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Gas Chromatography of Volatile Xenon Compounds. The Elution Behavior of Xenon Difluoride

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For the first time the gas chromatography of a volatile xenon compound is reported. In this paper the elution of XeF_2 from a Kel F 10 oil-Fluoropak column is described and discussed in terms of instrumental requirements and chemical and physical properties of XeF_2. Possibilities for further application of gas chromatography in the analysis of xenon compounds and in the determination of certain physicochemical parameters are pointed out.

INTRODUCTION

In this communication we wish to report the results of our preliminary research in gas chromatography of volatile xenon compounds. Ever since the discovery of xenon fluorides[1] and the investigation of their physical and chemical properties[2–5] it was very interesting to examine the gas chromatographic behavior of these extraordinary interesting compounds. Reviewing corresponding physical and chemical properties of XeF_2, XeF_4 and XeF_6 one can note the relatively high volatility of all of these compounds even at room temperature (vapor pressures: 4.5, 2.5 and about 25 mm Hg, respectively). Chemical reactivity or sensitivity increases regularly with the number of fluorine atoms in the molecule, ranging from the relatively inactive and stable XeF_2 up to the very reactive XeF_6. Some interesting properties of volatile xenon compounds are presented in Table I.

TABLE I

Some Physical Properties of Volatile Xenon Compounds

Compound	Subl. and m. p. ^{0}C	V. p. mmHg 330^0 K	ΔH_{subl} Kcal/mole
XeF_2	129	39.05	—13.2
XeF_4	117	27.01	—14.5
XeF_6	45 (m. p.)	23.4 (296^0 K)	—15.3
$XeOF_4$	— 46.2 (m. p.)	28 (298^0 K)	—

Considering the Table as well as other chemical properties of the compounds listed, it is obvious that there is a good reason for detailed gas chromatographic investigation of these materials. Further study will include separation, analysis and thermodynamics of adsorption, solution and complex formation of volatile xenon compounds. In this report the elution of xenon difluoride will be described and discussed.

EXPERIMENTAL

All measurements were performed with a home made gas chromatograph, equipped with Model 301 Gow Mac TC cell (nickel body and filaments) connected to the Model 40-05C power supply of the same manufacturer. Helium (Airco) dried with activated molecular sieves and at the flow rate of 20 ml/min was used as carrier gas. Both detector cell cavities were interconnected through the column in series. Detector current was set at 220 mA. The column, 4 feet × 1/8 inch teflon tubing, was packed with 15% Kel F-10 oil on Fluoropak 80 following the method of Juvet and Fisher[6]. High purity XeF_2 was prepared by the method of Holloway[7] and Streng *et al.*[8] while elemental fluorine, used in the preparation of XeF_2 as well as column conditioning, was obtained as described earlier[9,10]. A home made brass six port gas sampling valve (GSV) having 420 μl sample loop (1/8 inch copper »U« tube) was used for the sample injection. The column was kept at room temperature and conditioned with several injections of pure fluorine. A sample mixture, containing solid XeF_2 (in excess to create saturated vapor) F_2, and He as pressurizing agent, was prepared in a nickel pressure vessel and allowed to flow slowly through GSV. Usually, one or two injections of the above mixture immediately following the conditioning procedure was enough to obtain a well defined XeF_2 peak, recorded on a 10 mV recorder (Nuclear Institute »Jožef Stefan«) equipped with a Keithley preamplifier.

The pressure vessel containing the sample mixture, all ducts (1/8 inch copper tubes) and GSV were heated with a heating tape up to roughly 55° C in order to increase the partial pressure of XeF_2, amounting to about 39 mmHg at this temperature[3].

DISCUSSION

Gas chromatography of reactive fluorine compounds is at present a commonly accepted procedure for the analysis of these interesting and important compounds[11]. Regardless of this fact, however, there appeares to be some inconsistence in the literature dealing with the elution of light fluorine compounds[12,13]. Too high a sensitivity of XeF_2 towards moisture[14] or construction materials is not expected, but necessary precautions were undertaken. Materials exposed to the sample mixture were fluorine resistant and passivated as usual. On Fig. 1a a typical XeF_2 chromatogram is presented. Almost tailless, it is well separated from F_2 and HF contained in the first peak. The relatively short column used could not separate these two gases. Considering the vapor pressure of XeF_2 at the working temperature (55° C) the amount of HeF_2 injected was estimated to be about 10^{-6} moles. Although XeF_2 is reportedly[14] rather insensitive towards moisture, we have experienced a very interesting behavior of XeF_2 along this line. After thorough conditioning of the entire system with four or five injections of pure fluorine, the XeF_2 peak was well defined and reproducible. After several injections of the sample mixture, however, the XeF_2 peak started gradually to decrease in height until it disappeared almost completely, Fig. 1b. When a pure He—XeF_2 sample mixture was used, only traces of HF were recorded along with the well separated XeF_2 peak. Subsequent injections of this sample mixture caused the XeF_2 peak gradually to disappear while the tailing HF peak increased considerably. Repeated conditioning with F_2 restored the original XeF_2 peak reproducibly. This behavior

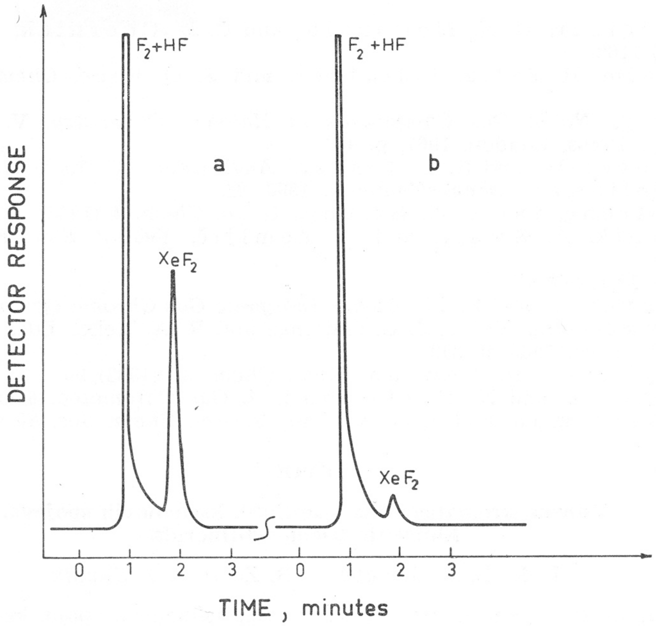

Fig. 1. Chromatograms of XeF_2. First (a) and sixth (b) injection after colum conditioning.

is simply attributed to the hydrolysis of XeF_2 with traces of moisture in the carrier gas. The literature data[14] stating that rapid hydrolysis of XeF_2 takes place at higher *p*H would not account for in here since conditioning with elemental F_2 will destroy all chemically active sites in the system which are basic in nature. The column was considered conditioned when an extremely sharp reproducible and tailless fluorine peak was obtained. On the other hand, there is no indication of chemical reaction between XeF_2 and the column packing.

Qualitative identification of XeF_2 was not carried out, although there is a certain gas chromatographic possibility for doing this, if using a reaction aftercolumn which permits only pure Xe enter the detector. It has been shown instead, however, that when the sample pressure vessel was cooled to 0^0 C with iced water, the XeF_2 peak disappeared completely (vapor pressure 1.7 mmHg). Such a behavior under the conditions of the experiment cannot be expected from either of the two other substances present, F_2 and HF.

Favorable retention properties of XeF_2 are very promising for future work on the analysis and separation of volatile xenon fluoride mixtures including gases like HF and F_2. On the other hand, considering the interesting local charge distribution in the molecules of xenon fluorides[3], certain specific molecular interactions with fluorinated liquid phase is expected. This investigation is currently under way and will be reported at a later date.

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IZVOD

Plinska kromatografija hlapljivih ksenonovih spojeva. Eluiranje ksenon-difluorida

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Prvi put je objavljeno eluiranje hlapljivoga ksenonova spoja, ksenon-difluorida, iz plinsko-kromatografske kolone. Uvjeti eluiranja ovog osjetljivoga spoja detaljno su diskutirani s obzirom na instrumentalne zahtjeve, uz fizička i kemijska svojstva ovoga spoja. Naglašena je daljnja mogućnost primjene plinske kromatografije za analizu hlapljivih ksenonovih spojeva, i određivanje nekih njihovih fizičko-kemijskih parametara.

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