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Volatile Compounds of β-Diketonates of Dioxouranium(VI) with Tetrahydropyran and Tetrahydrothiophene

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Abstract

Complexes of the type [UO_2(β-diket)$_2 \cdot n$B] where β-diket = $CF_3COCHCOR$ (R = CF_3, CH_3, C_4H_3S or C_6H_5 and denoted by HFAA, TFAA, TTA or BTA, respectively), B = tetrahydropyran (THP) and tetrahydrothiophene (THT) and n = 0.5–2.0, have been synthesized and characterised by infrared, ^{1}H NMR and mass spectral techniques. Vapour pressure of UO_2(HFAA)$_2 \cdot$THP was measured by the transpiration method between the temperature range of 323–391 K. The enthalpy of vaporisation of UO_2(HFAA)$_2 \cdot$THP was estimated to be 18.4 kcal/mol.

Introduction

Mixed ligand complexes of dioxouranium containing fluorinated β-diketones and tetrahydrofuran (THF) or trimethylphosphate (TMP) have recently been reported [1] to be volatile. Enhanced volatility of these compounds has been attributed to the close packing of fluorines in β-diketones and also to the presence of coordinated THF or TMP molecules. Such compounds of uranium have drawn much attention because of their potential use in isotope enrichement by laser induced separation techniques [2].

The present study with the tetrahydropyran (THP) and tetrahydrothiophene (THT) adducts of β-diketonates of dioxouranium(VI) was taken up to evaluate their volatility as compared to that of the THF adduct reported earlier [3–5]. It was also considered of interest to compare the ligating behaviour of β-diketones and THT with THF, as THT is supposed to form strong bonds because of its strong polarizability and available dπ-orbitals on sulphur atom.

Experimental

In general, UO_2(β-diket)$_2 \cdot$THP compounds were prepared by an extraction process [3] from an aqueous solution of uranyl nitrate and benzene solution of β-diketone and THP. The compounds UO_2(β-diket)$_2 \cdot n$THT on the other hand, were synthesized [4] either by refluxing $UO_3 2H_2O$ and β-diketone in a mixture of n-hexane and THT or by reacting anhydrous UO_2Cl_2 and thallium salt of β-diketone in 1:2 molar ratios in a mixture of n-hexane and THT. Compounds were handled in a dry box continuously flushed with dry nitrogen.

The analytical and physical data of the compounds are given in Table I. Infrared (IR) spectra 4000–200 cm^{-1} of the compounds were recorded as Nujol mull on a Perkin-Elmer Spectrometer model 577 using CsI optics. Proton NMR spectra of these compounds were recorded on a Varian A 60 spectrophotometer at 60 MC/s in $CDCl_3$ using trimethylsilane (TMS) as an internal standard. The mass spectrum of UO_2(HFAA)$_2 \cdot$THP was recorded on a Quadrupole mass spectrometer, Extranuclear, EMBA II at 40 eV and 1 milliampere emission current at 85 °C, and those of UO_2(HFAA)$_2 \cdot$2THT and UO_2(BTA)$_2 \cdot$THT were recorded on VG micromass 7070F mass spectrometer at ion source of 170–200 °C, 70 eV and 200 μA emission current. Vapour pressure measurements on compound UO_2(HFAA)$_2 \cdot$THP were carried out by the transpiration method. The details of experimental arrangements and the procedure were similar to that reported earlier [5]. The uranium content was determined by spectrophotometric and fluorometric methods.

Results and Discussion

The compounds are soluble in alcohol, ether, benzene and toluene but insoluble in carbontetrachloride, chloroform and n-hexane (except the HFAA compounds which are soluble in non-polar solvents also). Whereas none of the compounds UO_2(β-diket)$_2 \cdot n$THT could be sublimed, the compounds of the type UO_2(HFAA)$_2 \cdot$THP and UO_2(TFAA)$_2 \cdot$THP sublimed at 50–60 °C and 90–100 °C at 10^{-4} mmHg, respectively.

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TABLE I. Analytical Data of $[UO_2(\beta\text{-diket})_2 \cdot THP]$ and $[UO_2(\beta\text{-diket})_2 \cdot n THT]$

Compound	Colour	Melting point (°C)	Analysis					
			Found (%)			Calculated (%)		
			U	C	H	U	C	H
$UO_2(HFAA)_2THP$	yellow	84–85	30.4	22.1	2.9	30.9	23.4	1.6
$UO_2(TTA)_2THP$	golden yellow	196–198	29.5	32.4	2.4	28.8	31.6	2.8
$UO_2(BTA)_2THP$	dark yellow	158–159	29.5	37.6	4.1	30.3	38.2	2.8
$UO_2(TFAA)_2THP$	yellow	194–195	35.1	27.5	3.3	35.9	27.2	2.7
$UO_2(HFAA)_2THT$	yellow	136–138	31.5	20.8	1.4	30.8	21.8	1.3
$UO_2(TTA)_2THT$	dark orange	140–145	29.8	31.1	2.8	29.8	30.7	2.0
$UO_2(TFAA)_2 \cdot 0.5THT$	yellow	136–138	39.0	23.8	3.2	38.4	23.4	2.0
$UO_2(BTA)_2 \cdot 2THT$	orange	117–118	27.7	37.9	2.9	27.2	38.3	3.2

TABLE II. Infrared (cm^{-1}) Spectra[a] of $UO_2(\beta\text{-diket})_2 \cdot THP$ and $UO_2(\beta\text{-diket})_2 \cdot n THT$

Compound	$\nu(C=O)$	$\nu(C=C)$	$\nu(C-O-U)$	$\nu(C-O-C)$ or $\nu(C-S-C)$	$\nu_3(UO_2^{2+})$	$\nu(U-O)$	$\delta(UO_2^{2+})$
$UO_2(HFAA)_2 \cdot THP$	1647s, 1622m	1539m		1015sh, 807s	949s	532m, 335vw	263m, 246m
$UO_2(TFAA)_2 \cdot THP$	1624vsb	1534sb	1286sb	1025s, 795vs	922vs	519m, 398s	262s, 256sh
$UO_2(TTA)_2 \cdot THP$	1612s, 1598vs	1541vs	1315s	1026s, 795vs	932vs	502m, 350vw	267s, 250s
$UO_2(BTA)_2 \cdot THP$	1570m	1530vs	1310s	1019vs, 804s	936vs	470m, 356w	265s, 245m
$UO_2(HFAA)_2 \cdot THT$	1646m, 1616sh	1536w		665sh	949m	520w, 354w	262vw, 245vw
$UO_2(TFAA)_2 \cdot 0.5THT$	1624vs, 1600sh	1534m	1294vsb	670vw	926s	518vw, 408vw	293vw, 268vwb
$UO_2(BTA)_2 \cdot 2THT$	1566s	1530m	1315s	675w	923s	515m, 355vw	265m, 240w
$UO_2(TTA)_2 \cdot THT$	1613sb, 1583sh	1542mb	1314s	670sh	922s	502vw, 350vw	270w, 240w

[a] s = strong, m = medium, w = weak, sh = shoulder, vs = very strong, vw = very weak, b = broad.

Infrared Spectral Results

Infrared spectral data of the compounds are given in Table II. The carbonyl stretching frequency $\nu(C=O)$ for the complexes appears at a lower wave number (1650–1560 cm^{-1}) as compared to those for the respective free β-diketone (1680–1585 cm^{-1}). This establishes bonding through the carbonyl group [6, 7]. Bray and Kramer [8] have made detailed study of the infrared transition frequencies of uranyl and hexafluoroacetylacetonate moieties based on the relative basicity of the neutral ligands and the extent of oligomerization in the compounds. In the present study with the compounds $UO_2(HFAA)_2 \cdot THP$, $UO_2(TTA)_2 \cdot THP$, $UO_2(TFAA)_2 \cdot THP$ and $UO_2(BTA)_2 \cdot THP$ the neutral base THP provides uniform interaction with the UO_2 group. The β-diketonate anions, however, interact to different extents to the central UO_2 group and also with neighbouring uranyl compound molecules. It is, therefore, difficult to correlate the magnitude of the negative shift $\Delta\nu(C=O)$ with the basicity of β-diketonate anion, although the order of $\Delta\nu(C=O)$, 43, 38, 31 and 15 cm^{-1} falls in the line of HFAA, TTA, TFAA and BTA.

The newly observed strong bands in the region 1315–1286 cm^{-1} and 1540–1534 cm^{-1} are due to $\nu(C-O-U)$ and $\nu(C=C)$, respectively, and confirm the chelate formation by the β-diketonate ion. The tetrahydropyran molecule shows two characteristic strong bonds at 1090 and 818 cm^{-1} due to asymmetric and symmetric stretching of C–O–C band [9]. These bands shift to the 1015–1026 and 795–807 cm^{-1} regions for complexes, indicating the strong ligating behaviour of the THP molecule. In the case of the $UO_2(\beta\text{-diket})_2 \cdot n THT$ complexes, the $\nu(C-S-C)$ bands appear between 665–675 cm^{-1} as compared to 682 cm^{-1} for free tetrahydrothiophene [10], suggesting coordination to uranium.

The asymmetric stretching O=U=O, ν_3, for all these compounds appear as strong bands between 920–950 cm^{-1}. An attempt to correlate the basic nature of the β-diketone or THP and THT based on the position of the ν_3 band [11] does not seem to follow any uniform pattern. In the far infrared region, the $\nu(U-O)(\beta\text{-diket})$ bands appear as two (strong to medium) bands in the region 530 to 335 cm^{-1}, adding support to the conclusion that the chelated nature of β-diketones remains intact even

TABLE III. Characteristic Proton Magnetic Resonance (PMR) Frequencies in [$UO_2(\beta$-diket$)_2 \cdot$THP] and [$UO_2(\beta$-diket$)_2 \cdot n$THT] Complexes in $CDCl_3$[a]

Complex	Chemical shift (δ ppm)		
	Base protons		β-diketonate protons
	H'_b	H'_a	γ(CH)
$UO_2(HFAA)_2 \cdot$THP	4.85	2.15	6.75
$UO_2(TFAA)_2 \cdot$THP	4.30	1.86	6.24
$UO_2(TTA)_2 \cdot$THP	4.30	1.60	6.33
$UO_2(BTA)_2 \cdot$THP	4.28	1.52	6.53
$UO_2(HFAA)_2 \cdot$THT	4.13	2.16	6.66

[a] Other compounds $UO_2(\beta$-diket$)_2 \cdot n$THT were insoluble in $CDCl_3$. (H_b and H_a for THP and THT are 3.67, 1.62 ppm and 2.86, 1.98 ppm, respectively.)

after interaction with THP or THT. However, the ν(U–O)THP or ν(U–S) were difficult to assign because of the broad nature of the bands and the poor resolution of the spectra in the ν(U–S) region.

NMR Spectral Results

The proton NMR spectra of $UO_2(\beta$-diket$)_2 \cdot$THP complexes and $UO_2(HFAA)_2 \cdot$THT are given in Table III. Three distinct absorption bands have been observed for each complex. The δC–H proton of the β-diketonate ion appears between δ = 6.24 to 6.75 ppm as a sharp singlet. The other two bands appear between δ = 4.30 to 4.65 ppm and δ = 1.60 to 2.15 ppm, as a quintet and triplet, respectively, due to coordinated THP or THT molecules. In comparison, triplets appear at δ = 1.62 ppm (THP), 1.98 (THT) and quintet at δ = 3.67 ppm (THP) and 2.86 ppm (THT) for the neat ligands. The deshielding of these two bands shows drainage of the electron cloud from the oxygen or sulfur of the ligands to the UO_2^{2+} ion in the complex. In the case of $UO_2(HFAA)_2 \cdot$THP and $UO_2(HFAA)_2 \cdot$ THT complexes, the three bands have relative areas 1:2:2 confirming the molecular formula as UO_2-$[(CF_3CO)_2CH]_2 \cdot (CH_2)_5O$ and $UO_2[(CF_3CO)_2CH]_2 \cdot (CH_2)_4S$.

Mass Spectra

The cracking pattern of $UO_2(HFAA)_2 \cdot$THP and the relative intensities of the fragments are given in Table IV. Appearance of *m/e* at 770 shows the stability of the parent compound under mass spectrometric conditions. Electron impact mass spectra of $UO_2(HFAA)_2 \cdot$THT and $UO_2(BTA)_2 \cdot 2$THT show maximum masses of 684 and 700, respectively, showing instability of these complexes. The fragments corresponding to these masses can be formulated as $[UO_2(HFAA)_2]^+$, 684; $[UO_2(BTA)_2]^+$, 700.

Vapour Pressure of $UO_2(HFAA)_2 \cdot$THP

The vapour pressure of uranium-bearing species was calculated on the assumption that the uranium-bearing vapor species contains one atom of uranium per molecule. The ideal gas behaviour is assumed and the expression (1) is derived for the partial pressure of the vapor species [12].

$$p_u = \frac{n_u}{n_u + n_c} p \tag{1}$$

where p_u is the partial pressure of the vapor species*, p is the total pressure of the gas phase, n_u is the number of moles of the vapor species containing uranium atom transported by n_c moles of argon carrier gas. In order to establish the equilibrium transport conditions, several experiments were conducted at 365 K with different argon flow rates (1.2–5.0 l h^{-1}). A flow rate (3 l h^{-1}) within the plateau region obtained by the plot of apparent pressure of uranium-containing species *vs.* the flow rate was used in the subsequent measurements. The vapour pressure of $UO_2(HFAA)_2 \cdot$THP was measured in the temperature interval 323–391 K. The transpiration data results are presented in Table V

TABLE IV. Mass Spectra of $UO_2(HFAA)_2 \cdot$THP

m/e	Ion	Calculated mass	Relative intensities
770	$(UO_2(HFAA)_2 \cdot THP)^+$	770	18
701	$(UO_2[HFAA][CF_3COCHCO]THP)^+$	701	7
615	$(UO_2[HFAA][CF_3COCHCO])^+$	515	7
563	$(UO_2[HFAA]THP)^+$	563	100
477	$(UO_2[HFAA])^+$	477	66
427	$(UO_2[CF_3COCHCOF])^+$	427	4
289	$(UO_2F)^+$	289	27
270	$(UO_2)^+$	270	4

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*Measured in atm.

TABLE V. Vapour Pressure of $UO_2(HFAA)_2 \cdot THP$

Temperature[a] (K)	Ar passed (mol)	U collected (mol)	$-\log(p)$ (atm)
323	0.809	1.44×10^{-6}	5.75
323	0.670	0.945×10^{-6}	5.85
331	0.593	1.901×10^{-6}	5.49
331	0.635	2.08×10^{-6}	5.484
340	0.614	2.416×10^{-6}	5.405
340	0.491	3.256×10^{-6}	5.178
357	0.276	9.559×10^{-6}	4.461
365	0.289	14.6×10^{-6}	4.297
365	0.324	19.64×10^{-6}	4.218
365	0.461	25.42×10^{-6}	4.26
365	0.395	23.42×10^{-6}	4.227
370	0.511	29.41×10^{-6}	4.24
376	0.307	21.43×10^{-6}	4.156
387	0.225	41.81×10^{-6}	3.730
391	0.123	23.63×10^{-6}	3.720
391	0.133	24.16×10^{-6}	3.740

[a] ± 0.5 K.

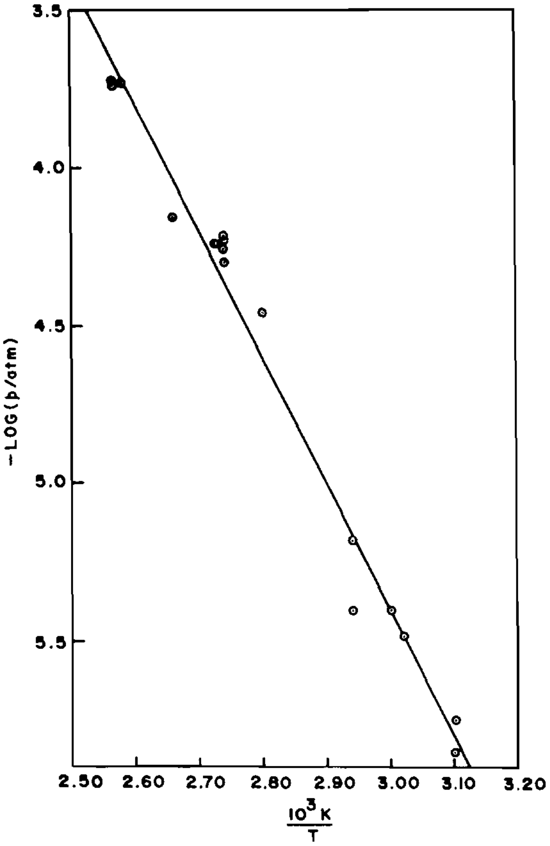

Fig. 1. Log p vs. $1/T$ of $UO_2(HFAA)_2 \cdot THP$.

and Fig. 1. A least-squares treatment of these values gave the expression (2) for the temperature dependence of pressure.

$$\log(pU) = (6.701 \pm 0.422) - (4.034 \pm 0.149)\,\frac{10^3\ K}{T} \qquad (2)$$

A second-law enthalpy of vaporisation (18.4 kcal/mol) was calculated from this expression. The vapour pressure calculated from eqn. (2) is almost an order of magnitude lower than that reported by Kramer *et al.* [3] for the compound $UO_2(HFAA)_2 \cdot THF$. This difference may be due to the difference in the two techniques; they measured total vapour pressure including the pressure due to decomposition products while in this work we measured only the vapours containing the uranium atom. The cause of this difference in the two methods is discussed in our previous paper [5]. The compounds $UO_2(HFAA)_2 \cdot THP$ and $UO_2(HFAA)_2 \cdot THF$ have similar vaporisation behaviour. However, the former has a smaller enthalpy of vaporisation compared to $UO_2(HFAA)_2 \cdot THF$ [5] ($\Delta H_v = 21.1$ kcal/mol); thus it will be more volatile at lower temperature. On this basis, it may be inferred that substituting THP for THF increases the intra-molecular bonding and decreases the intermolecular interactions in the solid.

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