

SPONTANEOUS ISOTHERMAL DECOMPOSITION OF THE URANYL CARBONATE COMPLEX $(\text{NH}_4)_4[\text{UO}_2(\text{CO}_3)_3]$ AT ROOM TEMPERATURE. PART II. INFRARED SPECTROSCOPY AND X-RAY ANALYSIS

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ABSTRACT

Progressive decomposition of $(\text{NH}_4)_4[\text{UO}_2(\text{CO}_3)_3]$ was followed by means of IR spectroscopy and X-ray analysis. The well-crystalline material is gradually changed into an amorphous one. Hydroxyls and water are the new constituents of the examined solid. The intensity and frequency of some IR adsorption bands remain unchanged, although about 87% of ammonium and carbonate components are decomposed; some other bands gradually disappear. The positions of IR active uranyl vibrations are observably changed only during the third kinetic stage of the decomposition.

INTRODUCTION

As stated in Part I of this series [1], changes in the appearance of ammonium uranyl carbonate (AUC) are accompanied by deep chemical changes leading to the formation of hydroxo carbonate solid phases containing water. In the present communication these results are compared with the results of infrared (IR) and X-ray investigation. By means of IR spectroscopy the presence of expected entities (OH^- and H_2O) can be confirmed together with the type of their bonding within the solid phase. Also, possible changes of the original AUC components preserved in the course of decomposition can be followed. Special attention should be paid to the antisymmetric valence vibration of the uranyl ion $\nu_3(\text{UO}_2)$ as its characteristic frequency can vary within a very broad range [2,3] depending on the properties of the coordination sphere of this central ion.

The positions of uranium atoms can be followed easily by means of X-ray diffraction analysis owing to their large mass (compared to the other atoms in the complex). As the crystal as well as molecular structure of AUC is known [4–6], the initial sample was used as a standard for tracing any structural changes taking place during the decomposition.

EXPERIMENTAL

The material investigated and the conditions of its self decomposition were described in Part I of this series [1]. Samples for physico-chemical measurements were taken at the same time as the samples for chemical analysis.

IR spectra were measured by a Perkin-Elmer 225 instrument in the range of $4000-200\text{ cm}^{-1}$. CsI windows and Nujol mull was mostly used, in several cases KBr discs were also employed.

X-ray measurements were performed using a HZG-3 diffractograph (German Democratic Republic) with a Co K_{α} anode, or a Czechoslovak Mikrometa instrument with a Cu K_{α} anode. Powder samples were pressed into a shallow cavity of the measuring cell. As the relative intensities of individual diffraction bands might be influenced by accidental mutual orientation of individual crystals in a measuring cell, diffraction pattern of one filled cell was recorded occasionally during a period of approx. one year. Whereas all intensities generally decreased with time, their relative values fluctuated together with an occasional change in the band position. Accordingly, similar effects observed later in individual AUC samples during the decomposition, may not be caused only by accidental orientation of the crystals; they seem to be inherent to the material investigated. An overlap with random position effect cannot, of course, be excluded.

RESULTS

In Table 1 numerical data from the IR spectrometric investigation of various AUC samples are collected. Some of the observed bands were present already in the initial AUC sample, some of them emerged during the decomposition.

*Original bands**Uranyl*

Both its IR active vibrations (the antisymmetric $\nu_3(\text{UO}_2)$ and the deformation $\nu_2(\text{UO}_2)$) preserve their considerable intensity during the whole decomposition. Their frequencies are changed only slightly (the former moderately increases whereas the latter decreases by about the same value), mostly during the decomposition stage C [1]. With regard to the considerable extent of decomposition observed the changes are really minor.

Carbonates

The ligands are supposed to be bidentate coordinated to a uranium atom in the plane perpendicular to the $\text{O}_1\text{-U-O}_1$ axis: the interpretation of the

TABLE 1

Infra-red spectral data (in cm^{-1})^a

Sample	$\nu(\text{U}-\text{O}_{\text{lig}})$	$\nu_2(\text{UO}_2)$	Water libration modes	$\nu_3(\text{CO}_3)$	$\nu_5(\text{CO}_3)$	$\nu_6(\text{CO}_3)$	$\nu_3(\text{UO}_2)$
W-0 ^b	235m-s	273s	460w,b	691m-s,sp	718s,sp ^c	843m,sp	853vw,sp
W-0	235m	272s	-	691m,sp	719s,sp	843w-m,sp	852vw,sp
W-1	231m	270s	-	691m,sp	720s,sp	846m,sp	856w,sp
W-2	235m	272s	-	690m,sp	719s,sp	845w-m,sp	854vw,sp
W-3	237m-s	272s	530vw	690m,sp	719s,sp	843w-m,sp	853vw,sp
W-4	240m,b	272s	525vvw	691m,sp	720s,sp	845w,sp	854vvw
W-5	240sh	271s,sp	400-530w ^c	691m,sp	720s,sp	845w,sp	857vvw
W-6	-	270s,sp	400-530w-m	691w-m,sp	720m,sp	846vw	-
W-7	-	271s	380-530m-s	690m,sp	719m-s,sp	844vw,sp	-
W-8	260sh	268s	380-530m-s	690w-m,sp	710m,sp	-	892s ^f
W-9	-	265m-s	380-530m-s	680vvw,vb	722m	788w	893 ^f
W-10	-	260s	380-530m-s	680vw,vb	722m	-	897 ^f
W-11	-	260s	380-530m-s	680w,b	727m	-	900s,b
W-12	-	260m-s	380-530m-s	680w,vb	728w	-	901vs
W-13	-	259m-s	380-530m-s	-	-	-	905vs
W-14 ^h	-	258m-s	380-530m-s	-	-	-	907vs
W-15	-	260w-m	380-530m-s	-	-	-	908vs

TABLE 1 (continued)

Sample	$\nu_2(\text{CO}_3)$	$\nu_4(\text{CO}_3)$	$\nu_4(\text{NH}_4)$	$\nu_1(\text{CO}_3)$	$\nu_2(\text{NH}_4)$
W-0 ^b	1050m-s,sp	1060w,sp	1085w	[1340vs	1430s]
W-0	1051m-sp	1060w,sp	1087vw	1515vs,b	1575sh
W-1	1052m-sp	1061w,sp	1073w	1520vs	1575sh
W-2	1052m,sp	1061w,sp	1080w	1515vs	1575sh
W-3	1050m,sp	1060w,sp	1080w	1515vs,b	1575sh
W-4	1053m,sp	1060vw,sp	1082vw	1515vs,b	1575sh
W-5	1052m,sp	1061w,sp	1080w	1518vs	1575sh
W-6	1054m,sp	1062vw,sp	1080w	1515vs,b	1575sh
W-7	1051m,sp	1060w,sp	1085w	1515vs	1575sh
W-8	1051w,sp	-	1085w ^g	1515vs	-
W-9	-	1073w	-	1515vs,b	1575sh,vv
W-10	-	-	1085w	1513s,b	-
W-11	-	-	1085w	1513s,b	-
W-12	-	-	1082w	1515s	-
				1512s	-
				1520s]	-
W-13	-	-	-	1518s	1620w-m
				[1382vs,sp	1396vs,sp
				[1382vs,sp	1520s]
W-14 ^h	-	-	-	1518s	1618w,b
				[1382vs,sp	1395vs
				1520s]	-
W-15	-	-	-	1518s	1619w-m
				[1343m,sp	1374m,sp]
				1520s	1623w-m

Nujol absorption,
not measured in
other media

TABLE 1 (continued)

Sample	$\nu(\text{NH})$ [8]	$\nu(\text{NH})$ [8]	$\nu(\text{NH})$ [8]	$\nu(\text{OH})$	$\nu(\text{OH})$
W-0 ^b	1735w	1780w	[2850m,b	3190vs,b	3540w,sh
W-0	1735vww	1780w	3020s,b]	3190s	3550vw,vvb
W-1	1736vw	1780w-m		3190s,b	3550vww,vb
W-2	1735vw	1780w		3195s	3560vw,vb
W-3	1738vw	1780w-m		3190vs	3550w,vb
W-4	-	1780w	Nujol absorption,	3200s	3550w,vb
W-5	-	1780w	not measured in	3190vs,b	3550w-m,vvb
W-6	-	1780w	other media	3190s,b	3550w-m,vvb
W-7	-	1780w-m		3200vs,b	3470m,vb
W-8	-	1780vw,b		3200s,b	3440m-s,vb
W-9	-	-		3200s,b	3450m-s,vb
W-10	-	-		3200s,b	3440m-s,vb
W-11	1765w-m,vvb	-		3200s,b	3440m-s,vb
W-12	-	-		3210s	3460m-s,b
W-13	-	-		3220s	3460m-s,vvb
W-14 ^h	-	-		3210s	3460m-s,vvb
W-15	-	-		3220s	3460s,vb

^a For the headings, see text. Symbols: s, strong; m, medium; w, weak; sh, shoulder; v, very; b, broad; sp, sharp. Measured in Nujol mulls, the values in brackets in KBr discs (W-12 to W-14) or Florube mulls (W-15).

^b Data from literature [8], the commentary in the text does not apply to them.

^c Additional [5]: 760vw, 789vw, 829vw,sp are given.

^d An additional band at 2110w given [8].

^e An atypical, broad band (see Fig. 1); for its quantitative interpretation see text.

^f For samples W-7 to W-10 additional bands were recorded: 972vw, 970vw, 970vw, 975vww, respectively.

^g Additional bands were recorded: 1162vw, 1178vw for W-8; 1152w-m for W-9; 1153vw, 1168vw for W-10; 1155vw, 1168vw for W-11; 1165vw,vb for W-12; 1150 for W-13.

^h This sample was measured 123 days after sample W-13, i.e. 608 days from the beginning of weathering; without chemical analysis.

individual carbonate vibrations is taken from the literature [7,8]. The valence vibration frequency $\nu_1(\text{CO}_3)$ (about 1515 cm^{-1}) as well as the intensity of the respective band remain practically constant during all three decomposition stages. Similarly it applies for the intensity of the $\nu_4(\text{CO}_3)$ valence vibration. The frequency of this vibration, however, is considerably shifted and split, from 1340 cm^{-1} for sample W-0 to a doublet at 1382 and 1396 cm^{-1} for the last sample. (Unfortunately, only the spectra of the samples on the margins of the whole set were taken and therefore the time correlation of the changes remains to be established.) Anyhow, this appreciable intensity of carbonate vibrations is preserved regardless of the considerably lowered carbon content (up to a C/U ratio of about 0.4) [1]. The symmetric $\nu_2(\text{CO}_3)$ frequency of about 1050 cm^{-1} is also unchanged but it is observable only during stages A and B.

From the other carbonate vibrations the in-plane deformation vibrations $\nu_3(\text{CO}_3)$ and $\nu_5(\text{CO}_3)$ are observable at 690 and 720 cm^{-1} , respectively. Their intensity is lowered and their frequency slightly shifted in the course of decomposition. The last one, the out-of-plane $\nu_6(\text{CO}_3)$ vibration about 844 cm^{-1} preserves its energy whereas its intensity gradually drops (up to sample W-7 inclusively).

Ammonium groups

Three valence vibration bands $\nu(\text{NH})$ at 2850, 3020, and 3190 cm^{-1} were observed in the initial AUC sample [8]. Only the last one could be observed in all samples whereas the former two were measured only at the margins of the investigated set. The frequency of the last valence vibration band was practically constant in all samples, the slight shift towards higher energies being caused perhaps by a distortion due to a stepwise increase of a new broad adsorption about 3500 cm^{-1} (see below). The considerable intensity of the discussed band was also preserved during the whole decomposition and its relationship to the N/U ratio is apparently non-linear (within the range 4.0–0.52) [1]. Both lower valence vibrations were not present in the spectra of the final samples (starting with sample W-12).

The deformation vibration $\nu_4(\text{NH}_4)$ at 1430 cm^{-1} , present in the initial sample, was not observed in any of the final samples (measured in KBr discs). The $\nu_2(\text{NH}_4)$ vibration (at 1678 cm^{-1} at the beginning), supposed to be activated in IR spectra by strong hydrogen bonds [8], was observed in all samples up to sample W-7 (its parameters are N/U = 1.46, C/U = 1.03). For the following sample W-8 (N/U = 0.89, C/U = 0.63) the band disappeared and, instead, a new band at 1620 cm^{-1} was observed with a slightly lowered intensity.

New vibration bands

They were observed in two regions; about 3500 cm^{-1} (valence vibrations of the hydroxyl group $\nu(\text{OH})$) and in the range $600\text{--}350\text{ cm}^{-1}$ (most probably libration modes of water molecules) [9].

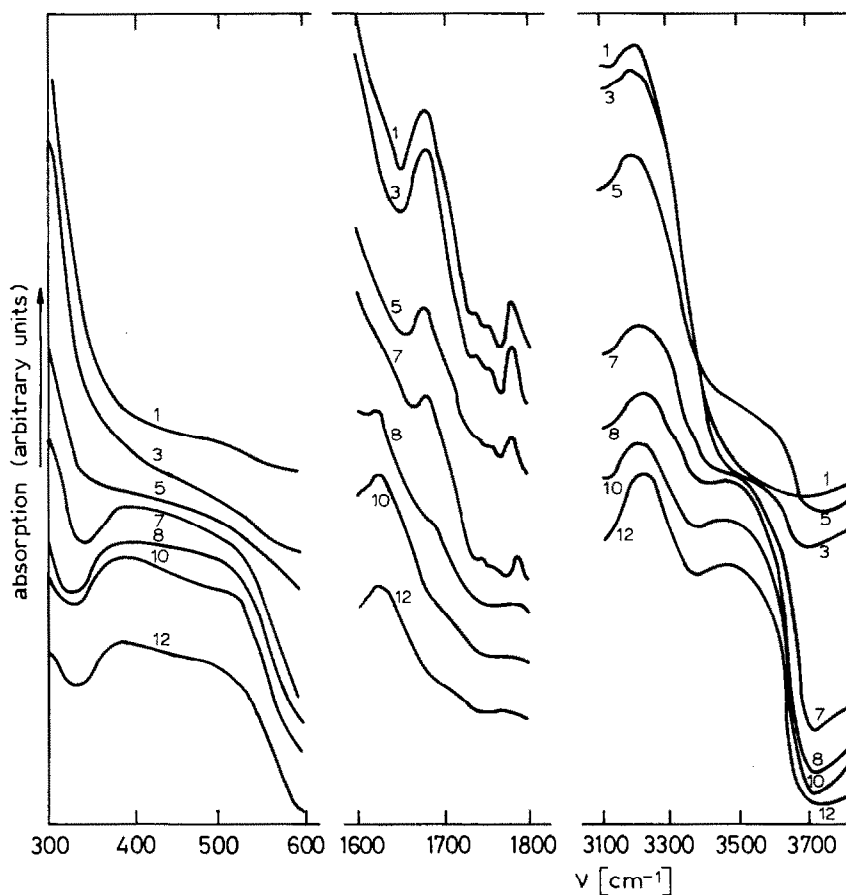


Fig. 1. IR spectra of the selected samples.

Both bands around 3500 cm^{-1} (Table 1) are strongly coupled and their resulting shape is clearly non-ideal. At the beginning of the decomposition a very weak to weak band near 3550 cm^{-1} was detectable whose intensity gradually increased (see Fig. 1). Later (approximately from sample W-7) a new band appeared about $3455 \pm 15\text{ cm}^{-1}$ that is more marked; the original band forms practically a shoulder.

Both these vibration bands should be assigned to hydroxyl vibrations $\nu(\text{OH}^-)$ differentiated by their chemical (bonding) state. The higher vibration frequency $\nu(\text{OH}^-)_{\text{H}_2\text{O}}$ could be assigned to water hydroxyls (water is present in small amounts as moisture at the beginning and later as a decomposition product), the lower band $\nu(\text{OH}^-)_{\text{OH}}$ to hydroxyls formed by decomposition (in observable quantities during the second decomposition stage).

In principle the IR data in the region of 3500 cm^{-1} confirm the results of the mass-balance calculations based on chemical analysis [1]. Already during

the first decomposition stage small but increasing quantities of hydroxyls were formed up to sample W-11. From chemical analysis alone (OH^-/U or $\text{H}_2\text{O}/\text{U}$ values) the maximum OH^- content was found in samples W-9 or W-10; this discrepancy can be explained by lack of experimental precision.

As to the new band in the low energy region, small indications around 530 cm^{-1} were observed starting with sample W-3. An evident curvature, observable around 400 cm^{-1} in sample W-5, becomes impressive beginning

TABLE 2

Numerical characteristics of the X-ray patterns ^a

AUC-0 [5]		W-0		W-1		W-2		W-3		W-4		W-5	
<i>d</i>	<i>I_r</i>	<i>d</i>	<i>I_r</i>	<i>d</i>	<i>I_r</i>	<i>d</i>	<i>I_r</i>	<i>d</i>	<i>I_r</i>	<i>d</i>	<i>I_r</i>	<i>d</i>	<i>I_r</i>
705	50	701	3	698	20	699	24	706	35	695	9	695	9
636b	90	633	100	633	100	631	100	635	100	635	100	628	100
597	80	595	15	592	73	593	40	600	25	601	5	592	16
530	80	529	13	528	28	528	56	532	24	577	3	540	2
								515	6	526	12	524	12
								505	4			489	2
488	10	489	3					494	4	494	2	466	3
468	20	466	7	467	15	466	7	483	4	466	8	453	2
439	50	437	16	438	26	437	15	442	8	436	11	437	3
432	50	429	22	430	9	431	17	432	12	432	14	429	6
386	80	385	28	385	35	387	29	87	12	384	3	385	4
376	50	375	17	375	33	376	26	377	20	375	13	374	4
351	50	350	12	351	26	350	29	352	20	351	6	350	7
344	15	343	4	344	6	344	5	344	6	343	3	342	3
331	50	331	11	331	20	330	14	330	12			330	3
328	50	327	4	323	20	328	15	327	sh	327	13	327	3
317 ^b	20	317	10	317	12	317	16	318	16	316	22	316	24
314	15	314	3	314	6								
312	20	311	11	310	16	312	14	312	10			311	2
298.8	20	297.8	6	298.4	14	299.7	10	301	4	298.2	5	297.8	3
293.0	15	292.3	4	293.2	5					293.2	3	292.3	2
289.0	15			288.6	sh					281.7	7	286.5	1
287.4	20	286.5	13	287.5	28	286.9	11	287.7	8				
280.8	15	279.9	6	280.6	9	280.2	4	281.4	6	279.8	7	279.9	3
273.9	50	273.5	20	274.0	42	273.9	25	275.0	20	274.4	21	273.5	9
267.4	15	266.6	6	266.9	5	267.5	4			265.1	3	266.7	1
264.4	10	264.2	2					263.7	4				
263.2	15	262.6	6	262.9	4	262.9	4						
260.8	15	260.1	4	261.0	2								
254.8	15					254.0	3						
248.3	20	248.0	4	248.4	11	248.0	4			247.2	4	248.0	2
245.0	50	244.3	15	244.8	23	244.8	26	245.4	20	243.9	18	244.4	3
235.2	20			234.9	6	234.6	18	234.3	4	234.5	3	235.1	1

^a Symbols: interplane distance *d* (in pm); relative intensity *I_r* (in % of the most intensive band in the given record); s, sharp; b, broad; v, very; sh, shoulder.

with sample W-7 (Fig. 1). The shape of this band is atypical (a long slowly-increasing plateau from about 530 to 380 cm^{-1}) which reveals its complexity. It can be assigned to the libration of water molecules [9] banded by a sequence of energies, apparently in voids of the solid left by the escaped volatile components (more probably the ammonium groups, which are similar to water in their ability to form hydrogen bridges).

The numerical data from X-ray analysis, complementing the IR spectro-

W-6		W-7		W-8		W-9		W-10		W-11		W-12		W-13	
<i>d</i>	<i>I_r</i>	<i>d</i>	<i>I_r</i>	<i>d</i>	<i>I_r</i>	<i>d</i>	<i>I_r</i>	<i>d</i>	<i>I_r</i>	<i>d</i>	<i>I_r</i>	<i>d</i>	<i>I_r</i>	<i>d</i>	<i>I_r</i>
692	11	704	10	712	100	712b	100	699b	100	703	100	691	100	680b	100
626	100	626	100	675	sh	665	sh					641	sh		
590	9	589	10	632s	37										
559	4														
524	6														
		460	4												
464	8	448	4												
		427	5	396	23	389	19								
437	4	387	3	382	17	382	sh								
429	6	370	3							370		370			
383	5	348	4			357		357							
374	7	337	3	340											
349	5	323	5												
343	3	315	18												
330	2	305	4	305											
327	9	298.5	4												
315	3	290.4	3												
		284.3	3												
310	2	273.5	4												
296.9	2	261.3	3												
292.0	4														
286.4	9														
279.6	7														
273.5	12														
265.4	2														
264.1	2														
261.6	2														
253.7	1														
249.9	1														
247.3	3														
244.1	8														
237.3	2														

^b Not cited here: 318 pm, $I_r = 15$.

^c Very broad band within the given limits.

scopic measurements are collected in Table 2. Structural changes of the investigated solid phases during the spontaneous decomposition as well as structural identity of our initial product AUC/W-0 with that published in the literature [5] are documented.

Apart from a general decrease in intensity, the basic diffraction pattern is preserved up to sample W-7. Only certain particular changes in intensity and sometimes in the position or occurrence of individual bands were recorded (e.g. samples W-3 to W-7 in the region of 530–430 pm; probably also certain shift of the most intensive bands from 635 to 628 pm in samples W-4 and W-5, was no artefact being confirmed by a control measurement on another apparatus with Cu K_{α} anode). A principal structural change takes place only starting with sample W-8. This sample contains a new, different crystal structure together with a minority of the original crystalline substance (characterized by its maximum, a distinct and sharp band at 632 pm).

According to the structural measurements it can be stated that the solid phase AUC/W-8 and all the following samples contain (besides a considerable amorphous fraction) a crystalline material different from all preceding phases belonging to decomposition period B: sample W-8 thus forms the boundary between the last two stages. This is in agreement with the IR data. According to the chemical analysis however, sample W-8 belongs still to the second period. In this sense the agreement of the two measurements is only approximate. The boundary between stages A and B cannot be found from structural measurements only as no principal structural change takes place there.

DISCUSSION

The assignment of the basic vibrational bands is clearcut for the initial AUC sample (see ref. 8 and the papers cited therein). To monitor the AUC decomposition by means of IR spectroscopy, a comparison with the spectra of the original substance is appropriate (any changes of the original bands as well as parameters of the new bands). Uranyl is the only unchanging part of the investigated phases whereas its surroundings are subjected to alterations. It is generally assumed that its antisymmetric frequency, $\nu_3(\text{UO}_2)$, reflects the resulting bonding state of the whole complex and may serve as an appropriate indicator of proceeding changes.

A calculation [3] for mononuclear complexes has shown that the most remarkable changes of the valence vibration $\nu_3(\text{UO}_2)$ take place under the influence of alterations in the force field of the surrounding ligands (i.e. of their electron-donating power, EDP), alterations in the ligands mass or in their U–L separation being much less significant. In the former case the $\nu_3(\text{UO}_2)$ frequency may be shifted by as much as 15 cm^{-1} (for coordination numbers 5 or 6) whereas in the latter case only by less than 2 cm^{-1} (for any coordination number).

To supplement empirically the above conclusions the influence of a crystal structure or of outer sphere cations on the $\nu_3(\text{UO}_2)$ frequency can be cited. In the IR spectra of the $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ complexes with the following cations NH_4^+ , K^+ , Na^+ , Rb^+ and Cs^+ , the $\nu_3(\text{UO}_2)$ frequency equals [3] 889, 880, 876, 875 and 863 cm^{-1} , respectively, so that the influence of the cations is undeniable. The gross difference of 26 cm^{-1} between the highest and lowest values is distinctly larger than the calculated maximum for the influence of ligand field in a mononuclear complex. The role of the crystal structure of the substances under study cannot be determined unambiguously because the structure of the last two compounds is not known (the analogous sodium compound is structurally different [10]). However, as the ammonium and potassium analogues are isomorphous [11] and their frequencies nevertheless differ by 9 cm^{-1} , this difference should be attributed merely to the influence of the cations: simultaneously the influence of crystal structure should be more or less negligible.

During the AUC decomposition no substitution of cations takes place, merely the original cation, NH_4^+ , is being lost from the solid phase. The unchanged $\nu_3(\text{UO}_2)$ values during stages A and B indicate that the resulting uranyl bonding state is, surprisingly, not influenced by the decomposition of more than 3/4 of the ammonium groups originally present ($n_{\text{w.8}} = 0.89$, $n_{\text{w.9}} = 0.67$ for the end of stage B or the beginning of stage C, respectively).

On the other hand, the $\nu_3(\text{UO}_2)$ value grows considerably (by more than 13 cm^{-1}) during stage C, where both ammonium and carbonate decomposition is very meagre (n from 0.65 to 0.52, c from 0.42 to 0.40, the latter difference being within the experimental error). As the concentrations of both new components, OH^- and H_2O , are also nearly constant during the last stage, a more complex reaction mechanism can be expected which cannot be reconstructed from the chemical composition of the investigated phases only.

The $\nu_3(\text{UO}_2)$ frequency can be observed [2,3] within the considerable range of 1000 to 700 cm^{-1} . This empirical fact indicates that the force constant of the $\text{U}-\text{O}_I$ bond is able to vary considerably within the class of uranyl compounds under consideration. An explanation of this fact was looked for in the interaction of primary ($\text{U}-\text{O}_I$) and secondary ($\text{U}-\text{O}_{II}$ or, more generally, $\text{U}-\text{L}$) bonds in which a strengthening of the former results in a weakening of the latter (and vice versa). Semiquantitative calculations, according to which primary uranyl bonds are influenced by EDP of ligands bonded to the equator of the uranium atom, seem to confirm this explanation [12,13]. In the usual interpretation [14,15] a ligand brings a certain electrostatic charge to the U atom that is proportional to the EDP of the ligands, thus weakening the $\text{U}-\text{O}_I$ bond because of repulsion from O_I oxygens. The $\nu_3(\text{UO}_2)$ values are also dependent on the uranyl coordination number.

Any experimental verification of this hypothesis is difficult as it is

practically impossible to find a series of uranyl compounds differing only by EDP of their ligands. Precipitated (hydrolytic) sodium [16] or ammonium [17] uranates may serve as a realistic approximation to this requirement. Each of the two types of uranyl compounds may differ above all by molar ratios of their cations which modify the electron-donor properties of the oxonium oxygen, i.e. the ligand to which they are bound.

A linear shift of the $\nu_3(\text{UO}_2)$ values from 960 to 860 cm^{-1} was found for the sodium compounds (Na/U varying from 0.0 to 1.0) whereas for ammonium uranates (NH_4/U from 0.0 to 0.7) the shift was non-linear from 960 to 900 cm^{-1} . The $\nu_3(\text{UO}_2)$ vs. Na/U linear relationship may be extrapolated up to the values of $\text{Na}/\text{U} = 2$ and 4, the respective compounds being $\alpha\text{-Na}_2\text{UO}_4$ and Na_4UO_5 . (In $\alpha\text{-Na}_2\text{UO}_4$ the $[\text{UO}_6]$ octahedra are linked by sharing edges into linear chains [18–20] whereas in $\beta\text{-Na}_2\text{UO}_4$ they form a plane by sharing vertices. The structure of Na_4UO_5 is again linear [21], similar octahedra being linked into chains by primary O_1 oxygens). The above-mentioned changes of the ν_3 frequency were interpreted as results of EDP enhancement of the bridge (oxonium) oxygen [17] >ONa , proportional to the sodium content. Anyhow they illustrate the significance of molecular structure for the spectral behaviour of the uranyl ion, in contrast to crystal structure. Four different crystal structures can be found within the above series of sodium uranates, with no observable effect on the linear relationship mentioned. As has been shown above, the $\nu_3(\text{UO}_2)$ values may vary really considerably in polymeric molecular structures.

According to the X-ray diffraction measurements, AUC weathering is accompanied by build-up of an amorphous fraction. The new crystalline component formed during stage C was hardly observable (see Table 2). As uranium atoms dominate in X-ray analysis (because of their large mass), their mutual separation must change in an irregular way during the decomposition, resulting in an increase of the amorphous component. In principle, partially modified molecular as well as crystal structures may be the case here.

A different situation can be expected after preponderant decomposition of the unstable components, when new molecular (and possibly also crystal) structures may be formed within which the role of newly-arisen components can dominate. Such a situation might take place notably during stage C where the decrease of chemical components is less important than the rearrangement of the respective molecular structure towards the final product, hydroxo carbonates or hydroxidic phases of the $\text{UO}_2(\text{OH})_2 \cdot x\text{H}_2\text{O}$ type [1]. These can no longer be mononuclear complexes as the supply of cationic coordination sites is at last partially saturated by the formation of double or triple hydroxyl bridges, thus giving rise to polynuclear complexes. That is the reason why the values of their $\nu_3(\text{UO}_2)$ frequency exceed the theoretical limits for mononuclear complexes. In principle, the investigated solids should consist of coordination-deficient mononuclear hydroxo carbonates

TABLE 3

Intensities of the selected frequencies ^a

Sample	$I[\nu(\text{NH})]_{\text{U}}$	$\frac{I[\nu(\text{NH})]_{\text{U}}}{(\text{N/U})_{\text{s}}}$	$I[\nu_1(\text{CO}_3)]_{\text{U}}$	$\frac{I[\nu_1(\text{CO}_3)]_{\text{U}}}{(\text{C/U})_{\text{s}}}$
W-0	1.045	0.261	1.210	0.401
W-1	1.098	0.294	1.277	0.445
W-2	1.032	0.291	1.212	0.446
W-3	1.096	0.337	1.157	0.457
W-4	1.007	0.338	1.156	0.498
W-5	1.131	0.481	1.452	0.839
W-6	0.967	0.531	1.325	0.989
W-7	1.048	0.718	1.240	1.204
W-8	1.069	1.201	1.252	1.987
W-9	1.098	1.639	1.221	2.907
W-10	1.131	1.714	1.243	3.032
W-11	1.013	1.634	1.248	3.044
W-12	1.049	1.748	1.138	2.845
W-13	0.855	1.538	0.913	2.227
W-14	0.989	—	0.947	—
W-15	1.011	1.944	0.864	2.107

^a Because of various degree of decomposition of the individual samples, the height of the $\nu_3(\text{UO}_2)$ peak was taken as an internal standard, i.e. $I[\nu(\text{NH})]_{\text{U}} = I[\nu(\text{NH})]/I[\nu_3(\text{UO}_2)]$, etc.

(derived from AUC) during decomposition stages A and B, and of polynuclear hydroxo carbonate phases during stage C.

As to the decomposition components, the behaviour of the $\nu(\text{NH})$ and $\nu_1(\text{CO}_3)$ vibration bands (at 3190 and ca. 1520 cm^{-1} , respectively) is remarkable as their intensities remain practically constant during the whole recorded decomposition (i.e. n decreased from 4.0 to ~ 0.6 , c from 3.0 to ~ 0.4), see Table 3. Any consistent explanation seems to be rather difficult. From a molecular point of view it is evident that the vibration intensities under consideration cannot be linearly related to the number of corresponding N–H or C–O bonds in the complex. It looks as if these frequencies belong to a certain non-changing configuration (probably containing uranyl ions) and not only to the decomposing entities.

The other ammonium and carbonate frequencies gradually weaken and finally disappear in the course of decomposition (Table 1). The $\nu_2(\text{NH}_4)$ frequency at 1678 cm^{-1} , activated by strong hydrogen bonds (see the discussion above) is observable up to sample W-7 (Fig. 1). A similar band around 1620 cm^{-1} appears in the following samples, assigned to the water deformation vibration $\delta(\text{H–O–H})$. This should mean that the initial system of strong hydrogen bonds is preserved approximately till the end of the second decomposition stage and that the gradual increase in water content found its expression only after removing these strong bridges (the consider-

TABLE 4

Water libration bands

Sample	Area of the water libration bands ^a	H ₂ O/U from Table 2 of Part I [1]	Area of H ₂ O libration band/(H ₂ O/U) ^b	H ₂ O libration, expressed relatively in % ^c
W-5	20.8	0.59	35.3	39.4
W-6	39.1	0.62	63.1	70.4
W-7	55.7	0.64	87.0	97.1
W-8	68.3	0.71	96.2	107.4
W-9	80.1	0.835	95.9	107.0
W-10	64.5	0.81	79.6	88.8
W-11	64.5	0.72	89.6	100.0
W-12	66.2	0.74	89.5	99.9
W-13	60.9	0.68	89.6	100.0
W-15	76.5	0.64	119.5	133.4

^a Area of the $\nu_3(\text{UO}_2)$ band taken as an internal standard; the other areas given in percent of this standard.

^b A quotient of the two preceding columns; the average for samples W-7 to W-13 is equal to 89.6 ± 5.2 (i.e. $\pm 5.8\%$).

^c The average of the preceding column related to the average value 89.6, see footnote b.

able and comparable H₂O/U values in samples W-5 and W-6 did not result [1] in any appearance of the $\delta(\text{H}-\text{O}-\text{H})$ band in the corresponding spectra).

As to the intensities of $\nu(\text{OH})$ frequency around 3500 cm^{-1} (either from hydroxyls or from water molecules), their exact evaluation is impossible because of the band overlap in the second half of the decomposition (Fig. 1 and Table 1). In principle however, they increase with decomposition which corresponds to the increasing content of the respective components. Their behaviour is thus different from that of the $\nu(\text{NH})$ frequencies discussed above.

The unusually flat band at $530\text{--}380 \text{ cm}^{-1}$ (Fig. 1 and Table 1) was assigned to molecular water libration modes [9]. To verify this assignment the peak area was compared with the water content as determined by chemical analysis. The results in Table 4 show that as soon as the band is fully developed including the low-energy side (valid for sample W-7 and the following ones), its area is really directly proportional to the calculated water content [1], with a reasonable standard deviation of $\pm 5.8\%$. This result can be thus taken as an independent IR spectrometric determination of water. The less decomposed samples with underdeveloped (W-5, W-6) or missing (below W-5) low-energy edge of the discussed band do not fit with the above linear relationship (Table 4). The type of bonding to the crystal lattice of the generated molecular water is accordingly not uniform in all samples and, as follows from the flat shape of the band, the water in one sample could be bonded by several different values of energies.

SUMMARY

This communication completes the results of chemical analysis [1]. IR spectroscopic data confirm that the formation of hydroxyl groups and of water molecules takes place during the self decomposition of AUC (as was supposed [1]). This follows from the observed characteristic frequencies and sometimes also from the areas of some absorption bands (water libration). The correlation with the results of chemical analysis is generally good. In other cases [e.g. $\nu(\text{NH})$ and $\nu_1(\text{CO}_3)$] the vibration intensities remain unexpectedly constant in the course of the whole decomposition although 85–90% of the initially present ammonium or carbonate ions were decomposed. At the same time other frequencies fade out with the progressing decomposition. No consistent explanation of this unexpected effect could be found except for the general conclusion that the intensities of the above valence vibration bands are not proportional to the number of corresponding bonds in the investigated solids.

Irregular changes in the position of uranium atoms, induced by the decomposition of unstable AUC components, are detected as a growth of the amorphous portion of the solid phase.

The resulting changes in molecular structure should be reflected in changes of the vibration frequencies of uranyl as a central ion. Its anti-symmetric frequency, constant during the first two decomposition stages (up to $n = 0.69$, $c = 0.63$) seems to indicate a qualitative (and in principle, also quantitative) rigidity of its inner coordination sphere, though the carbonate ligands are gradually decomposed and can be substituted (to a certain extent) by hydroxyls having different coordination properties including EDP. In other words, despite the considerable decrease in content of both unstable components, the investigated solids remain modified carbonate phases during the first decomposition stage with coordination-deficit complexes and the uranyl coordination number gradually decreasing below six. During the second stage this coordination number remains perhaps constant and close to six so far as the average coordination number of hydroxyls is close to three (see Part I, Table 8) [1].

The last decomposition stage differs from the former two, above all, by a shift of the uranyl anti-symmetric frequency. A polymeric molecular structure can be proposed, i.e. not carbonate complexes modified by hydroxyls but, in principle, hydroxo complexes with a carbonate component in this case.

The final—at least metastable—product of the AUC decomposition is the hydroxo carbonate of the approximate formula $(\text{NH}_4)_{0.52}[\text{UO}_2(\text{CO}_3)_{0.41}(\text{OH})_{1.73}](\text{H}_2\text{O})_{0.61}$. Its uranyl coordination number can be formally equal to six (as far as the mean coordination number of hydroxyls is three, then it holds true $(2 \times 0.41) + (3 \times 1.73) = 6.01$) or lower (e.g. $(2 \times 0.41) + (2 \times 1.73) = 4.28$). Because of their unusual character, the IR spectra provide no authoritative clue for solving this question.

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