Inorganica Chimica Acta, 81 (1984) 83–89

Formation of the Ammonium-Uranyl-Carbonate Complexes of the Type $(NH_4)_4[UO_2(CO_3)_3]$, Prepared by Precipitative Re-extraction

V. BARAN, F. ŠKVOR and V. VOSEČEK

Nuclear Research Institute, 250 68 Řež, Czechoslovakia

Received March 2, 1983

The paper describes results of the precipitative re-extraction of the uranium(VI) from the tri-n-butylphosphate organic phase using ammonium carbonate aqueous solutions with various composition. Based upon the results, the appropriate chemism is proposed. The resulting crystalline precipitates, generally denoted as AUC, can be described by formula $(NH_4)_x[UO_2(CO_3)_y]$, *with x and y mostly equalling 4 and 3, respectively, but sometimes having smaller values. The solids are characterized by means of chemical, X-ray and IR analysis. Some peculiarities as for the water content in the AUC solid are also given. Mixing the two starting liquid phases in a pre-selected ratio using an agitated flow-through reactor is recommended as the most reliable practical preparation procedure.*

Introduction

Ammonium–uranyl–carbonates, usually abbreviated in AUC, are of increasing technological importance [1–5]. In the present paper a novel preparation route based upon precipitative re-extraction of uranium from kerosene solutions of tri-n-butylphosphate will be described. The results were obtained during an investigation of the UF_6-to-UO_2 reconversion consisting of the following steps: UF_6 hydrolysis in solution of a nitrate the cation of which—such as Ca, Fe(III), Al—firmly binds or precipitates fluoride ions; direct uranium extraction from the hydrolysate by means of 30% TBP solution [4, 6, 7]; solidification of the uranium by its precipitative re-extraction in the form of AUC (or, as a possible alternative, re-extraction of uranium into aqueous phase and gelation into microspheres); AUC–UO_2 transformation.

The authors believe that the mechanism of the complex formation within the aqueous phase is in principle the same as in the case of usual mixing of two aqueous solutions. On the other hand, some differences are conceivable: for instance, in the crystal shape and dimensions of crystallites because of a controlled uranyl transport from organic to aqueous phase, together with a possible influence of the surface properties on the phase boundaries *etc.*

Experimental

The uranium-containing organic phase was prepared from an aqueous uranyl nitrate solution with 30 vol.% solution of tri-n-butylphosphate in kerosene. The aqueous precipitative solutions were prepared by dissolution of solid ammonium hydrogen carbonate, NH_4HCO_3; solutions with a higher ammonia content, $i = N/C > 1$, were prepared by addition of ammonia to the former solution. Preparing the solution from gaseous NH_3 and CO_2 is possible, but not convenient for a laboratory scale.

The precipitative re-extraction was realized by mixing both solutions under stirring, either using the usual titration technique, or by dosing the solutions in a preselected molar ratio of the components into an agitated flow-through reactor. The easily filterable precipitate was washed by a small portion of water, then more thoroughly by ethanol or acetone, and dried in air at room temperature. The as-received crystalline powder was usually easily flowing, without any compaction.

The uranium content was determined gravimetrically, with accuracy better than 0.5% rel.; ammonia after its release and absorption in 4% boric acid by titration with sulfuric acid using a mixed indicator; the carbonate content after decomposition of a sample in boiling sulfuric acid (1:1) and absorption and weighing the evolved carbon dioxide on ascarite. Because precision of the former procedure is better than 3% rel. and of the latter up to 5% rel., the values of the experimental N/U ratios are more reliable than those of C/U ones.

IR spectra were taken using mostly a Perkin-Elmer 225 spectrometer, in several cases a Beckman IR 20A was used. The spectra were measured in the 4000–200 cm^{-1} region in Nujol or Voltalef mulls using KBr, NaCl or CsI windows. X-ray diffraction patterns

0020-1693/84/$3.00

were measured by a Mikrometa apparatus with chamber radius 114.6 mm and nickel filtered CuK_α radiation.

Symbols: Terms belonging to aqueous or organic phase have subscripts w or o, resp.; those belonging to states before and after precipitative re-extraction are denoted by a and p, resp. (from the Latin word ante and post); s stands for stoichiometric, S for solid. Concentrations are in brackets, molar ratios in parentheses, G stands for an amount, relative or absolute. The gross characteristics of the uranium carbonate solid is based upon the following conventional formula: $(NH_4)_\alpha[(UO_2)_\beta(OH)_\gamma(CO_3)_\delta(H_2O)_\epsilon]$ = AUC $\alpha\beta\gamma\delta\epsilon$ so that AUC 41030 is the abbreviation for $(NH_4)_4[UO_2(CO_3)_3]$, AUC 32135 for $(NH_4)_3[(UO_2)_2(OH)(CO_3)_3(H_2O)_5]$, *etc.*

Results and Discussion

General

Not taking here into account the precipitative solutions with i = N/C (the ammonia-to-carbon dioxide ratio) higher than 2, the carbonate aqueous solution for the precipitative re-extraction can be composed of ammonium carbonate, $(NH_4)_2CO_3$, with i = 2.0; of ammonium hydrogen carbonate, NH_4HCO_3, with i = 1.0; or of a solution with composition between these limits, $(NH_4)_i(H)_jCO_3$, with $i + j = 2.0 > i > j$. Of all the chemical forms of CO_2 in water [8] there are the ionic ones, CO_3^{2-} and HCO_3^-, which will be first of all taken into account from the present point of view. From ^{13}C NMR studies [8, 9] it follows that fast hydrogen exchange takes place—each ion has its own peak position or, if both present, merely a single peak appears proportionally to the mole fraction of the ions. It indicates that the rate of the hydrogen exchange reaction is faster than the registration time of the PMR method (about a microsecond, or less).

It is pertinent to ask why the difference in behaviour of the two ions as ligands in relation to uranyl as central ion is so large—while CO_3^{2-} anions bind the uranyl ion very strongly (formation constant of the tricarbonate complex ranges within $10^{18}-10^{23}$, see refs. [8, 10, 11]), uranyl complexes with HCO_3^- ligands have not been described [10]. Because the ability of the uranyl ion to form strong complexes with bidentate oxygenated ligands can be considered quite common [12], combination of this rule with the above mentioned ability of the carbonate ionic forms to exchange their hydrogen ion easily may be sufficient to explain the observed situation by the assumption that in the course of the formation of the uranyl–carbonate bond, $UO_2^{2+}-CO_3^{2-}$, the hydrogen carbonate ion dissociates its hydrogen. Schematically: $(UO_2HCO_3)^+ \rightarrow UO_2CO_3 + H^+$. An internal acidification of the system, proportional to the number of such bonds formed, would be an inevitable consequence of this reaction mechanism. Fortunately, it can be checked experimentally because the evolved acid should react with both carbonate ionic forms and enhances thus stoichiometry of the overall reaction (see below).

A crystalline solid, corresponding to the formula $(NH_4)_4[UO_2(CO_3)_3]$ with N/U = 4.0 and C/U = 3.0, is formed under sufficient surplus of the carbonate ions above the stoichiometric ratio; *e.g.*, $q = (CO_2/U)_{prep}$ equal to about 20 is given in ref. [10]. When a smaller surplus is applied, crystalline phases with lower ammonium and carbonate content, nevertheless with very similar X-ray diffraction patterns as well as IR spectra, may arise [13]. For them formula $(NH_4)_x[UO_2(CO_3)_y]$ will be used; the lowest experimental values found [13] were x = N/U = 2.7 and y = C/U = 2.3.

Re-extraction using carbonate solution with i = N/C = 2.0

The stoichiometric reaction for this case is described by eqn. (1) for which the preparative quotient, $q = (CO_2/U)_{prep}$, equals 3, *i.e.* $q_s = 3.0$. When a surplus of the carbonate ions is used, then $q > q_s = 3.0$ and the term $(q - q_s)(NH_4)_2CO_3$ should be added to the righthand side of the equation

$$UO_2(NO_3)_2 + 3(NH_4)_2CO_3 = (NH_4)_4[UO_2(CO_3)_3] + 2NH_4NO_3 \qquad (1)$$

In the course of the reactions no carbon dioxide is released [14] (we suppose here the organic phase without an acid and the closed system). Too high values of q will not be in favour of the re-extraction because the surplus of carbonates in the mother liquor will hinder the transfer of uranium into the aqueous phase (from the opposite, extractive point of view an electrolyte in the aqueous phase works as a salting-out agent; simultaneously it will suppress solubility of the tricarbonate solid [10, 15]).

The role of a higher i = N/C ratio ought to be very similar. The selected data in Table I indicate that these expectations are fulfilled: see the data in columns R_f, R_c, $[U]_{pw}$ and $[U]_{po}$. As for the other components of the aqueous phase, with increasing i = N/C and q/q_s only the values of $[NH_3]_{pw}$ increase distinctly, the concentrations of nitrates being constant and those of carbonates decreasing.

Re-extraction using carbonate solution with i = N/C = 1.0

The reaction for the stoichiometric case is described by eqn. (2).

$$UO_2(NO_3)_2 + 6NH_4HCO_3 = (NH_4)_4[UO_2(CO_3)_3] + 2NH_4NO_3 + 3H_2CO_3 \qquad (2)$$

In contrast to eqn. (1) the stoichiometric quotient q_s is now doubled to 6.0; its value of 3.0 would be

TABLE I. The Effect of i = N/C Composition of the Aqueous Phase[a].

No.	i = N/C	q_s[b]	q/q_s	$(pH)_{pw}$	$[U]_{po}$	R_c[c]	R_f[c]	$[U]_{pw}$	$[CO_2]_{pw}$	$[NO_3]_{pw}$[d]	$[NH_3]_{pw}$
1	1.00	6.0	0.67	7.58	0.0011	7.5	154	0.0082	0.092	0.610	0.654
2	1.21	5.0	0.80	7.40[e]	0.0028	10.4	60	0.0292	0.204	0.603	0.942
3	1.80	3.3	1.21	9.19	0.0032	4.4	52	0.0140	0.577	0.603	1.154
4	2.18	3.0	1.33	9.60	0.0037	4.4	45	0.0162	0.355	0.600	2.151
5	3.07	3.0	1.33	9.92	0.0058	1.9	28	0.0108	0.302	0.593	3.295

No.	$G(U)_{po}$ mmol.	%	$G(U)_S$ mmol	%	x = $(N/U)_S$	y = $(C/U)_S$	X-ray identification
1	0.11	0.6	16.47	96.7	1.89	2.00	AUC 11113[16]
2	0.28	1.6	15.13	88.8	3.08	2.61	close to AUC 41030
3	0.32	1.9	15.93	93.6	3.92	2.87	AUC 41030
4	0.37	2.2	15.76	92.5	3.91	2.89	AUC 41030
5	0.58	2.4	15.85	93.1	3.96	3.01	AUC 41030

[a] As for symbols see Experimental. All concentrations are given in mol·dm^{-3}. For all samples it holds true: q = $(CO_2/U)_{prep}$ = 4.0; $G(U)_{ao}$ = 17.03 mmol; $G(CO_2)_{aw}$ = 66.71 mmol; $[U]_{ao}$ = 0.1703 mol·dm^{-3}; $[CO_2]_{aw}$ = 1.20 mol·dm^{-3}. [b] See eqn. (4c). [c] R_c = The re-extraction coefficient expressed by uranium concentrations in both liquid phases, $R_c = [U]_{pw}/[U]_{po}$. R_f = the formal re-extraction coefficient expressed by the uranium, lost from and remained in the organic phase, $R_f = ([U]_{ao} - [U]_{po})/[U]_{po}$. [d] The calculated values based upon the assumption that concentration of nitrates in organic phase is double that of uranium. [e] Certain decrease in $(pH)_{pw}$ of the first system with AUC 41030 or so in comparison with the systems of hydroxo carbonates found commonly, see below.

insufficient here (see eqn. (2a) below) because 4 ammonium groups are necessary for formation of the AUC complex and 2 other ones for equilibrating the nitrates, as illustrated by eqn. (2). If 3 carbonate ions are bound per uranium, then 3 hydrogen ions are to be released (eqn. (2a)). Their reaction with other hydrogen carbonates (eqn. (2b)) provides the 3 missing ammonium groups, as well as the unstable carbonic acid decomposing at room temperature (at least partially): $3H_2CO_3 = 3H_2O + 3CO_2$. Written chemically:

$$UO_2(NO_3)_2 + 3NH_4HCO_3 = NH_4[UO_2(CO_3)_3]^{3-} + 3H^+ + 2NH_4NO_3 \qquad (2a)$$

$$3H^+ + 3NH_4HCO_3 = 3NH_4^+ + 3H_2CO_3 \qquad (2b)$$

Equations (2a) and (2b) give after summation the overall eqn. (2), explaining both the enhanced q_s and the evolution of carbon dioxide bubbles during preparation.

These expectations were checked experimentally with two ways of reaching the preparative values q = $(CO_2/U)_{prep}$—the qs were adjusted either by gradually higher portions of the same hydrogen carbonate solution (Table II, Nos. 1–4 and 8–9), or by the same volume of the solution with gradually higher $[CO_2]_{aw}$ concentrations (Table II, Nos. 5–8).

The value of q_s found for the formation of AUC 41030 phases lies between 6.0 and 7.0; bearing in mind the finite values of the complexity constants, the value may be considered to be in accord with the theoretical prediction. The carbon dioxide is really evolved but the decomposition of carbonic acid, H_2CO_3, is incomplete.

Chemical composition of the AUC 41030 solids is sufficiently close to theory, requesting $G(UO_2)_S$ = 51.71%, $G(NH_4)_S$ = 13.82%, and $G(CO_3)_S$ = 34.47%, with the only exception of sample No. 6 (q = 7.0).

At the same q = 6.0, contacting the organic phase with different aqueous volumes brings about clear differences in composition of the solids (Nos. 4 and 5); higher uranium and carbonate concentrations are more favourable for reaching higher $(N/U)_S$ and $(C/U)_S$ ratios. Nevertheless, it probably holds true only when the q's are close to q_s, say q_s ±1, because with q distinctly higher than q_s (Nos. 8 and 9, q = 9.0 and 10.0) both solids are quite similar.

Re-extraction using carbonate solutions with i = N/C between 1.0 and 2.0

Similarly to eqns. (1) and (2) one can write here:

$$UO_2(NO_3)_2 + q_s(NH_4)_i(H)_jCO_3 = (NH_4)_4[UO_2(CO_3)_3] + 2NH_4NO_3 + (q_s - 3)H_2CO_3 \qquad (3)$$

Again, for $q > q_s$ the additional term $(q - q_s)(NH_4)_i(H)_jCO_3$ should be added to the right-hand side of eqn. (3), nevertheless, the value of q_s for this case is unknown, except that it lies between 6.0 and 3.0 for i = 1.0 and 2.0, respectively (see eqns. (2) and (1)).

TABLE II. Data on the Precipitative Re-extraction using NH_4HCO_3[a].

No.	q	q/q_s	$[U]_{hyp}$[b]	$[CO_2]_{aw}$	$[U]_{pw}$	$[NH_3]_{pw}$	$[CO_2]_{pw}$	$(N/C)_{pw}$	$G(UO_2)_S$ %	$G(NH_4)_S$ %	$G(CO_3)_S$ %	Σ(UNC)[d] %	$(N/U)_S$	$(C/U)_S$	X-ray patterns[a]
1	4.07	0.68	0.467	1.90					57.21	7.14	30.72	95.07	1.87	2.42	AUC 11113[16]
2	4.35	0.73	0.437	1.90					60.45	8.13	26.44	95.02	2.08	1.97	AUC 11113
3	5.40	0.90	0.352	1.90					59.05	8.84	32.92[c]	100.81	2.24	2.51	AUC 11113
4	6.00	1.00	0.317	1.90					56.46	10.69	31.35	98.50	2.84	2.50	AUC 11113
5	6.00	1.00	0.211	1.27	0.051	0.801	0.212	3.8	61.07	7.66	29.77	98.50	1.88	2.19	AUC 11113
6	7.00	1.17	0.211	1.48	0.039	0.671	0.227	3.1	52.48	12.43	36.65[c]	101.56	3.55	3.14	AUC 41030
7	8.00	1.33	0.211	1.69	0.027	0.799	0.296	2.7	51.76	13.49	35.56	100.81	3.90	3.09	AUC 41030
8	9.00	1.50	0.211	1.90	0.022	0.964	0.397	2.4	51.70	13.21	34.65	99.56	3.83	3.02	AUC 41030
9	10.00	1.67	0.190	1.90	0.021	1.060	0.509	2.1	51.47	13.32	35.10	99.89	3.87	3.07	AUC 41030

[a] As for symbols see Experimental. All concentrations in brackets are given in mol·dm^{-3}. $[U]_{ao}$ = 0.4435 mol·dm^{-3}. [b] $[U]_{hyp}$ is a hypothetical concentration calculated on the assumption that all uranium was transferred into the aqueous phase prior to any reactions. [c] These results seem to be rather high. [d] Sum of the preceding three columns.

The appropriate numerical value of the stoichiometric quotient q_s can be determined from material balance of the components in eqn. (3). For ammonia it holds true: $i \cdot q_s = 4 + 2 = 6$ so that $q_s = 6/i$; for hydrogen we have: $j \cdot q_s = 2(q_s - 3)$, whence again

$$q_s = 6/(2 - j) = 6/i \qquad (3a)$$

This reveals immediately why only the last three samples in Table I are pure AUC 41030 phases—it is because their q = 4.0 is slightly but sufficiently higher than the appropriate q_s's, the opposite being the case for the first two samples.

From eqn. (3a) it also follows that, in theory, the composition of the carbonate precipitative solution fully determines the value of q_s, *i.e.* the stoichiometry of the reaction. In practice, a value of q greater than q_s should be applied in order to obtain the pure AUC 41030 phase without an over-stoichiometric surplus of the carbonates (see also below).

The chosen value of i = 1.56 of the carbonate precipitative solution leads to $q_s = 6.0/1.56 = 3.85$. In accord, pure AUC 41030 phases were formed at $q \geqslant 4.0$ at both initial uranyl concentrations in the organic phase.

Furthermore, the results in Table III document that the re-extraction efficiency, judged from the residual uranium concentration in the organic phase $[U]_{po}$ as well as from the re-extraction coefficiencts, R_f or R_c, is much better when a pure carbonate AUC 41030 phase, instead of a hydroxo carbonate one, can be formed. In addition, the efficiency generally gets better with higher q's.

The starting $[U]_{ao}$ value also plays an important role in the interconnections. It follows from quite different courses of the relationship $[U]_{po}$ (or R_f) *vs.* q for the two $[U]_{ao}$ values—for the higher one the curve approaches to a horizontal line whereas for the lower one it goes steeply up (both curves intercept at q equal approximately to 5.6, compare also R_f and R_c values in Table III).

The different behaviour could be caused by different changes of uranium concentration during re-extraction—it either declined (Nos. 3–5) when the $[U]_{ao}$ values were higher than the $[U]_{hyp}$ ones (see note b in Table II), or increased in the opposite case of Nos. 7–9, Table III. The described changes happened because the initial $[U]_{ao}$ concentrations decreased 2.4 times whereas the carbonate concentrations remained unchanged, so that for the same q's 2.4 times smaller volumes should be used. The kinetics of the uranium transport through the liquid–liquid interface and some properties of the solid as well (*e.g.*, the $(N/U)_S$ ranges and the $(C/U)_S$ values in Table III, or the sum ΣUNC for samples Nos. 7–9, see also below) are also influenced. It should be concluded therefore that not only the value of q but also the relation of concentrations of the components—and, thus, the appropriate volumes—participating in

TABLE III. Data on the Experiment with i = N/C = 1.56[a].

No.	q[b]	q/q_s	$\frac{V_{aw}}{V_{ao}}$[c]	(pH)[d]	$[U]_{po}$	$[U]_{pw}$	R_f[e]	R_c[e]	ΔR_f	ΔR_c	$[NH_3]_{pw}$	$[CO_2]_{pw}$	$(N/C)_{pw}$
1	1.5	0.39	0.500	4.47	0.0965	0.0021	3.2	0.0			1.257		
									206.3	18.9			
2	3.0	0.78	1.000	7.62[d]	0.0019	0.0360	209.5	19.0			0.972	0.128	7.6
									289.5	31.2			
3	4.0	1.04	1.331	7.54[d]	0.0008	0.0401	499.0	50.1			0.859	0.150	5.7
									166.7	−2.0			
4	5.0	1.30	1.664	8.26	0.0006	0.0289	665.7	48.2			1.095	0.307	3.6
									133.3	6.8			
5	6.0	1.56	2.012	8.48	0.0005	0.0275	799.0	55.0			1.260	0.438	2.9
6	3.0	0.78	0.416	7.85[d]	0.0526	0.0383	2.2	0.7			1.144	0.135	8.5
									56.4	15.5			
7	4.0	1.04	0.555	7.65[d]	0.0028	0.0454	58.6	16.2			0.945	0.299	3.2
									126.0	23.0			
8	5.0	1.30	0.693	8.38	0.0009	0.0353	184.6	39.2			1.026	0.305	3.4
									1484.4	267.8			
9	6.0	1.56	0.832	8.50	0.0001	0.0307	1669.0	307.0			1.206	0.405	3.0

No.	$(UO_2)_S$ %	$(NH_4)_S$ %	$(CO_3)_S$ %	Σ(UNC)[g] %	$(N/U)_S$	$(C/U)_S$	X-ray patterns
1	64.98	5.41	19.54	89.93	1.25	1.35	AUC 32135[17]
2	57.95	8.92	31.04	97.91	2.30	2.41	AUC 32135
3	52.56	12.97	34.25	99.78	3.69	2.93	AUC 41030
4	52.39	12.95	34.84	100.18	3.70	2.99	AUC 41030
5	52.38	12.97	34.92	100.27	3.71	3.00	AUC 41030
6	72.91	2.31	18.14	93.63	0.47	1.14	amorphous
7	54.76	10.96	31.10	96.86	3.00	2.56	AUC 41030
8	51.84	12.11	31.33	95.28	3.50	2.72	AUC 41030
9	51.82	12.78	32.54	96.84	3.71	2.84	AUC 41030

[a] As for symbols see Experimental. For i = 1.56 it holds j = 0.44, q_s = 3.85. $[CO_2]_{aw}$ was 1.202 mol·dm^{-3} for all systems. All concentrations in brackets are given in mol·dm^{-3}. [b] $[U]_{ao}$ = 0.400 mol·dm^{-3} holds for Nos. 1–5, 0.167 mol·dm^{-3} for Nos. 6–9. [c] The volume ratios of aqueous and organic phase used. [d] $(pH)_{aw}$ was 9.50. The decrease of the pHs for the first system with AUC 41030 phase in comparison with the preceding one was always found. [e] R_f, R_c = the re-extraction coefficients, see note [c] in Table I. ΔR_f and ΔR_c = difference of the neighbouring values. All values rounded off to within tenths. [f] The gravimetric results given; spectrophotometric ones, not cited here, were very close to them. [g] Sum of the preceding three columns. The sums for Nos. 7, 8 and 9 should be close to 100% similarly as it is for Nos. 3, 4 and 5; the reason for this discrepancy see the text.

the reactions plays its undeniable role within the precipitative re-extraction.

Equation (3) holds for the theoretical formula $(NH_4)_4[UO_2(CO_3)_3]$ with N/U = 4.0 and C/U = 3.0. Nevertheless, when q is close to q_s certain observable deviations in molar ratios, $(N/U)_S$ and $(C/U)_S$, can be identified [13], as one can also see from Tables II and III. In such cases the formula of the complex solid should be rewritten in the following way: $(NH_4)_x[UO_2(CO_3)_y]$ with x = 2(y − 1) or y = (x/2) + 1 from the electroneutrality condition. Then, we can rewrite the equation as follows:

$$UO_2(NO_3)_2 + q_s(NH_4)_i(H)_jCO_3 = (NH_4)_x[UO_2(CO_3)_y] + 2NH_4NO_3 + (q_s \cdot j/2)H_2CO_3 \qquad (4)$$

The stoichiometry condition for ammonia has now the form: $i \cdot q_s = x + 2 = 2y$, and that for carbonates: $q_s = y + q_s \cdot j/2$, hence for both cases

$$q_s = (x + 2)/i = 2y/i \qquad (3b)$$

In comparison with eqn. (3a), (x + 2) or 2y substitutes for 6 so that in the most general case

$$q_s = (x + 2)/i = 2y/i \leqslant 6/i \qquad (3c)$$

and the value of q_s depends upon the composition of both the precipitative solution and—up to a certain limit—the AUC precipitate itself.

Open and Marginal Questions

As for the chemical forms of the carbon dioxide and their amounts in the aqueous mother liquors, the amounts of CO_2, really evolved during the reactions at room temperature, are distinctly smaller compared with the theoretical H_2CO_3 amount. In accord with basic monographs this indicates that only a part of carbon dioxide forms the acid and, possibly, decomposes. The other part remains dissolved in the supernatant because of its weaker hydration. After at least 10 min. boiling the overall amount of the evolved CO_2 meets the theoretical requests.

So far as the $[NH_3]_{pw}$ concentrations are concerned, Tables II and III point out that their anionic counterbalance, consisted of carbonate plus nitrate and hydroxyl ions, is insufficient if all the ammonia had the form of ammonium cations. It is reasonable to suppose, therefore, that a substantial part gets a non-ionic form, most likely that of the undissociated NH_4OH.

In a series of experiments, not described here, it was found that formation of the AUC solid may be considerably influenced by other factors than merely the preparative molar ratios, q's. Even though the AUC precipitate behaves correctly, *i.e.* it settles quickly within the aqueous phase, not interfering with quick separation of both liquid phases, sometimes its settling as well as separation of the liquids are much more difficult. Because this ill-behaviour took place merely when the technique of titrating the organic with the aqueous phase was applied, the cause is most likely connected with transformation of a hydroxo carbonate solid phase, arisen at earlier stages, into the AUC one. Such transformation is possible but it is not straightforward. According to our experience, the most practical and reliable way of AUC preparation is mixing the two liquid phases in a preselected ratio in an agitated flow-through reactor.

The formula of tetraammonium tricarbonato uranylate, $(NH_4)_4[UO_2(CO_3)_3]$—AUC 41030 in our abbreviation—does not contain water in any form in accord with literature quotations [10]. Also our analytical results are in line with it because the sum of all three basic components of AUC 41030 is very close to 100% (see Tables II and III and ref. [13]; includingly our other rather numerous data, not cited in the present paper), with the only exception of samples Nos. 7–9 in Table III. One can tentatively suppose that a presence of some molecular water is the reason for this finding. Then, starting from an average of the sums ΣUNC amounting 96.3 ± 0.7%, about one mole of water per formula unit can be calculated.

The presence of water can be unequivocally proved by means of the IR spectra where it manifests itself by ν(OH) frequencies at 3540 cm^{-1} (a shoulder on strong ν(NH) peak) [13] and libration modes [18] round 400 cm^{-1}; the deformation frequency slightly above 1600 cm^{-1} is hidden in very strong carbonate peaks. This conclusion is based upon IR and thermal analysis of the analogous tricarbonato uranylate complexes of other metal cations such as Tl(I), Ag, Na, K, and Ba (only the latter, in contrast to the others, nominally forms hydrates [10]), the spectra of which have quite distinct water peaks in the mentioned regions [19]. This suggests that their crystal lattices (may) contain molecular water even when formally they are not hydrated; the ν(OH) peak is, in these cases, quite evident because it does not interfere with much stronger ν(NH) peaks of the ammonium groups.

We tried to quantify the water amount in the individual samples Nos. 7–9. This cannot be done starting from chemical analyses because the differences (up to 100%) caused by the water are strongly influenced by the summed errors of the determination, so we used the heights of the selected peaks in the IR spectra. The results, gathered in Table IV, indicate that the amount of water is roughly the same in samples 8 and 9, being approximately one half of that of sample 7. Because in average all the samples contain approximately one water molecule (see above), sample No. 7 contains, perhaps, 1.4H_2O/U, the others about 0.7H_2O/U.

TABLE IV. Infra-red Analysis of the Water Content, Relative Intensities of the Selected Peaks[a].

Sample No. (Table III)	3540/3180 %	400/3180 %	3540/885 %	400/885 %
7	53.7	64.5	55.1	66.2
8	22.5	25.7	24.8	28.2
9	23.8	28.6	26.2	31.4

[a] The peaks at 885 cm^{-1} (uranyl antisymmetric frequency) and at 3180 cm^{-1} (ammonium N–H stretching frequency) of the AUC complexes were used as internal standards. Frequency 3540 cm^{-1} belongs to ν(OH) stretch of water, that round 400 cm^{-1} to water libration [18]. Intensities of these peaks are expressed in per cent relatively to the standards, all peaks in the heading being denoted directly by their wavenumbers.

It is pertinent to recall here that the main difference in the way of preparation of the AUC samples with and without water content was that of the initial concentration $[U]_{ao}$ and its relation to the values of $[U]_{hyp}$ (see above). This reveals that lower values of $[U]_{ao}$ favour formation of solid phases that are able to embed into themselves about one water molecule per uranium.

IR spectra of samples Nos. 8 and 9 are closely similar one to each other, and with the exception of the presence of water to the other AUC phases as well [13]; nevertheless, that of No. 7 differs from them in that some of the carbonate bands are not so sharp and/or intense, one of the two in-plane and the out-of-plane deformation is missing, two of the three stretching frequencies are shifted *etc.* Even though it is difficult to claim a hydroxo carbonate phase (*e.g.* its antisymmetric uranyl frequency has not been changed, its X-ray pattern is that of AUC 41030), it clearly indicates certain minor changes in the properties of the coordinated carbonate ligands. Also the higher water content (*ca.* 1.5H_2O/U) may be connected with the phenomenon of subtle interchanges from the carbonato to hydroxo carbonato uranyl coordination compounds.

References

1 K. G. Hackstein and F. Plöger, *Atomwirtschaft, 12,* 524 (1967).
2 V. Mathieu, *Trans. Am. Nucl. Soc., 28,* 327 (1978).
3 S. G. Brandberg, *Nucl. Technol., 18,* 177 (1973).
4 V. Baran, *At. Energy Rev., 17,* 891 (1979).
5 Yi-Ming Pon, Che-Bao Ma, Nien-Nan Hsu, *J. Nucl. Mater., 99,* 135 (1981).
6 E. Lillyman, F. C. Mascall and C. G. Mathers, *Brit. Pat.* 1 449 122 (1976); *US Pat.* 3 928 538 (1975).
7 C. W. Blumfields, *Nucl. Eng. Int., 24,* 32 (1979), No. 281.
8 T. M. Abbott, G. W. Buchanan, P. Kruus and K. C. Lee, *Canad. J. Chem., 60,* 1000 (1982).
9 E. T. Strom, D. E. Woessner and W. B. Smith, *J. Am. Chem. Soc., 103,* 1255 (1981).
10 I. I. Chernyayev, 'Uranium Complex Compounds' (in Russian), p. 17. Nauka, Moscow (1964).
11 S. Ó. Cinnéide, J. P. Scanlon and M. J. Hynes, *J. Inorg. Nucl. Chem., 37,* 1013 (1975).
12 L. Cattalini, U. Croatto, S. Degetto and E. Tondello, *Inorg. Chim. Acta Rev., 5,* 19 (1971).
13 V. Baran, *Coll. Czech. Chem. Commun., 47,* 1269 (1982).
14 L. Mayo, *J. Inorg. Nucl. Chem., 43,* 2133 (1981).
15 N. P. Galkin, A. A. Mayorov and U. D. Veryatin, 'Uranium Concentrates Reprocess Technology' (in Russian), p. 62. Atomizdat, Moscow (1960).
16 I. I. Chernyayev, V. A. Golovnya and G. V. Ellert, *Zhur. Neorg. Khim., 6,* 376 (1971).
17 I. I. Chernyayev, V. A. Golovnya and G. V. Ellert, *Zhur. Neorg. Khim., 6,* 386 (1971).
18 K. Ohwada, *J. Inorg. Nucl. Chem., 41,* 1145 (1979).
19 V. Baran and J. Vachuška, unpublished results.