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THERMAL DECOMPOSITION OF BARIUM DIOXODIAQUAPEROXYOXALATO URANATE(VI) HYDRATE

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Abstract

Barium dioxodiaquaperoxyoxalatouranate was obtained by reaction of uranyl nitrate with oxalic acid and then hydrogen peroxide in the presence of barium ion. The complex was subjected to chemical analysis. The thermal decomposition behaviour of the complex was studied using TG, DTG and DTA techniques. The solid complex salt and the intermediate product of its thermal decomposition were characterized using IR absorption and X-ray diffraction spectra. Based on data from these physico-chemical investigations the structural formula of the complex was proposed as $Ba[UO_2(O_2)(C_2O_4)(H_2O)_2]\cdot H_2O$.

Keywords: barium salt, IR data, peroxy, thermal analysis, uranium(VI), X-ray diffraction

Introduction

Uranyl ion forms numerous complexes with sulphate, carbonate and oxalate anions. The interest in the present work lies in the preparation and characterisation of the 1:1 complex species. 1:1 peroxyuranates that were described in literature [1] are of four types. Compounds of formula $M^IHU_2O_9\cdot nH_2O$, $M_2^IU_2O_9\cdot nH_2O$ and $M_2UO_5\cdot nH_2O$ have been obtained by the reaction of uranyl nitrate on alkaline hydrogen peroxide [2, 3] and as decomposition products of alkaline solutions of triperoxy uranates [4, 5]. Owing to an intrinsic interest in [6, 7] and practical use of [8, 9] peroxometal compounds there has been an upsurge of research in their chemistry. Although peroxoactinides are known [10, 11] molecular complexes are rather scanty [12, 13]. This aspect of uranium is complicated [10] and $[UO_2(O_2)]\cdot nH_2O$ (n=2 or 4) is best characterised. In addition $[UO_2(O_2)L]$, L=Ph_3PO, Ph_3AsO or pyridine N-oxide [12] and a few diperoxouranium(VI) complexes with Schiff bases as coligands [13] are known. The compound $[UO_2(O_2)]\cdot 4H_2O$ oxidises olefins to epoxides and oxidative- cleavage products [9]. It has been observed [11] that $[UO_2]^{2+}$ re-

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acts with H_2O_2 to generate $[UO_2(O_2)]$ in solution and caused to anticipate a similar reaction in the presence of an appropriate coligand would provide an access to molecular peroxo-complexes of the metal.

As with molybdenum and tungsten, the peroxide chemistry of uranium is confined to the +6 oxidation state; in view of the small potential for the +6/+5 change (0.063 volts). The best characterised peroxy derivative is tetroxide (commonly called uranyl peroxide), $UO_4 \cdot nH_2O$ (where n is 2 or 4); many peroxyuranates are known, in which the ratio of peroxide to uranium is 3:1, 5:2, 2:1, 3:2, 1:1 and 1:2 and in addition to these, a series of mixed ligand peroxy compounds have been described. In general, the peroxide content increases with pH; acids decompose the compounds to uranium(VI) salts and oxygen, while the triperoxyuranate ion is stable at pH 12–14.

In the present work barium dioxodiaquaperoxyoxalatouranate(VI) complex was prepared by reaction of UO_2^{2+} with oxalic acid and then hydrogen peroxide in the presence of barium ion. The thermal decomposition of the complex has been studied and a detailed account of the mechanism has been worked out on the basis of the thermal data, infrared spectroscopic and X-ray diffraction studies.

Experimental

Instrumentation

Thermal analysis unit

SEIKO combined thermal analysis system (TG/DTA-32), temperature programmable thermal balance, made in Japan and platinum crucible as container is used for taking curves in air. The rate of heating is fixed to10°C min^{-1}, and sensitivity of the instrument is 0.1 mg.

Infrared spectra

The infrared spectra of the complexes are recorded on Shimadzu FTIR-8201 PC Infrared Spectrophotometer in KBr pellets.

X-ray diffraction data

X-ray diffractometer of Rich Seifert & Company (made in Germany) attached to a microprocessor is used for taking X-ray diffraction patterns at wavelength of CuK_α=1.540598 Å.

Preparation and analysis

The barium dioxodiaquaperoxyoxalatouranate(VI) complex salt is prepared by adopting the following procedure [14]:

About 1.0 g (1.99 mmol) sample of $UO_2(NO_3)_2 \cdot 6H_2O$ was dissolved in water (10–15 cm^3) followed by addition of concentrated solution of barium hydroxide solution with stirring until yellow precipitate ceased to appear. The yellow precipitate was filtered off and washed free of barium and nitrate ions. To an aqueous suspension of the product was added 4 cm^3 (10 mmol) of concentrated solution of oxalic acid to obtain a clear solution, which was stirred for ca 5 min. A 25 cm^3 (220.5 mmol) sample of 30% H_2O_2 was added, while the $U:C_2O_4:H_2O_2$ ratio was maintained at 1:1:111 and the solution was stirred for ca 15 min followed by careful addition of the barium hydroxide solution until pH was raised to 6, where upon a yellow product just began to appear. An equal volume of ethanol was added with occasional stirring to obtain yellow microcrystalline complex of barium dioxodiaquaperoxy and oxalatouranate(VI). The compound was allowed to settle for ca 20 min, separated by centrifugation, purified by washing with ethanol (3–5 times) and finally dried in vacuo over silica gel. The compound thus obtained is tested to confirm the absence of nitrate.

The reaction of hydrogen peroxide with uranyl ion leading to a complex peroxy uranate(VI) of a definite composition is highly dependent on the pH of the reaction medium. Thus, evaluation of an appropriate pH for successful synthesis of a peroxy uranate species is emphasized to be an important prerequisite. The suitable pH for bringing about coordination of both peroxide and oxalate with the uranyl center was ascertained to be 6. The compounds isolated at a relatively lower pH (e.g. ca 4) on being analyzed did not show the occurence of peroxide to the desired level (i.e, $U:O_2^{2+}$ as 1:1), indicating therefore that the O_2^{2+} uptake process was in progress but did not reach the $U:O_2^{2+}$ ratio of 1:1.

The compound was analysed for its uranium(VI), oxalate, peroxide and water content. Uranium(VI) was estimated by photochemical reduction with alcohol [15] whereas oxalate [16] and peroxide [17] by volumetric titration with standardised cerium(IV) sulphate. Water content was determined by difference and from thermal data. The results of the analyses are shown in Table 1.

Table 1 Chemical analysis data of barium dioxodiaquaperoxyoxalatouranate(VI)

Composition/%					Mole ratio	Possible formula
U(VI)	$C_2O_4^{2-}$	O_2^{2-}	Ba^{2+*}	H_2O^*	$U(VI):C_2O_4^{2-}:O_2^{2-}$	
40.96	14.96	5.35	23.58	9.29	1.03:1.02:1	$Ba[UO_2(O_2)C_2O_4(H_2O)_2]\cdot H_2O$

[*] Calculated from the formula

Results and discussion

Thermal analysis

Thermogravimetric analysis (TG)

The pyrolysis curve of barium dioxodiaquaperoxyoxalatouranate(VI) hydrate and the data obtained are shown in Fig. 1 and Table 2 respectively. From the curve it is evident that the complex loses three molecules of water between 30 and 149°C in two steps until the anhydrous salt is finally obtained. The mass loss corresponds to 8.97% on the TG curve against the calculated value of 9.29%. The next step indicates the de-

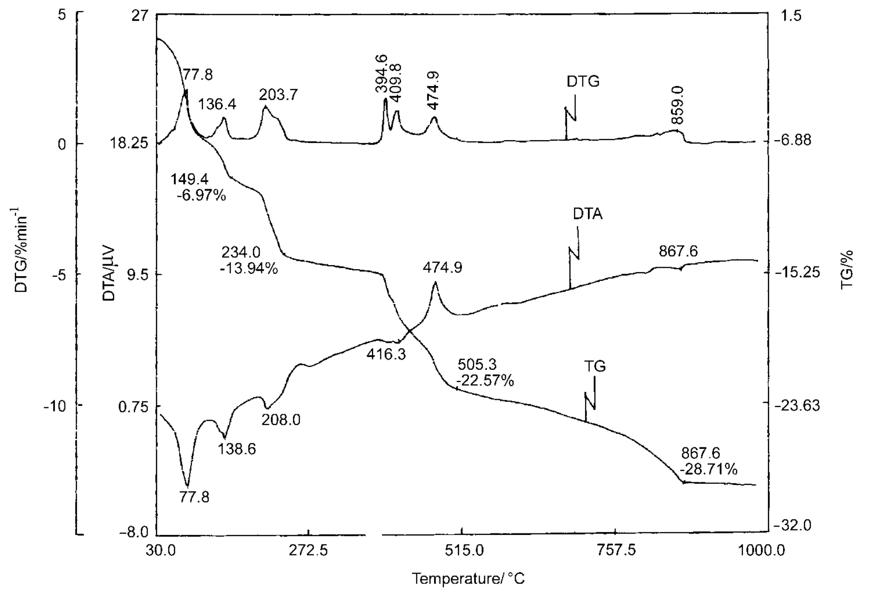

Fig. 1 TG/DTG/DTA curves of barium dioxodiaquaperoxyoxalatouranate(VI) hydrate

composition of the anhydrous product to a carbonate intermediate $BaCO_3{\cdot}UO_4$ with the expulsion of carbon monoxide upto 234.0°C. The mass loss corresponding to this step is 13.94% against the calculated value of 14.11%.

Table 2 Summary of the thermal decomposition of the barium salt

Mass of comp.	Step no.	Temperature/°C		Mass loss/%		Possible decomposition product (intermediate)
		starting	ending	obs.	calc.	
8.00 mg	1	30.0	149.4	8.97	9.29	$Ba[UO_2(O°_2)C_2O_4]$
	2	149.4	234.0	13.94	14.11	$BaCO_3{\cdot}UO_4$
	3	234.0	505.3	22.57	21.69	$BaCO_3$+BaU_2O_7
	4	505.3	~700.0	24.80	24.44	$BaUO_4$
	5	~700.0	867.6	28.71	27.19	BaO+UO_2

After 234°C the TG curve shows that the intermediate is relatively stable upto 381.6°C and then the decomposition of the carbonate intermediate is continuous indicating the formation of barium carbonate and barium diuranate intermediates with the expulsion of carbon dioxide upto 505.3°C. The observed mass loss amounts to 20.95% against the calculated value of 20.65%. The resulting intermediate products i.e., barium carbonate and barium diuranate react together to form monouranate [18] with the expulsion of carbondioxide which further decomposes to form BaO and UO_2 [19]. The observed mass loss is 28.71% while the calculated value is 27.19%.

Differential thermogravimetric analysis (DTG)

DTG results of the barium salt of the complex are shown in Fig. 1. There are apparently five significant peaks in the DTG curve in support of the mass loss pattern of decomposition of barium dioxodiaquaperoxyoxalatouranate(VI) hydrate. The first prominent peak lying at 77.8°C describes the dehydration of the complex due to loss of one molecule of crystal water. A sharp peak at around 136.4°C may be attributed to the loss of two molecules of coordinated water to give rise to the anhydrous product. The peak at 203.7°C corresponds to the decomposition of the anhydrous complex to the formation of $BaCO_3 \cdot UO_4$. This is followed immediately by the formation of barium carbonate and barium diuranate intermediates, which is indicated by sharp peaks at 394 and 409.8°C. The next peak at 474.9°C may be due to the formation of barium monouranate, which is formed by the reaction of the intermediates viz. barium carbonate and barium diuranate. The resulting barium monouranate eventually decomposes to uranium dioxide and barium oxide, which is shown by a small peak at 859.0°C.

Differentital thermal analysis (DTA)

From Fig. 1 it is clear that the dehydration of barium dioxodiaquaperoxyoxalato uranate(VI) hydrate is indicated by endothermic peaks with ΔT_{min} at 77.8 and 138.6°C indicate the loss of one crystal and two coordinated water molecules in a stepwise manner. The endothermic peak with ΔT_{min} at 208°C on the DTA curve can be associated with the partial decomposition of the anhydrous product to give $BaCO_3 \cdot UO_4$. A small endothermic peak with ΔT_{max} at 416.3°C indicates the decomposition of $BaCO_3 \cdot UO_4$ to give $BaCO_3$ and BaU_2O_7. An exothermic peak with ΔT_{max} at about 474.9°C corresponds to the formation of $BaUO_4$ from a reaction between intermediates $BaCO_3$ and BaU_2O_7. Barium monouranate subsequently decomposes into barium oxide and uranium dioxide, which is shown by a small endothermic peak at 867.6°C.

Infrared spectra of barium dioxodiaquaperoxyoxalatouranate(VI)

IR spectra of barium dioxodiaquaperoxyoxalatouranate(VI) trihydrate and the products obtained by heating the complexes at 200 and 450°C and cooled to room temperature are given in Fig. 2 A, B and C and Table 3 respectively. The spectrum of the barium complex also shows distinctly strong and sharp absorption band at 897 cm^{-1} which may be assigned to the νU=O(trans-linked O=U=O) [20] a broad and medium peak at 725 cm^{-1} attributed to the νO-O(the peroxy modes) [21–24] and a small band at 600 cm^{-1} to the $\nu U\text{-}O_2$ bond. In this spectrum a triangularly bonded bidentate peroxide is also indicated, in which O_2^{2+} group is bound to UO_2^{2+} center and IR modes due to the coordinated $C_2O_4^{2+}$ ligand (at 1628 cm^{-1}) showing the presence of a chelated oxalato group [25, 26]. The symmetric and asymmetric stretching bands of H–O–H appear on the spectrum at 3500 and 3160 cm^{-1}. The δH–O–H at 1628 cm^{-1} in the IR spectrum of the compound also resembles in its shape and position to those generally observed for coordinated water [27, 28].

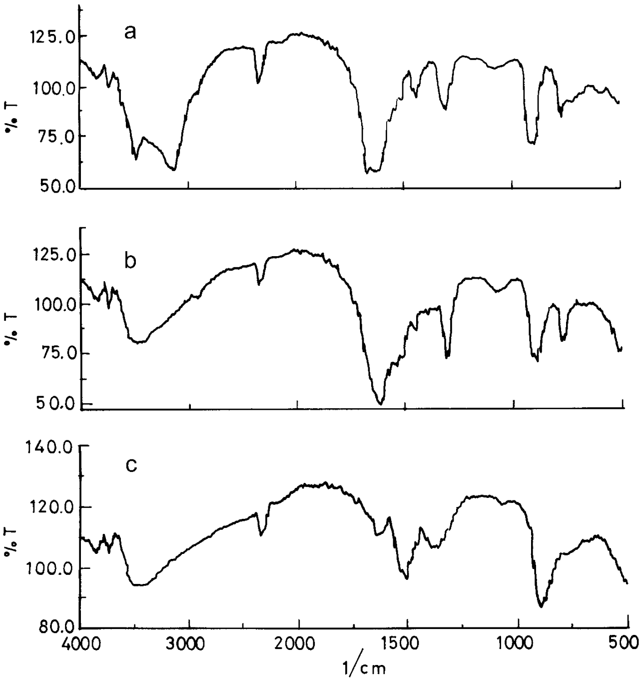

Fig. 2 Infrared spectrum of barium dioxodiaquaperoxyoxalatouranate(VI) hydrate (a); Infrared spectrum of barium dioxodiaquaperoxyoxalatouranate(VI) after heating to 200°C (b);
Infrared spectrum of barium dioxodiaquaperoxyoxalatouranate(VI) after heating to 450°C (c)

Table 3 Infrared absorption data of barium dioxodiaquaperoxyoxalatouranate(VI) and the decomposition products

Complex			Band assignment
Original/cm^{-1}	Heated at 200°C/cm^{-1}	Heated at 450°C/cm^{-1}	
3500 w 3160 b,s	3500 b	3500 b	$\nu_{as,s}$(H–O–H)
1674 b 1628 w	1675 m,b	1650 b, w	ν_a(C=O)+δ(H–O–H)
	1525 sp,m	1510 sp,m	ν_s(C–O) due to CO_3^{2-}
1449 m 1316 m	1470 w 1320 m	1370 b,m	ν_s(C=O)+δ(O–C=O)
1090 b,w 897 sp,s	1070 b,w 900 sp,s	1085 b,w 900 sp,s	ν(U=O)
725 w	770 m		ν(O–O)
600 b,w	650 vw		ν(U–O_2)

b=broad, m=medium, s=strong, sp=sharp, sh=shoulder, w=weak

The spectra of the first and second decomposition products of the barium complex may be discussed in a manner different from those of the calcium complex [29] because of the difference in the decomposition temperatures picked for the study. The intermediates obtained at the specified temperatures are for the decomposition of the original complex. According to the thermal decomposition mechanism, the product at 200°C is carbonate intermediate where as the one at 450°C is presumably due to the intermediates barium carbonate and barium diuranate. The broad bands at about 3500 cm^{-1} for the first and the second decomposition products obtained by heating the

Table 4 X-ray diffraction data of barium dioxodiaquaperoxyoxalatouranate(VI) and the products after heating it to 200 and 450°C, compared with uranium(VI) oxalate and barium oxalate

Ba^{2+} complex	Complex heated to 200°C	Complex heated to 450°C	$UO_2C_2O_4$	BaC_2O_4	$BaC_2O_4 \cdot H_2O$
				5.030_x	
26.60_1		8.781_4		4.64_2	
8.207_1		8.083_4		4.43_4	
5.819_x		6.72_5		4.300_8	5.520_5
		5.710_6	4.87_6	4.09_6	5.140_x
4.816_1		4.623_5	4.57_6	3.540_x	4.100_5
4.215_1		4.326_5	4.46_x	3.23_2	
3.376_5		4.171_x		2.908_6	
3.135_1		3.395_5		3.12_6	
2.937_1		3.283_6		3.80_4	
2.632_1		3.734_5		3.05_6	
2.228_1		2.514_5		3.58_2	
2.113_1	2.0261_6	2.293_4		2.963_4	
2.008_1		1.893_4		2.716_1	
1.969_1		1.936_4		2.563_4	
1.629_1	1.2895_x	1.638_4		2.536_2	
		5.308_5		2.514_2	
		1.812_5		2.490_2	
				2.462_1	
				2.404_1	
				2.353_1	
				2.329_4	
				2.314_4	
				2.275_1	
				2.227_2	

original complex to 200 and 450°C respectively and cooling to room temperature may be due to absorption of moisture from atmospheric air.

X-ray diffraction data

X-ray diffraction data of barium dioxodiaquaperoxyoxalatouranate(VI) and that of the product obtained after heating the original complex to 200°C and cooling are given in Table 4 along with those of uranium(VI) oxalate and barium oxalate for comparison.

The data in the table clearly show that the heated product obtained at 200°C is an individual compound and not a mixture of barium and uranyl oxalates. The decomposition product was subjected to the usual acid test for the presence of carbonate and the same was confirmed. The complex was also heated to 450°C and maintained at this temperature for half an hour and the product obtained in this manner was tested for the presence of carbonate by the usual acid test. The result of this test indicates the presence of carbonate in the product.

Mechanism:

From the thermal data it is possible to assign the following possible mechanism for the step-wise thermal decomposition of the complex:

$$\mathrm{Ba[UO_2(O_2)C_2O_4(H_2O)_2]\cdot H_2O} \xrightarrow{30-149.4\,^\circ\mathrm{C}} \mathrm{Ba[UO_2(O_2)C_2O_4]}$$

$$\xrightarrow{149.4-234\,^\circ\mathrm{C}} \mathrm{BaCO_3\cdot UO_4} \xrightarrow{234-505.3\,^\circ\mathrm{C}} \mathrm{BaCO_3+BaU_2O_7}$$

$$\xrightarrow{505.3-\sim 700\,^\circ\mathrm{C}} \mathrm{BaUO_4} \xrightarrow{\sim 700-867.6\,^\circ\mathrm{C}} \mathrm{BaO+UO_2}$$

Overall:

$$\mathrm{Ba[UO_2(O_2)C_2O_4(H_2O)_2]\cdot H_2O} \rightarrow \mathrm{BaO+UO_2+3H_2O+O_2+CO_2+CO}$$

Literature [30] shows that uranyl ion (which has a linear structure) has conventionally been assumed to be the centre of the complex, as it does not take part in the inner-sphere substitution reactions and remains unchanged. Besides, uranyl ion exhibits six coordinations and hence, it can be concluded from the results of the above investigation that the complex is having octahedral structure with composition $\mathrm{Ba[UO_2(O_2)C_2O_4(H_2O)_2]\cdot H_2O}$.

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