductivity detector was equipped with nickel filaments. A doser of special construction was used for introduction of the sample (Fig. 1). The doser was placed in a special box filled with a dry inert gas

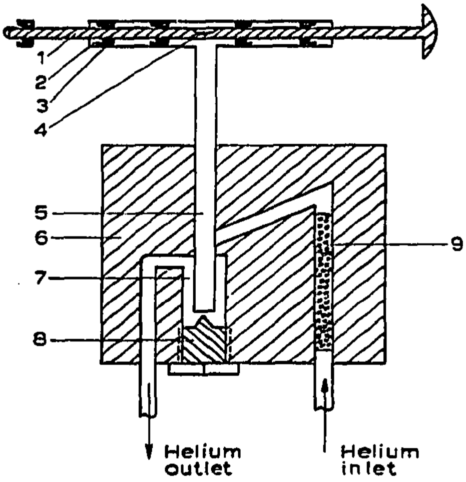

Fig. 1. Solid doser. 1, Pivot (monel); 2, tube (monel); 3, gasket; 4, pit for solid samples; 5, vaporizer tube (nickel); 6, vaporizer block (copper); 7, vaporizer chamber (nickel); 8, seal (nickel); 9, tube with metal powder for pre-heating the carrier gas.

(argon) and mounted on the cover of the chromatograph oven. Containers for samples and a torsion balance for weighing samples were placed in the same box.

Columns. A PTFE tube (140 × 0.4 cm) packed with 20% Kel-F 10 on the PTFE solid support Polychrom-1 (30–60 mesh) was used as the column for GC analysis. The packing was conditioned for 8 h at 100° in a stream of dry helium, and then a slow (*ca.* 20 ml/min) stream of gaseous fluorine was passed through the column and a few large samples (about 200 mg total) of a mixture of XeF_2 and XeF_4 (*ca.* 1:1) were introduced into the column at 40°.

The same method of pre-conditioning was used for the preparative column.

Technique

For introduction of the sample, the pivot (1) was pulled out until the pit (4) was outside the horizontal tube (2). A solid sample was placed in the pit, and the pivot was pushed into its original position and turned through 180° so that the sample dropped through the vertical tube (5) into the vaporizer chamber (7).

For the quantitative analysis of XeF_2 and XeF_4, a calibration graph of peak area *versus* weight of sample was used. This relationship was linear over the range 0–20 mg for both substances. The sensitivity was about 0.1% and the precision ±5%. By introducing a mixture of XeF_2, XeF_4 and XeF_6 into the column, three main peaks were recorded on the chromatogram (Fig. 2). Peaks 1 and 2 were identified as XeF_2 and XeF_4, respectively, by means of IR spectroscopy of the eluted substances. Peak 3 was presumably XeF_6, although no detailed examination of this product was carried out except IR spectroscopy of the crude mixture. The most important impurity in all instances was hydrogen fluoride. For the quantitative determination of this impurity, the gas chromatograph was calibrated with gaseous hydrogen fluoride by means of a special stainless-steel vacuum system.

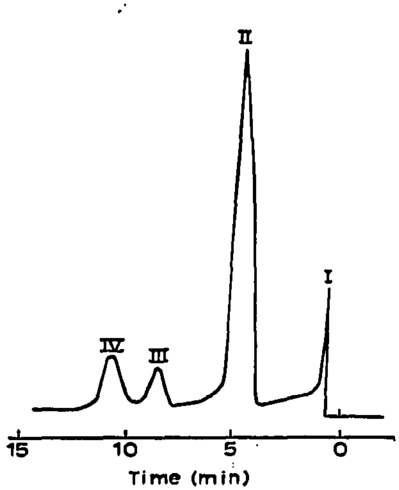

Fig. 2. Chromatogram of xenon fluorides. Conditions: column, PTFE, 140 × 0.4 cm; packing, 20% Kel-F 10 on Polychrom-1; column and detector (katharometer) temperature, 40°; vaporizer temperature, 120°; sample size, 8 mg; carrier gas flow-rate, 45 ml/min. I, HF (0.5%); II, XeF_2 (68.5%); III, XeF_4 (13%); IV, XeF_6 (18%).

Preparative-scale separation

Preparative-scale GC was carried out on a PTFE column (130 × 0.8 cm) with the same packing; the helium flow-rate was 140 ml/min and the column temperature 40°. The components were removed from the column in quartz traps cooled to —20° by means of an ice–salt mixture. The outlet tubes were cooled with liquid nitrogen so as to prevent back-diffusion of atmospheric moisture into the traps. Up to 60 mg of the original mixture of XeF_2 and XeF_4 (*ca.* 1:1) could be separated in a single run. The purity of the collected components was examined on the analytical column. The purity achieved was greater than 99.5%; the remainder was almost entirely hydrogen fluoride.

The attempt to obtain pure XeF_6 failed owing to its reaction with quartz, accompanied by explosions of the oxygen-containing compounds formed.

DISCUSSION

As shown above, if the apparatus is properly protected from moisture, GC can be used successfully for analytical and preparative-scale separations of xenon fluorides.

The good reproducibility of these experiments is important. By the successive introduction of equal amounts of samples, the heights of the chromatographic peaks were nearly constant. These results are in disagreement with the decrease in peak heights described by Zado *et al.*[2], and we cannot explain this discrepancy. We can only emphasize that satisfactory reproducibility can be obtained only after careful purification of the carrier gas and passivation of the apparatus used.

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