VAPOUR PRESSURE OF BIS(1,1,1,5,5,5-HEXAFLUORO-2,4-PENTANEDIONATO) DIOXOURANIUM-TETRAHYDROFURAN

M.S. GILL

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085 (India)

(Received 19 August 1985)

ABSTRACT

The vapour pressure of $UO_2(HFA)_2THF$ (HFA = hexafluoroacetylacetonate, THF = tetrahydrofuran) was measured by the transpiration method in the temperature range 320–394 K. The enthalpy of vaporisation of $UO_2(HFA)_2THF$ was estimated to be 21.1 kcal mol^{-1}.

INTRODUCTION

Recently there has been a revival of interest in the synthesis and characterisation of volatile uranium compounds as a consequence of the advent of laser isotopic enrichment [1–3]. Most of these studies considered UF_6 as the model and attempted to substitute other ligands for fluorine. Thus uranium borohydride, chlorides, alkoxides, amides, etc., have been prepared and characterised [1]. Though many of these compounds exhibit reasonable volatility ($U(BH_4)_4$, 0.1 torr at 293 K [3], $U(OCH_3)_6$ distills at 360 K and 0.01 mm Hg) [4], the strong affinity of uranium for oxygen renders them extremely reactive towards oxygen and/or moisture.

Realising that the chemical reactivity of such compounds, even when they show sufficient volatility, would make them unsuitable for their intended use, during the past few years chemists have concentrated their attention on uranyl compounds [5–10]. If appropriate ligands could be found to form stable uranyl complexes, it is possible to have uranium compounds with reasonable vapour pressures. $UO_2(HFA)_2 \cdot THF$ (HFA = hexafluoroacetylacetonate; THF = tetrahydrofuran) is one such compound that has been studied due to its potential use in laser isotope enrichment [5,6]. It has been shown to be volatile, but its vapour pressure as a function of temperature is not well established. We report vapour pressure measurements between 320 and 394 K using an all-glass transpiration assembly.

EXPERIMENTAL

Preparative and handling work was carried out in an argon-filled dry box. Tetrahydrofuran (BDH) was dried using $LiAlH_4$ and purified by fractional distillation. Hexafluoroacetylacetone was obtained from Koch Light Laboratories and used after distillation at 343 K. The compound $UO_2(HFA)_2THF$ was prepared following the procedure reported in the literature [6]. The purity of the compound was checked by elemental analysis.

A schematic diagram of the transpiration assembly and details of the collector are shown in Fig. 1. Pure, dry argon carrier gas was first passed through columns of copper-based catalyst (BASF), molecular sieves (4A) and finally through phosphorus pentoxide before it was introduced into the transpiration assembly. The flow rates were regulated and measured with a glass capillary flow meter [11] which was previously calibrated.

After the furnace had reached the desired temperature, the sample was transferred into the boat which was then brought into position. The sample was allowed to attain thermal equilibrium and the temperature was then determined with a calibrated chromel–alumel thermocouple. During all these operations, argon flowed away from the collector and, hence, no vapours condensed inside the collector. After the sample attained the desired temperature, argon flow was reversed and the carrier, saturated with vapours, allowed to pass through the collector. A known amount of carrier gas was passed and, at the end, the direction of argon reversed again. The collector was removed and the uranium compound in the collector was dissolved in concentrated nitric acid. The quantity of uranium was determined by spectrophotometric and fluorimetric methods.
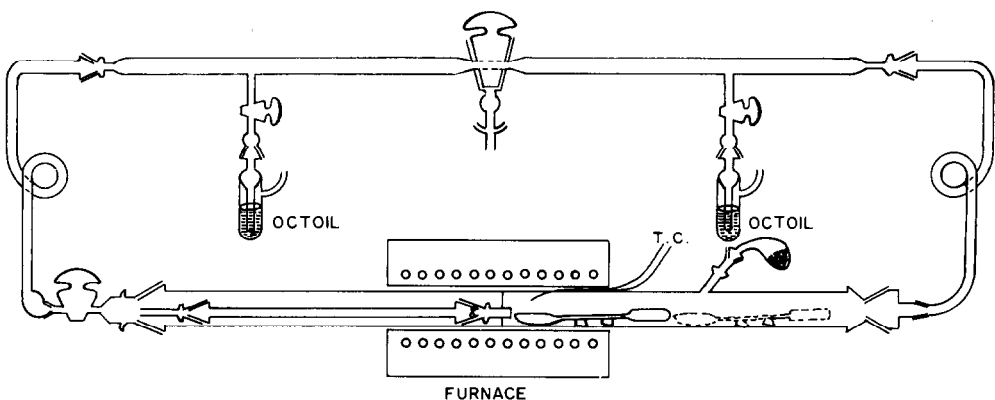

Fig. 1. Transpiration assembly.

RESULTS AND DISCUSSION

From the experimentally determined quantity of uranium-bearing species, n_U moles, transported by a known amount of argon, n_A moles, the vapour pressure of uranium bearing species p_U was calculated using an equation derived by assuming ideal behaviour of the vapour [12]. Since in any transpiration experiment it is necessary to establish equilibrium conditions between the vapour and a condensed phase [13], several experiments were first conducted at 357 K with different argon flow rates (0.6–5.26 l h^{-1}). The flow rate found to be within the plateau region (3 l h^{-1}), obtained by plotting apparent uranium-containing species pressure vs. flow rate, was used in subsequent measurements. The transpiration data results are presented in Table 1 and Fig. 2. A least-squares treatment of these values gave the expression below (1) for the temperature dependence of pressure

$$\log(\,p_U/\text{atm}) = (8.497 \pm 0.422) - (4.668 \pm 0.150)\frac{10^3\ \text{K}}{T} \tag{1}$$

A second-law enthalpy of vaporisation (21.1 kcal mol^{-1}) was calculated from this expression.

There are two main differences between the present work and that reported by Kramer et al. [6] on the vapour pressure of this compound. The vapour pressures reported in the former work are considerably higher. At

TABLE 1

Vapour pressure of $UO_2(HFA)_2THF$

| Temp. (K ± 0.5)	No. of moles of argon passed	No. of moles of uranium collected	$-\log p$ (atm)
320	0.528	0.52×10^{-6}	6.01
320	0.756	0.52×10^{-6}	6.16
331	0.744	1.26×10^{-6}	5.77
331	0.561	0.98×10^{-6}	5.76
343	0.510	2.6×10^{-6}	5.29
353	0.292	0.8×10^{-5}	4.56
357	0.66	2.1×10^{-5}	4.49
357	0.385	1.36×10^{-5}	4.45
357	0.389	1.26×10^{-5}	4.49
373	0.483	4.2×10^{-5}	4.06
373	0.269	2.2×10^{-5}	4.07
373	0.342	2.31×10^{-5}	4.17
381	0.223	3.46×10^{-5}	3.81
381	0.213	3.36×10^{-5}	3.80
394	0.240	9.94×10^{-5}	3.38
394	0.219	9.12×10^{-5}	3.38
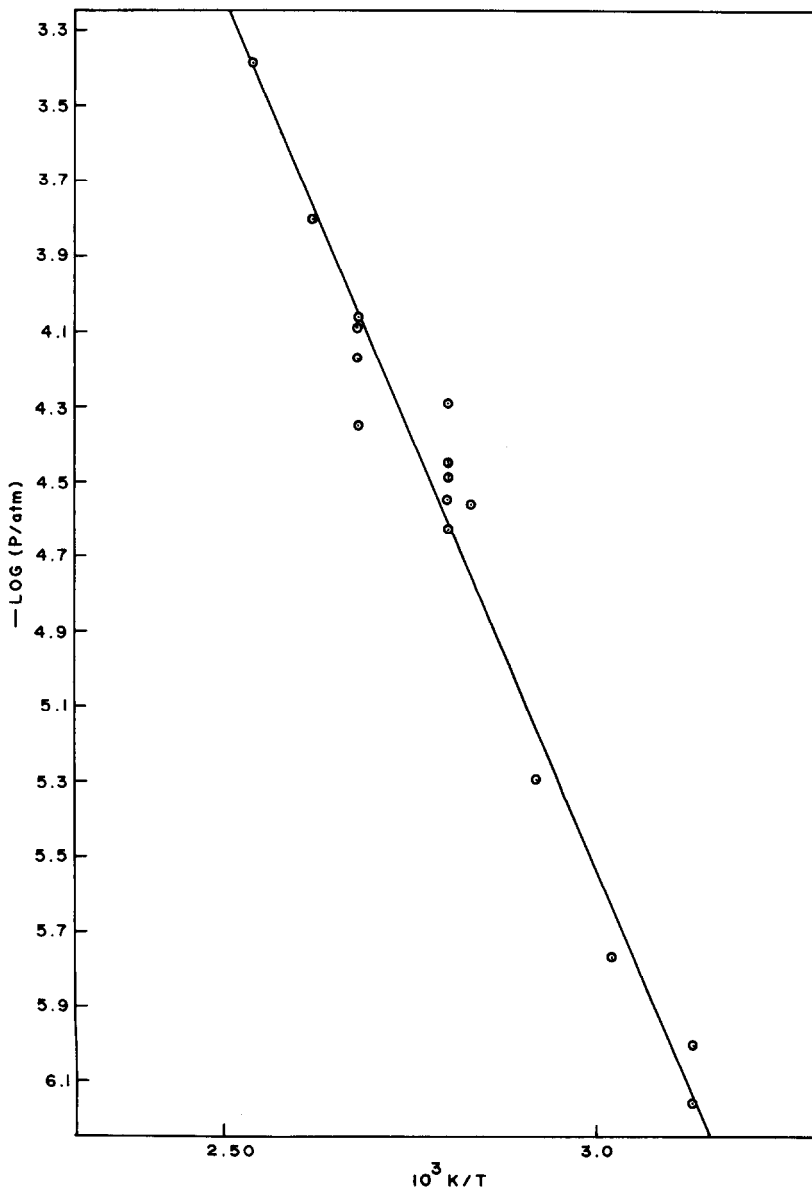
Fig. 2. Log p vs. $1/T$ of $UO_2(HFA)_2THF$.

373 K, their vapour pressure is an order of magnitude higher. Consequently, the enthalpy of vaporisation (14 kcal mol^{-1}) derived from these measurements is much lower than that obtained in the present work.

Since Kramer et al. [6] used the tensimetric method to measure the vapour pressure, the measured pressure will be that due to the presence of all the gaseous species, including any non condensable vapours. In the present case, since only uranium-bearing species present in the vapour phase are esti-

mated, the pressure of other non-uranium-bearing species will not be involved in pressure computation. If some simultaneous decomposition occurred with vaporisation of $UO_2(HFA)_2THF$, then the total pressure recorded by the static method would be higher. This will also be reflected in the calculated enthalpy values. This could be a reason for the difference in the data of the two experiments. In the transpiration method, the decomposition reaction would not alter the transport process provided there is always sufficient undecomposed sample in the boat and the decomposition product in the boat is less volatile.

The following experiment was carried out in support of the above explanation. A sufficient quantity of the sample enclosed in a glass vial was heated to ~ 363 K. The vapours formed were analysed by gas chromatography. In all such experiments, the presence of free THF was observed, suggesting the following decomposition reaction.

$$UO_2(HFA)_2THF = UO_2(HFA)_2 + THF(g) \tag{2}$$

$UO_2(HFA)_2$ is comparatively less volatile [9] than $UO_2(HFA)_2THF$ and, hence, will not contribute to the transport of uranium-containing vapours. Reaction (2) would significantly increase the total vapour pressure over $UO_2(HFA)_2THF$.

The significantly higher values reported by Kramer et al. [6] would, thus, presumably correspond to the total pressure of THF(g) and $UO_2(HFA)_2THF$ and not to the equilibrium reaction (3)

$$UO_2(HFA)_2THF(s) = UO_2(HFA)_2THF(g) \tag{3}$$

It is probable that their reported lower enthalpy value may correspond to reaction (2) and not to (3). In view of this analysis, eqn. (1) probably represents reaction (3).

ACKNOWLEDGEMENTS

REFERENCES

1 J.H. Coleman and T.J. Marks, U.S. Patent 4 097 384 (1978).
2 A. Edward, E.A. Cuellar and T.J. Marks, Inorg. Chem., 20 (1981) 2129.
3 N. Ghiassee, P.G. Clay and G.N. Walton, Inorg. Nucl. Chem. Lett., 16 (1980) 149.
4 M.S. Gill, S.C. Jain and G.S. Rao. B.A.R.C. Rep. I-736, 1982.
5 D.M. Cox, R.B. Hall, J.A. Horsley, G.M. Karmer, P. Rabinowitz and A. Kaldor, Science, 205 (1979) 390.

6 G.M. Kramer, M.B. Dines, R.B. Hall, A. Kaldor, A.J. Jacobson and J.C. Scalon, Inorg. Chem., 19 (1980) 1340.

7 E.T. Maas Jr., G.M. Kramer and R.G. Bray, J. Inorg. Nucl. Chem., 43 (1981) 2053.

8 J. Taylor, A. Ekstrom and C.H. Randall, Inorg. Chem., 17 (1978) 3285.

9 A. Ekstrom, H. Loeh, C.H. Randall, L. Szego and J.C. Taylor, Inorg. Nucl. Chem. Lett., 14 (1978) 301.

10 G.M. Kramer, E.T. Maas and M.B. Dines, Inorg. Chem., 20 (1981) 1415.

11 O.M. Sreedharan, S.R. Dharwadkar and M.S. Chandrasekharaiah, B.A.R.C. Rep. I-239, 1973.

12 U. Merten and W.E. Bell, in J.L. Margrave (Ed.), Characterisation of High Temperature Vapours, Wiley, New York, 1967, pp. 99–104.

13 M.S. Chandrasekharaiah, M.D. Karkhanavala and S.N. Tripathi, J. Less-Common Met., 80 (1981) 9.