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SPONTANEOUS ISOTHERMAL DECOMPOSITION OF THE URANYL CARBONATE COMPLEX $(NH_4)_4[UO_2(CO_3)_3]$ AT ROOM TEMPERATURE. PART III. MECHANISM OF THE DECOMPOSITION. STABILITY OF THE URANYL MOLECULAR ORBITALS

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ABSTRACT

A mechanism for the spontaneous decomposition of ammonium uranyl carbonate starting with the dissociation of ammonium groups and continuing by further reactions is proposed and discussed. Two simultaneous reaction paths, which differ in their proportion of participation in the overall result, are considered for the first two reaction stages, and neutralization of hydrogen and hydroxyl ions takes place during the third stage. The results agree with the mass-balance calculations.

The IR active frequencies are not shifted observably until the third stage where changes of chemical composition are only minor. New experimental material for discussion of some basic problems of uranyl bonding is supplied.

INTRODUCTION

The presence of ammonium groups in ammonium uranyl carbonate (AUC) can be taken as the principal source of its instability at room temperature. The instability of ammonium compounds as compared with sodium or potassium analogues can be well illustrated experimentally. For instance, sodium and potassium AUC analogues decompose at temperatures of 350 and 500 °C, respectively [1]; Na_2CO_3 and K_2CO_3 are also more stable than $(NH_4)_2CO_3$, etc. Ammonium groups are supposed to dissociate at room temperature in the solid phase, yielding gaseous ammonia that escapes irreversibly in an open system: $(NH_4^+)_s \rightarrow (NH_3)_g + (H^+)_s$. Hydrogen cations have to remain within the solid phase to preserve its electroneutrality. Quite analogous proton transfer leading to the evolution of gaseous ammonia at the beginning of thermal decomposition was reported for some other ammonium and tetraalkylammonium compounds [2].

The hydrogen ions, whose amount is determined first of all by the physical conditions (temperature, force fields within the solid phase, etc.),

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may take part in a variety of chemical reactions—first of all with coordinated carbonates and, in subsequent steps, also with various intermediates and reaction products such as HCO_3^-, OH^-, H_2O, and NH_3 (the last one being involved in the equilibrium $NH_4^+ \rightleftharpoons NH_3 + H^+$). In carbonate systems the hydrogen ion moves very fast [3,4] with respect to the reaction $HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$. At the same time very firm uranyl carbonate complexes are known (UO_2^{2+}-CO_3^{2-}) whereas no data about hydrogen carbonate complexes have yet been published [1,5]. As the hydrogen ion remains within the solid phase after the release of an ammonia molecule, the following step of the decomposition reaction is presumed, explaining at the same time the formation of hydroxyl ions

$$(H^+)_s + (CO_3^{2-})_s = (HCO_3^-)_s \Rightarrow (CO_2)_g + (OH^-)_s \qquad (1)$$

According to eqn. (1), the composition of the gaseous stream should be equal to $(N/C)_g = (NH_3)_9/(CO_2)_g = 1.0$. As the $(HCO_3^-)_s$ decomposition is certainly not instantaneous, another reaction is supposed to take place simultaneously

$$(H^+)_s + (HCO_3^-)_s = 2(H^+)_s + (CO_3^{2-})_s = (H_2CO_3)_s \Rightarrow H_2O + (CO_2)_g \qquad (2)$$

The origin of water is explained in this way together with the composition of the volatile stream $(N/C)_g = 2.0$. By analogy, the third reaction

$$(H^+)_s + (OH^-)_s = H_2O \qquad (3)$$

could be significant in later stages of the AUC decomposition in which the $(OH/U)_s$ ratio is higher. Nevertheless the sums of eqns. (1) + (2) and (1) + (3) are identical

$$2(H^+)_s + (CO_3^{2-})_s = (H_2CO_3)_s \Rightarrow H_2O + (CO_2)_g$$

therefore, hereinafter only eqns. (1) and (2) will be formally taken into account.

This simple scheme is, above all, able to explain the origin of hydroxyl ions and of water during the AUC decomposition; some quantitative correlations based on it, may also be attempted.

CALCULATIONS OF THE DECOMPOSITION

The key entity of the presumed mechanism is $(HCO_3^-)_s$, which either decays into a hydroxyl ion according to eqn. (1) or reacts with a hydrogen ion according to eqn. (2), yielding a molecule of water. Knowing the $(OH^-/U)_s$ and (H_2O/U) values accurately, the relative reaction rates p_1 and p_2 for both reaction paths could be established ($p_1 + p_2 = 1$). However, as the accuracy of the above experimental data is insufficient for the calculation, the average composition of the volatile fraction $\phi(N/C)_g$ will be used instead. (Especially for stage A the variance of H_2O/U values is large; for all stages partial drying may also take place—see below.) For stages A and B these values are equal to 1.5 and 1.3, respectively (see Table 5 of Part I [6]).

After re-writing the above equations as follows

$$\left[(NH_4^+)_s + (CO_3^{2-})_s = (OH^-)_s + (CO_2)_g + (NH_3)_g\right] \cdot p_1 \tag{4}$$

$$\left[2(NH_4^+)_s + (CO_3^{2-})_s = H_2O + (CO_2)_g + 2(NH_3)_g\right] \cdot p_2 \tag{5}$$

their sum is equal to

$$\begin{aligned}&(p_1 + 2p_2)(NH_4^+)_s + (CO_3^{2-})_s \\ &\quad = p_1(OH^-)_s + p_2(H_2O) + (CO_2)_g + (p_1 + 2p_2)(NH_3)_g\end{aligned} \tag{6}$$

and the following relationships based on eqn. (6) are valid

$$(N/C)_g = p_1 + 2p_2$$

$$(OH^-)_s = p_1(CO_2)_g = [p_1/(p_1 + 2p_2)](NH_3)_g$$

$$H_2O = p_2(CO_2)_g = [p_2/(p_1 + 2p_2)](NH_3)_g$$

The amounts of hydroxyl ions and water produced can thus be independently calculated from both volatile components. Practically, the analytical data per mole of uranium for the neighbouring solid samples i and $(i+1)$ can provide the amounts of the volatilized components: $(\Delta c)_g = (c_i - c_{i+1})_s$ or $(\Delta n)_g = (n_i - n_{i+1})_s$, where $c = (C/U)_s$ and $n = (N/U)_s$. Total amounts of hydroxyl ions or water, formed up to a selected decomposition point, can be obtained by summation of the appropriate partial differences.

The values of $(\Delta c)_g$ and $(\Delta n)_g$ are given in Table 5 of Part I [6]. The values of $(OH/U)_s$ and (H_2O/U) were calculated for $p_1/p_2 = 0.5/0.5$ in stage A and for $p_1/p_2 = 0.7/0.3$ (and alternatively also for $p_1/p_2 = 0.8/0.2$ which is at the margin of experimental error) in stage B. With respect to the decrease of the n values and persistence of the c ones, during stage C only the neutralization of hydroxyl ions by hydrogen ions was assumed (eqn. 3) causing an increase of H_2O/U and a decrease of $(OH/U)_s$ values; $NH_4^+ \Rightarrow NH_3 + H^+$ and $H^+ + OH^-/U \Rightarrow H_2O/U$.

The results of the above calculations are summarized in Table 1 from which the following conclusions may be drawn:

(1) The values of the same parameter $(OH/U)_s$ or (H_2O/U), independently calculated from $(\Delta c)_g$ and $(\Delta n)_g$ are in acceptable agreement (see Part A of Table 1).

(2) For stage B and $p_1/p_2 = 0.7/0.3$, the $(OH/U)_s$ values calculated from $(\Delta c)_g$ are always higher than those calculated from $(\Delta n)_g$, the sum of the differences equalling 0.322. When $p_1/p_2 = 0.8/0.2$ is supposed, then the $(OH/U)_s$ values from both sources are mutually interchanging with the sum of their differences equal to -0.019. It indicates higher confidence of the latter alternative.

TABLE 1

Comparison of various results for parameters $(OH/U)_s$ and H_2O/U

Part A, Partial results based on the supposed decomposition mechanism

Sample	$(OH/U)_s$ calculated from:		H_2O/U calculated from:		Remarks
	$(\Delta n)_g$	$(\Delta c)_g$	$(\Delta n)_g$	$(\Delta c)_g$	
W-1	0.087	0.065	Numerically identical with $(OH/U)_s$ data		$p_1/p_2 = 0.5/0.5$
W-2	0.150	0.140			
W-3	0.250	0.235			
W-4	0.340	0.340			
$W_{A/B}$	0.407	0.470			
W-5	0.639 (0.694)	0.701 (0.734)	0.506 (0.479)	0.569 (0.536)	$p_1/p_2 = 0.7/0.3$
W-6	0.924 (1.047)	0.974 (1.046)	0.628 (0.567)	0.686 (0.614)	(values in parentheses
W-7	1.118 (1.287)	1.191 (1.294)	0.711 (0.627)	0.779 (0.676)	valid for $p_1/p_2 = 0.8/0.2$)
W-8	1.425 (1.667)	1.471 (1.614)	0.843 (0.722)	0.899 (0.756)	
$W_{B/C}$	1.527 (1.794)	1.618 (1.782)	0.887 (0.754)	0.962 (0.798)	
W-9	1.50 (1.76)	1.59 (1.75)	0.92 (0.78)	0.99 (0.83)	Only neutralization
W-10	1.49 (1.75)	1.58 (1.74)	0.93 (0.79)	1.00 (0.84)	$(NH_4^+ = NH_3 + H^+;\ H^+ + OH^- = H_2O)$
W-11	1.45 (1.71)	1.54 (1.70)	0.97 (0.83)	1.04 (0.88)	based on decrease of the value
W-12	1.43 (1.69)	1.52 (1.68)	0.98 (0.85)	1.05 (0.90)	of *n* (Table 1 of Part I) [6]
W-13	1.38 (1.64)	1.47 (1.63)	1.03 (0.90)	1.10 (0.95)	was supposed
W-15	1.35 (1.61)	1.44 (1.60)	1.06 (0.93)	1.13 (0.98)	

Part B, Averaged results of both calculations (from $(\Delta n)_g$ as well as $(\Delta c)_g$, see Part A)

Sample	Results calculated supposing the decomposition mechanism		Results of the mass-balance calculations (Table 2 of Part I)		Differences given as balance – calculated values	
	$(OH/U)_s$	H_2O/U	$(OH/U)_s$	H_2O/U	Δ_{OH}	Δ_{H_2O}
W-1	0.08	0.08	0.0	0.35	−0.08	0.27
W-2	0.15	0.15	0.11	0.22	−0.04	0.07
W-3	0.24	0.24	0.19	0.20	−0.05	−0.04
W-4	0.34	0.34	0.34	0.06	0.0	−0.08
W-5	0.67 (0.71) [a]	0.54 (0.51) [a]	0.89	0.59	0.22 (0.18) [b]	0.05 (0.08) [c]
W-6	0.95 (1.05)	0.66 (0.59)	1.14	0.62	0.19 (0.09)	−0.04 (0.03)
W-7	1.15 (1.29)	0.74 (0.65)	1.40	0.64	0.25 (0.11)	−0.10 (−0.01)
W-8	1.45 (1.63)	0.87 (0.74)	1.63	0.71	0.18 (0.00)	−0.16 (−0.03)
W-9	1.54 (1.76) [a]	0.96 (0.81) [a]	1.83	0.84	0.29 (0.07)	−0.12 (0.03)
W-10	1.53 (1.75)	0.97 (0.82)	1.84	0.81	0.31 (0.09)	−0.16 (−0.01)
W-11	1.49 (1.74)	1.01 (0.86)	1.80	0.72	0.31 (0.06)	−0.29 (−0.14)
W-12	1.47 (1.69)	1.02 (0.88)	1.80	0.74	0.33 (0.11)	−0.28 (−0.14)
W-13	1.42 (1.64)	1.07 (0.93)	1.73	0.67	0.31 (0.09)	−0.40 (−0.26)
W-15	1.39 (1.61)	1.10 (0.96)	1.72	0.64	0.33 (0.11)	−0.46 (−0.32)

[a] See remarks in Part A of the Table.

[b] The overall sum of Δ_{OH} in stage B equals 0.84, or (0.38); the same in stage C is 1.88, or (0.53).

[c] Analogously to footnote b, the sum in stage B equals −0.25, or (0.07); in stage C −1.71, or (−0.90).

(3) For stage C with the reaction mechanism of $(OH^-/U)_s$ neutralization into H_2O/U (i.e. decrease of the former and increase of the latter), the constant differences in $(OH/U)_s$ values obtained from $(\Delta n)_g$ or $(\Delta c)_g$ equal to 0.09 for $p_1/p_2 = 0.7/0.3$, or -0.01 for $p_1/p_2 = 0.8/0.2$; as for H_2O/U, the differences are 0.07 or 0.05. Again, the alternative of $p_1/p_2 = 0.8/0.2$ gives more consistent agreement.

(4) In Part B of Table 1, the mean calculated values of $(OH/U)_s$ as well as H_2O/U are being compared with the same parameters resulting from the mass-balance calculations [6]; for stages B and C, regardless of the diversity in their reaction mechanisms, parameters Δ_{OH} and Δ_{H_2O} are smaller when $p_1/p_2 = 0.8/0.2 = 4.0$ is supposed.

(5) As to the H_2O/U values (Table 1, Part B), the agreement of calculated and mass-balance results for stage A is very poor; due to a considerable uncertainty of the latter (they were evaluated as small differences of great numbers [6]) the former results should be preferred. For stages B and C the mass-balance calculations are far more precise [6] and as far as stage B is concerned, the agreement is really better. Again, $p_1/p_2 = 0.8/0.2$ is preferable.

During stage C a gradual decrease in H_2O/U values with time was observed though, according to the suggested mechanism, the opposite should be true. This disagreement can be explained by subsequent desiccation of the samples, reflected only in the mass-balance calculations based on chemical analysis. [For $(OH/U)_s$ values no such disagreement was observed.]

(6) From the mere acceleration of the overall decomposition rate in stage B compared to that in stage A it can be stated only that at least one of the reaction paths, p_1 or p_2, within stage B should be accelerated but no definite conclusion can be drawn for the other one. Nevertheless, by means of conversion of the overall rates, p_A and p_B, into the rates of the individual reaction paths in both stages (i.e. $p_A p_1$ vs. $p_B p_1$; $p_A p_2$ vs. $p_B p_2$) it can be found that the latter path providing water conserves its velocity in both stages whereas the former one providing hydroxyls accelerates by about four times. The appropriate numerical data are given in Table 2.

(7) An acceptable agreement can be generally reached between the mass-balance calculations (based on chemical analysis) and calculations based on the proposed mechanism. The most acceptable ratio of the partial rates of both simultaneous reactions (producing hydroxyl ions and water), p_1/p_2, is equal to one for stage A and to four for stage B. For stage C, the idea of neutralization of hydroxyl and hydrogen ions accompanied most probably by partial desiccation of the solid is satisfactory.

(8) No explicit explanation of the above mentioned behaviour could be found except for the general statement that changes in rates and mechanism of the decomposition are caused by changes in properties of the solid, especially in the time-dependent chemical composition. The course of the individual partial reactions, summarized in the following scheme, should be

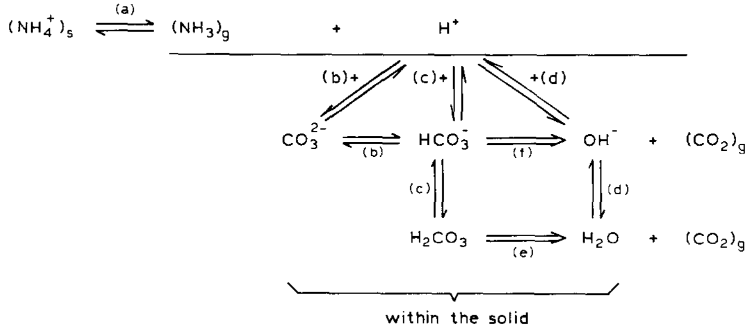
TABLE 2

Decomposition rates of individual reactions

Variable for calculation of p_X	Starting values			Calculated values				
	p_X [a]	p_1	p_2	$p_X \cdot p_1$	$p_X \cdot p_2$	$\frac{p_B}{p_A}$	$\frac{p_B \cdot p_1}{p_A \cdot p_1}$	$\frac{p_B \cdot p_2}{p_A \cdot p_2}$
n	$p_A = -0.00659$	0.5	0.5	−0.00330	−0.00330	2.36		
	$p_B = -0.01556$	0.7	0.3	−0.01089	−0.00467		3.30	1.42
		0.8	0.2	−0.01245	−0.00311		3.77	0.94
c	$p_A = -0.00451$	0.5	0.5	−0.00226	−0.00226	2.62		
	$p_B = -0.01183$	0.7	0.3	−0.00828	−0.00355		3.66	1.57
		0.8	0.2	−0.00946	−0.00237		4.19	1.05
M_w	$p_A = -0.34903$	0.5	0.5	−0.17452	−0.17452	2.38		
	$p_B = -0.83030$	0.7	0.3	−0.58121	−0.24909		3.33	1.43
		0.8	0.2	−0.66424	−0.16606		3.81	0.95

[a] The values are taken from Table 3 of Part I [6]. The overall reaction rate constant, p_X, stands for p_A or p_B.

controlled by details of molecular arrangement of the individual solid components.



The complexity of the situation may be illustrated by some molecular structural data. For instance, the number of N · · · O contacts (within the range 270–320 pm) necessary for formation of the hydrogen bridges is equal to six or eight for the first or second crystallographic type of ammonium groups, respectively [7]. With regard to the other condition for the formation of H-bridges [the R(H · · · O) separation being less than 240 pm], it was concluded that one ammonium group has four and the other six hydrogen bonds of various lengths and (N–H · · · O) angles [7]. According to another paper [8], the ammonium groups have more than four hydrogen bridges, which may bring about certain disarrangement of H-atoms in the structure of NH_4^+ ion.

VIBRATIONAL-SPECTROSCOPIC BEHAVIOUR

The resulting bonding state of the uranyl ion in a complex can be directly followed by IR spectroscopy, first of all by means of the marked $\nu_3(UO_2)$ anti-symmetric vibration. Namely, the parameters of the primary $U–O_I$ uranyl bond are generally supposed to depend sensitively on the parameters of coordinated ligands. In addition to the $\nu_3(UO_2)$ frequency, the deformation one $\nu_2(UO_2)$ can be found in the spectra; its values, however, are not so diagnostic.

The $\nu_3(UO_2)$ frequency values in various uranyl compounds are rather diverse. They can be mostly found within the range 1000–800 cm^{-1} [9], which corresponds to an almost twofold difference in the $U–O_I$ bond strength. There have been, of course, many attempts to interpret such remarkable changes in connection with the properties of the inner coordination sphere, as is briefly described in Part II of this series [10].

Most of the IR spectroscopic investigations compare the behaviour of the uranyl ion coordinated to various ligands: with different mass, bonding type and strength, symmetry of the inner coordination sphere, with different mutual influence of the components of the solid, etc.

The unique character of AUC and of its decomposition products consists in the possibility of following the vibration-spectroscopic behaviour of the uranyl ion coordinated to a ligand that gradually leaves the coordination sphere. To apply the above criteria, the mass of an individual ligand drops to zero and the symmetry of the inner coordination sphere decreases regardless of the behaviour of the other ligands (they may remain in their original positions, or be rearranged; or the original ligand can be substituted by another one in the course of decomposition). Distinct changes of the $\nu_3(UO_2)$ frequency (together with the frequencies of the other parts of the complex) must be expected as a result of certain (at least) quantitative changes in bonding interaction of the central ion as well as of lowering its symmetry.

It was however shown experimentally that both $\nu_3(UO_2)$ and $\nu_2(UO_2)$ frequencies remain unchanged during the first two decomposition stages (see Table 1 from Part II) [10], though 86.0% of carbonates together with 82.5% of ammonium groups originally present decomposed (see Table 7 of Part I) [6]. As to the frequencies of the ammonium and carbonate groups, the intensities of $\nu_1(CO_3)$ and $\nu_4(CO_3)$ valence vibrations remain unchanged (the energy of the latter increasing slightly) and the same is valid for the ν(N–H) vibration around 3200 cm^{-1}. The other ammonium and carbonate frequencies disappear sooner or later (Table 1 in Part II) [10]. The spectroscopic behaviour of the investigated samples thus corresponds to a situation in which the components of the inner and outer coordination spheres gradually disappear and, at the same time, the bonding state of the central ion remains unchanged. In other words, the intensity of some vibrations correspond to the number of the respective bonds in the molecule, whereas some other intensities (and, mostly, also the vibration energies) are independent of chemical composition of the solids. For the latter class of vibrations the starting energetic structure is virtually preserved although both coordination spheres undergo deep transformation. Two qualitatively different types of vibration modes seem to exist in the investigated solids.

Both uranyl frequencies are moderately shifted only during the third decomposition stage, where merely 4.5% of NH_4^+ and 0.7% of CO_3^{2-} are decomposed (Table 7 of Part I) [6]. It is thus obvious that both energy and intensity of some vibration bands are not particularly dependent on a degree of decomposition; they are more influenced by other factors and only loosely or indirectly connected with chemical composition.

Any far-reaching conclusions would be premature but it looks as if the uranyl bonding orbitals, determining the bond situation within the uranyl complex in the very beginning, preserved their energy as well as spatial orientation even after preponderant decomposition of the coordination sphere. A molecular (additive) point of view seems to be rather inadequate here because some non-additive stabilizing factor of the solid phase structure as a whole probably plays its role.

What alternative interpretation can be found? The assumption of independence of the $\nu_3(UO_2)$ frequency on the properties of the central ion coordination sphere would contradict all generally accepted concepts as well as lots of experimental material. An acceptable explanation of the broad interval of the observed vibration energies (cited above) would have to be found as well.

Regardless of any future interpretation it seems to be indisputable that the vibration-spectroscopic behaviour of the investigated uranyl carbonate complexes is quite different from that of other related compounds (e.g. halogen complexes, complexes with various substituted ligands, or with various cations and the same complex anion) or ammonium [11] and sodium uranates [12] whose $\nu_3(UO_2)$ frequency is systematically shifted. The vibration properties of sodium uranates with varying cation content may serve as a good example of such behaviour. For Na/U between 0 and 1.0, a linear relationship between 960 and 860 cm^{-1} is valid that can be further extrapolated [13,14] as far as to 775 and 590 cm^{-1} for α-Na_2UO_4 and Na_4UO_5, respectively.

The type of bonding of uranyl in a variety of its compounds is probably not universal and may vary considerably. This information may be of importance when formulating or evaluating empirical formulae as, e.g. Badger's rule, determining a relationship between the size of the uranyl ion and its $\nu_3(UO_2)$ frequency. Several versions of this rule have been published [15], some of them rather controversial [16].

SUMMARY

The proposed mechanism, though quite simple, explains quantitatively the course of the spontaneous AUC decomposition. The formation of hydroxyls and of water, experimentally proved in the previous communications [6,10], is shown to be the result of the internal solid phase processes (and not of a reaction, e.g. with air humidity).

It is not easy to interpret the varying rate of the decomposition (i.e. to explain why it is constant only within some limits of solid phase composition). An explanation should be connected with some details of the molecular structure with many hydrogen bonds of various strengths. Though our sample, prepared by precipitative reextraction from a tributylphosphate solution [6], was (according to IR spectra, chemical composition and X-ray analysis) identical with the AUC prepared from aqueous solutions, any catalytic influence of trace quantities of organic substances cannot be excluded. Nevertheless even the AUC monocrystals, grown only in aqueous medium, also decomposed observably [6].

The systems examined provide a new opportunity for investigating the influence of surrounding ligands on uranyl as the central ion, viz. in the case when ligands originally present leave the solid phase. Based on IR spectra it can be stated that the uranyl bonding in carbonate complexes can be different from that in other types of oxygenated compounds (e.g. in precipitated or high-temperature uranates). First of all, the uranyl $U-O_I$ bond in carbonate complexes seems to be less sensitive to changes in the symmetry or overall electron-donating power of the ligand surroundings.

The system of uranyl molecular orbitals formed in the original AUC seems to preserve its principal features until a considerable portion of the carbonate ligands is decomposed.

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