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# SPONTANEOUS ISOTHERMAL DECOMPOSITION OF THE URANYL CARBONATE COMPLEX $(NH_4)_4[UO_2(CO_3)_3]$ AT ROOM TEMPERATURE. PART I. CHEMICAL ANALYSIS

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## ABSTRACT

Spontaneous changes in the chemical composition of $(NH_4)_4[UO_2(CO_3)_3]$ are described. The effect takes place in the air at room temperature and is accompanied by changes in appearance. The decomposition proceeds as a linear process in three consecutive stages and the final (meta)stable product is a nearly-amorphous substance with carbon-to-uranium and nitrogen-to-uranium ratio of about 0.5. In the course of the decomposition the solid phase probably gains hydroxyl groups as well as water.

## INTRODUCTION

The title compound, ammonium uranyl carbonate (usually abbreviated to AUC) is explicitly described as stable when dry [1]. This fact is in agreement with thermoanalytical data. An observable thermal decomposition of AUC begins at 80 °C with a maximum at 150 °C [1], or, according to a recent source [2], at 150 °C with a maximum at 200 °C. Some other authors, however, show that the compound $UO_2CO_3 \cdot 2(NH_4)_2CO_3$, identical to the AUC, loses ammonia at room as well as elevated temperature [3].

In accordance with this, certain visual changes of the AUC complex were observed after prolonged storage in the air. Its bright yellow colour with a greenish tint was changed towards orange together with some loss of transparency. These effects were observed on powders with a particle diameter of about 0.01 mm as well as on monocrystals [4] with edges of approximately 2–3 mm. We attempted to perform chemical analysis of the AUC powders during their storage in order to learn whether the visual effects are accompanied by any measurable chemical or physico-chemical changes.

## EXPERIMENTAL

An AUC sample prepared by precipitative reextraction [5] was used for the experiments. As we had not found any description of a similar decomposition experiment, some experimental details were not clear at the beginning (e.g. the length of the experiment, the analytical methods used, etc.) and the amount of sample necessary had to be estimated. Due to this

TABLE 1

Chemical analysis—experimental results [a]

| Sample | $\Sigma/\Delta$ [b] | % $NH_4$ | % $UO_2$ | % $CO_3$ | $\Sigma$(NUC) (%) |
|---|---|---|---|---|---|
| W-0 | 0/0 | 13.71 | 51.13 | 34.32 | 99.16 |
| | | 83/6.06 | 33/0.65 | 206/6.00 | 322/3.25 |
| W-1 | 28/28 | 13.09 | 52.33 | 33.42 [c] | 98.84 [c] |
| | | 34/2.60 | 3/0.06 | 167/5.00 | 204/2.06 |
| W-2 | 64/36 | 12.73 | 53.67 | 32.40 [c] | 98.80 [c] |
| | | 25/1.96 | 43/0.80 | 162/5.00 | 230/2.33 |
| W-3 | 107/43 | 12.02 | 55.40 | 31.20 | 98.62 |
| | | 66/5.49 | 24/0.43 | 59/1.89 | 149/1.51 |
| W-4 | 153/46 | 11.39 | 57.47 | 29.60 [c] | 98.46 [c] |
| | | 6/0.53 | 29/0.50 | 148/5.00 | 183/1.86 |
| W-5 | 209/56 | 9.58 | 61.10 | 23.43 | 94.10 |
| | | 25/2.61 | 8/0.13 | 60/2.56 | 93/0.99 |
| W-6 | 241/32 | 7.92 | 65.25 | 19.38 | 92.55 |
| | | 20/2.53 | 14/0.21 | 71/3.66 | 105/1.13 |
| W-7 | 267/35 | 6.70 | 68.61 | 15.74 | 91.05 |
| | | 3/0.45 | 10/0.15 | 82/5.21 | 95/1.04 |
| W-8 | 302/35 | 4.41 | 74.11 | 9.41 | 87.93 |
| | | 10/2.27 | 18/0.24 | 60/6.38 | 88/1.00 |
| W-9 | 336/34 | 3.40 | 76.39 | 7.20 | 86.99 |
| | | 3/0.88 | 8/0.10 | 44/6.11 | 55/0.63 |
| W-10 | 366/30 | 3.36 | 76.63 | 6.93 | 86.59 |
| | | 10/2.98 | 6/0.08 | 68/9.81 | 84/0.97 |
| W-11 | 398/32 | 3.22 | 77.29 | 7.06 | 87.57 |
| | | 8/2.48 | 6/0.08 | 26/3.68 | 40/0.46 |
| W-12 | 433/35 | 3.12 | 77.43 | 6.82 | 87.37 |
| | | 10/3.21 | 4/0.05 | 24/3.52 | 38/0.43 |
| W-13 | 485/52 | 2.84 | 78.02 | 7.10 | 87.96 |
| | | 10/3.52 | 10/0.13 | 41/5.77 | 64/0.73 |
| W-14 | 608/123 | only IR spectra were taken | | | |
| W-15 | 952/344 [d] | 2.74 | 78.42 | 7.02 | 88.18 |
| | | 10/3.65 | 8/0.10 | 70/9.97 | 88/1.00 |

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[a] For each sample the average experimental values $\phi_{exp}$ (in mass percent) of the corresponding determinations are given (above), followed by the standard deviation $\sigma$ (below, expressed in hundredths of a percent, e.g. 87 instead of 0.87), and the relative standard deviation $\sigma_{rel}$ (after the fraction line, expressed in % of $\sigma_{exp}$). The mean values of $\sigma_{rel}$ for all samples were 2.68% for $NH_4$, 0.26% for $UO_2$, and 4.96% for $CO_3$.

[b] Duration of the experiment since the beginning ($\Sigma$) or since the previous analysis ($\Delta$).

[c] The value determined by graphic interpolation; to it the relative deviation of $\sigma_{rel} = 5\%$ (see footnote a) was ascribed enabling us to calculate $\sigma$ together with other data for $\Sigma$(NUC).

[d] 467 days from W-13; from the beginning up to the end of the real decomposition, 520 days elapsed, i.e. $\Delta = 35$ days from W-13.

vagueness, some pertinent measurements were not performed (e.g. some carbon determinations, the IR spectra in the region of Nujol absorption, or a more precise determination of the final stage of the decomposition) and the experiments had to be terminated because the sample was used up. All these apparent shortcomings can be remedied only by repetition of the experiment.

The weathering itself was performed by spreading an AUC powder sample on a Petri dish covered by a sheet of filter paper. The sample was left in the air at room temperature and stirred approximately every three days.

The determinations of uranium (gravimetric), nitrogen (by absorption of $NH_3$ after sample decomposition), and carbon (by absorption of $CO_2$ after decomposition) were performed as in the previous work [5]. The assumed accuracies of $< 0.5\%$, $< 3\%$, and $< 5\%$, respectively, were confirmed in practice (see Table 1).

Most symbols are explained later in the text. The subscript s is used for the solid phase, g for the gaseous phase. The errors of the analytical determinations are expressed as the standard deviation $\sigma$ or the relative standard deviation $\sigma_{\mathrm{rel}}$.

## RESULTS

The data from the chemical analysis are collected in Tables 1 and 2 and their graphical presentation in Figs. 1 and 2. It can be shown that the spontaneous decomposition of AUC in air at room temperature is a three-stage process within the period of time studied. The observed chemical changes are linear within each of the three stages denoted A, B and C, and the equation $y = px + q$ is valid for each of them.

The quantities $n = \mathrm{N/U}$, $c = \mathrm{C/U}$, or the molecular weight $M_{\mathrm{w}}$ may be substituted for the dependent variable $y$ into this equation; $x$ stands for time and the relevant parameters $p$ and $q$, calculated by linear regression, are summarized in Table 3.

To determine the boundaries $x_{\mathrm{A/B}}$ and $x_{\mathrm{B/C}}$ between the stages A, B and C, the intercepts of the relevant straight lines were calculated (see Table 4). These are in a good agreement with the graphical presentation. Nevertheless the corresponding values of $y_{\mathrm{A/B}}$ and $y_{\mathrm{B/C}}$ can be determined only approximately because the assumption of exact linearity is certainly not fulfilled in the vicinity of both intercepts. In spite of this systematic simplification the calculated boundary values of $y$ were used for further calculations because no other value would have been better substantiated.

The end of stage C could not be determined exactly because of insufficient amounts of the sample. Its calculation was based on the data concerning sample W-15, for which only a slightly increased uranium content, compared to the previous analysis (467 days ago), was found (see Table 1).

TABLE 2

Chemical analysis—recalculated results [a]

| Sample | $n=$ N/U | $c=$ C/U | $(N/C)_s$ | OH/U | $H_2O/U$ | Molecular weight [b] ($M_w$) | Starting mass (%) |
|---|---|---|---|---|---|---|---|
| W-0 | 4.01 | 3.02 | 1.33 | −0.03 [e] | 0.25 [c] | 528.2 [d] | 100 |
| | 11/2.7 | 14/4.6 | | 26/1154 | 4.3/17.2 | 45.5/8.6 | |
| W-1 | 3.74 | 2.87 | 1.30 | 0 | 0.35 | 516.1 | 97.71 |
| | 5/1.3 | 14/5.0 | | 19/– | 6.0/17.2 | 44.5/8.6 | |
| W-2 | 3.55 | 2.72 | 1.31 | 0.11 [e] | 0.22 | 503.2 | 95.27 |
| | 10/2.8 | 16/5.8 | | 26/233 | 3.8/17.1 | 43.1/8.6 | |
| W-3 | 3.25 | 2.53 | 1.28 | 0.19 [e] | 0.20 | 487.4 | 92.28 |
| | 19/5.9 | 6/2.3 | | 25/133 | 3.5/17.3 | 42.1/8.6 | |
| W-4 | 2.98 | 2.32 | 1.28 | 0.34 | 0.06 | 469.9 | 88.96 |
| | 2/0.6 | 12/5.3 | | 14/41.2 | 0.6/10.5 | 24.7/5.3 | |
| W-5 | 2.35 | 1.73 | 1.36 | 0.89 | 0.59 | 442.0 | 83.68 |
| | 6/2.7 | 5/2.7 | | 11/12.5 | 5.3/9.0 | 19.9/4.5 | |
| W-6 | 1.82 | 1.34 | 1.36 | 1.14 | 0.62 | 413.9 | 78.36 |
| | 5/2.7 | 5/3.9 | | 10/8.9 | 5.9/9.5 | 19.8/4.8 | |
| W-7 | 1.46 | 1.03 | 1.42 | 1.40 | 0.64 | 393.6 | 74.52 |
| | 1/0.6 | 6/5.4 | | 6/4.6 | 4.4/6.9 | 13.5/3.4 | |
| W-8 | 0.89 | 0.63 | 1.41 | 1.63 | 0.71 | 364.4 | 68.99 |
| | 2/2.5 | 4/6.6 | | 6/3.9 | 5.6/7.9 | 14.4/3.9 | |
| W-9 | 0.67 | 0.42 | 1.60 | 1.83 | 0.84 | 353.5 | 66.93 |
| | 1/1.0 | 3/6.2 | | 3/1.8 | 4.1/4.9 | 8.7/2.5 | |
| W-10 | 0.66 | 0.41 | 1.61 | 1.84 | 0.81 | 352.4 | 66.72 |
| | 1/1.9 | 2/5.0 | | 3/1.7 | 3.5/4.3 | 7.5/2.1 | |
| W-11 | 0.62 | 0.41 | 1.51 | 1.80 | 0.72 | 349.4 | 66.15 |
| | 1/1.3 | 1/2.2 | | 2/0.9 | 2.1/2.9 | 5.1/1.5 | |
| W-12 | 0.60 | 0.40 | 1.50 | 1.80 | 0.74 | 348.8 | 66.04 |
| | 1/1.6 | 1/2.1 | | 2/1.0 | 2.2/2.9 | 5.1/1.5 | |
| W-13 | 0.55 | 0.41 | 1.34 | 1.73 | 0.67 | 346.1 | 65.52 |
| | 1/2.2 | 1/3.2 | | 2/1.4 | 2.1/3.1 | 5.4/1.6 | |
| W-15 [f] | 0.52 | 0.40 | 1.30 | 1.72 | 0.64 | 344.2 | 65.16 |
| | 1/2.5 | 2/5.0 | | 3/1.8 | 3.2/5.0 | 7.6/2.2 | |

[a] Initial values are taken from Table 1. Under each calculated value the standard deviation $\sigma$ (in hundredths, e.g. 11 instead of 0.11) and the relative standard deviations $\sigma_{rel}$ (in %, after the fraction line) are given. The value $(N/C)_s = n/c$ is the residual nitrogen to carbon molar ratio in the solid phase. The molar ratio OH/U was calculated from the electroneutrality condition: $OH/U = 2 + n - 2c$, $\sigma_{OH^-/U} = \sigma_n + \sigma_c$. The calculation of $H_2O/U$ and $M_w$ is described in the text. The standard deviation of $M_w$ values was calculated as the sum of all the components, the standard deviation of $H_2O/U$ estimated as double this value.

[b] Theoretical value of $M_w$ for sample W-0 is 522.26 [1]; our calculated value of 528.2 differs by 1.1%.

[c] Valid for experimental values; for $n = 4.0$, $c = 3.0$ and $U_{exp}$, $H_2O/U$ equals 0.33.

[d] The value of 524.4 was calculated by linear regression from the experimental points of the kinetic period A.

[e] The result has not a single valid figure.

[f] As for sample W-14; see Table 1.

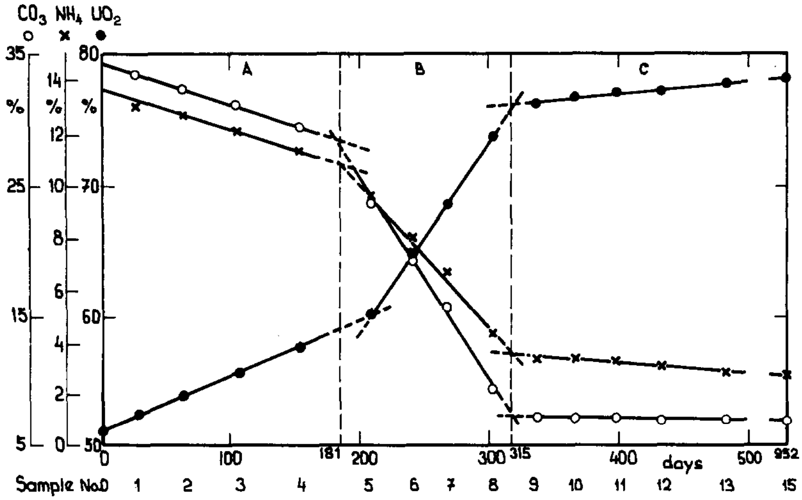

Fig. 1. Geometrical presentation of the direct analytical data.

This value did not agree with the straight line for stage C. The sample W-15 was therefore assumed to be stable (or metastable) and the uranium content of the sample was taken at the end of stage C. The overall period of decomposition was thus estimated to be about 520 days. The constant composition of the solid phase after 520 days was confirmed also by the determination of the other components, in a good agreement with the values obtained by linear extrapolation of $n = \mathrm{N/U}$ and $c = \mathrm{C/U}$.

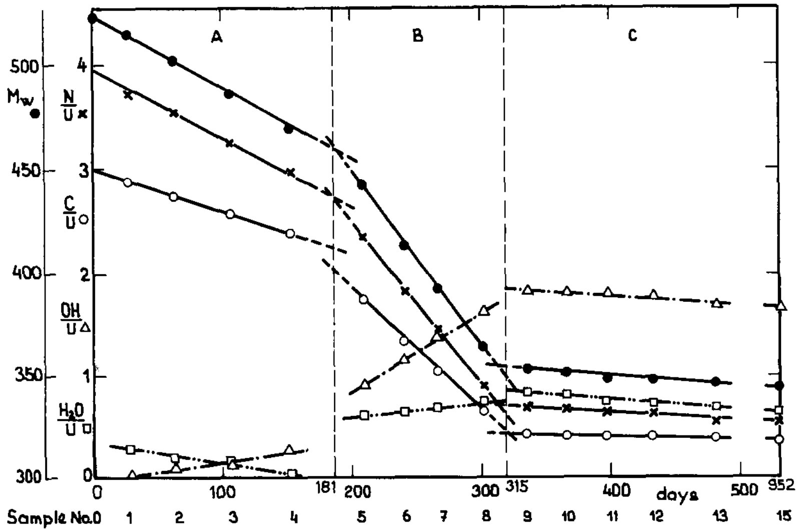

Fig. 2. Geometrical presentation of the recalculated analytical data.

TABLE 3

Data on kinetic stages [a]

| Kinetic stage | $y = \mathrm{N/U} = n$ | $y = \mathrm{C/U} = c$ | $y = M_w$ |
|---|---|---|---|
| A | $p = -0.0065856$ | $p = -0.0045111$ | $p = -0.34903$ |
| | $q = 3.970$ [b] | $q = 3.010$ [b] | $q = 524.4$ [b] |
| | $r = 0.9968$ | $r = 0.9995$ | $r = 0.9975$ |
| B | $p = -0.0155635$ | $p = -0.0118308$ | $p = -0.83030$ |
| | $q = 5.5948$ | $q = 4.1964$ | $q = 615.0$ |
| | $r = 0.9995$ | $r = 0.9999$ | $r = 0.9998$ |
| C | $p = -0.0008572$ | $p = -0.0000718$ | $p = -0.05007$ |
| | $q = 0.9650$ | $q = 0.4390$ | $q = 370.2$ |
| | $r = 0.9903$ | $r = 0.5902$ [c] | $r = 0.9834$ |

[a] In the linear relationship $y = px + q$, valid for each of the kinetic stages, $p$ = rate constant, $x$ = time; $r$ = correlation coefficient between $x$, $y$ variables.

[b] Compare with the theoretical values for the initial compound $n = 4.00$, $c = 3.00$, $M_w = 522.26$; the deviation is always less than 1%.

[c] Values of $c$ nearly constant in time.

Similar data could have been derived (with less accuracy owing to the analytical methods used) from the determination of ammonium groups. The determination of carbonate groups, however, cannot be used for this purpose as their content remains more or less constant during stage C.

The total of all the analyzed components Σ(NUC) in Table 1 amounts to 100% only for the initial sample, the difference from 100% increasing with time. This effect can be explained by the presence of some other component that was not determined by the chemical analysis. The requirement of electroneutrality for any chemical compound, present during the decomposi-

TABLE 4

Boundary values between the kinetic stages [a]

| $y$ | Calculated boundary values $x$ for various $y$ variables (days) | | Values of $y$ for: | |
|---|---|---|---|---|
| | $x_{A/B}$ | $x_{B/C}$ | $x = 181$ days, i.e. $y_{A/B}$ | $x = 315$ days, i.e. $y_{B/C}$ |
| $n$ | 181.0 | 314.8 | 2.78 | 0.70 |
| $c$ | 162.1 | 319.5 | 2.06 | 0.42 |
| $M_w$ | 188.3 | 313.7 | 461.2 | 354.5 |
| Selected boundary value $x$ | 181 | 315 | | |

[a] The subscripts A/B or B/C stand for the boundary values between the kinetic stages A and B, or B and C, respectively.

tion of AUC, can be expressed as $2 + n = 2c$, with the charge of cations on the left and that of anions on the right hand side of this equation. Substituting experimental data for $n$ and $c$ we found that in nearly all cases the positive charge prevailed. Thus, a negatively charged component that was not determined analytically had to be present. Supposing that this negative particle is hydroxyl (see Discussion below), the values of OH/U can be easily calculated, equalling $2 + n - 2c$.

Even after recalculation of the mass balance including the hydroxyl groups, the value of 100% was not reached. The samples were therefore assumed to contain water as a non-ionic component (see Discussion).

As the determination of uranium was the most precise, the content of the non-ionic component was calculated from the comparison of the experimental value of uranium content and the same quantity estimated from the sum of all ionic components (i.e. $NH_4^+$, $UO_2^{2+}$, $CO_3^{2-}$, and $OH^-$). The experimental value $U_{exp}$ was lower in all cases.

The content of the non-ionic component, expressed as the ratio $H_2O/U$, was apparently the least precise of all the components of the AUC solid phase as all experimental as well as computational errors are accumulated in it.

The resulting molecular weights $M_w$ were calculated, too, and are also given in Table 2.

The results discussed above characterized the composition of the solid AUC during various stages of decomposition. For a better understanding of the process it is appropriate to follow the composition of the volatile components, i.e. above all, the molar ratio $(N/C)_g$. The relevant values of the differences $(\Delta n)_g = (n_i - n_{i+1})_s$ and $(\Delta c)_g = (c_i - c_{i+1})_s$ can be evaluated from Table 1 for each experimental point. The average composition of the volatile component $\phi(N/C)_g$ for the three separate stages of the process can be calculated from these individual values. The same value of $\phi(N/C)_g$ can also be calculated from decomposition rates expressed for the individual points as $p(y)_i = (\Delta y/\Delta x)_i$ (where $y = n$ or $c$), from the equation $\phi(N/C)_g = p(n)_i/p(c)_i$ and, finally, the decomposition rate $p(y)$ can be calculated by linear regression (see Table 3).

The three techniques of the evaluation of the gaseous phase composition should, in principle, fit together well. Nevertheless, the third method enables us to calculate $\phi(N/C)_g$ even for stage C, where the former two methods fail because of zero values of the expressions in the denominator.

The numerical values calculated by the three given methods are shown in Table 5. It can be seen that the slight difference in the gaseous phase composition, observed for stages A and B, is statistically irrelevant. The value of $\phi(N/C)_g = 11.94$ for period C only means that ammonia is evolved much quicker than $CO_2$, the evolution rate of which is nearly zero.

The non-integer values of $\phi(N/C)_g$ for periods A and B can be explained if at least two parallel decomposition processes characterized by integer

TABLE 5

Characteristic of the composition of the volatile fraction

(A) Individual results

| Stage | $\Delta x$ (days) | $(\Delta y)_s$ [a] | $(\Delta n)_g$ [a] | $(\Delta c)_g$ [a] | $(N/C)_g = (\Delta n/\Delta c)_g$ | $\phi(N/C)_g$ | $p_n \times 10^3 = \Delta n/\Delta x$ | $\phi p_n \times 10^3$ | $p_c \times 10^3 = \Delta c/\Delta x$ | $\phi p_c \times 10^3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| A | 28 | W0 – W1 | 0.26 | 0.13 | 2.00 | 1.54 ± 0.30 | 9.29 | 6.91 ± 1.38 | 4.64 | 4.45 ± 0.18 |
| | 36 | W1 – W2 | 0.19 | 0.15 | 1.27 | | 5.28 | | 4.17 | |
| | 43 | W2 – W3 | 0.30 | 0.19 | 1.58 | | 6.98 | | 4.42 | |
| | 46 | W3 – W4 | 0.27 | 0.21 | 1.29 | | 5.87 | | 4.57 | |
| | 28 | W4 – $W_{A/B}$ | 0.20 | 0.26 | 0.77 [b] | | 7.14 | | 9.29 [b] | |
| B | 28 | $W_{A/B}$ – W5 | 0.43 | 0.33 | 1.30 | 1.31 ± 0.10 | 15.36 | 15.34 ± 1.01 | 11.79 | 11.83 ± 0.27 |
| | 32 | W5 – W6 | 0.53 | 0.39 | 1.36 | | 16.56 | | 12.19 | |
| | 26 | W6 – W7 | 0.36 | 0.31 | 1.16 | | 13.85 | | 11.92 | |
| | 35 | W7 – W8 | 0.57 | 0.40 | 1.43 | | 16.29 | | 11.43 | |
| | 13 | W8 – $W_{B/C}$ | 0.19 | 0.21 | 0.90 [b] | | 14.62 | | 16.15 [b] | |
| C | 21 | $W_{B/C}$ – W9 | 0.03 | 0.00 | – | [c] | 1.43 | 0.90 ± 0.17 | – | |
| | 30 | W9 – W10 | 0.01 | 0.01 | – | | 0.33 | | – | |
| | 32 | W10 – W11 | 0.04 | 0.00 | – | | 1.25 | | – | |
| | 35 | W11 – W12 | 0.02 | 0.01 | – | | 0.57 | | – | |
| | 52 | W12 – W13 | 0.05 | −0.01 | – | | 0.96 | | – | |
| | 344 [d] | W13 – W15 | 0.03 | 0.01 | – | | 0.86 | | – | |

(B) Averaged results

| $\phi(N/C)_g$ from data | stage A | stage B | stage C |
|---|---|---|---|
| $(\Delta n/\Delta c)_g$, Table 5 | 1.54 ± 0.30 (± 19.2%) | 1.31 ± 0.10 (± 7.6%) | – |
| $(\phi p_n/\phi p_c)_g$, Table 5 | 1.55 ± 0.20 (± 13.1%) | 1.30 ± 0.09 (± 6.9%) | – |
| $(p_n/p_c)_s$, Table 3 | 1.46 | 1.32 | 11.94 |

[a] $(\Delta y)_s = (y_i - y_{i+1})_s = (\Delta y)_g$, i.e. the change in composition of the solid determines composition of the volatile phase. The amount of evolved gaseous components is given by the decomposition equation $(y_0 - y)_s = -px + q$, valid for $y = n$ or $y = c$, $x$ being time. Hence, $dy/dx = p$ and $p_n/p_c = (dn/dx)/(dc/dx) = \Delta n/\Delta c = \phi(N/C)_g$.

[b] This value was not included in the respective average. Deviation of this value from the others might be connected with lack of precision in determination of the boundary limits between decomposition stages.

[c] For stage C, values of $(\Delta c)_g$ are practically zero, and $(N/C)_g$ cannot be calculated.

[d] For sample W-14 see Table 1.

values of $\phi(N/C)_g$ take place simultaneously. A quantitative verification of this hypothesis will be attempted in the following discussion.

## DISCUSSION

Three distinct kinetic periods of the AUC decomposition are apparent in all the following relationships, see Figs. 1 and 2, and Table 3. The fastest decomposition takes place during the second period B, the slowest one during the last period C. The ratios of the respective rate constants are given in Table 6 and it can be concluded that the ratios $p_A/p_B$ are practically independent of the variable ($n$, $c$, or $M_w$) used for the calculation. On the other hand, the other two ratios $p_A/p_C$ and $p_B/p_C$ are variable-dependent. Their values are similar for $n$ and $M_w$ whereas for the kinetic variable $c$ they are strikingly different. The mechanism of the third kinetic period of the AUC decomposition is most probably different from the first two periods as far as the $CO_2$ evolution is concerned.

The parameter $M_w$ can be regarded as the most complex one as experimental ($n$, $c$) as well as calculated (OH, U, $H_2O/U$) variables are included in its determination. The kinetic constants ratios in Table 6 calculated for $M_w$, are very similar to those for the parameter $n$ for all three stages of the decomposition, whereas for the parameter $c$ the agreement is limited to stages A and B. During stage C, the $c$ values are nearly constant in time and a low value of the correlation coefficient $r$ was therefore found for this parameter and stage C (see Table 3).

The boundary values $x_{A/B}$ and $x_{B/C}$ and the corresponding values of $y$ are given in Table 4. To characterize the degree of changes during the individual stages more objectively the values are also summarized in Table 7 together with some complementary data. It is apparent from these data that already during period A the changes in the composition of solid AUC are considerable. Nearly one third of the ammonia and the carbonate component were decomposed and the amount of water and hydroxyl ions in the solid phase became appreciable. The changes during period B were even more conspicuous although period B is shorter than period A (134 instead of

TABLE 6

Relative decomposition rates for individual kinetic stages

| Parameters calculated from variable | $p_A/p_B$ | $p_C/p_B$ | $p_C/p_A$ | $p_B/p_A$ | $p_B/p_C$ | $p_A/p_C$ |
|---|---|---|---|---|---|---|
| $n$ | 0.423 | 0.055 | 0.130 | 2.36 | 18.2 | 7.68 |
| $c$ | 0.381 | 0.006 | 0.016 | 2.62 | 164.8 | 62.82 |
| $M_w$ | 0.420 | 0.060 | 0.143 | 2.38 | 16.7 | 6.97 |

TABLE 7

Characteristics of the decomposition stages

| Variable | $y$ equal to | | | | Corresponds to atomic ratios in a cell [a] | | Remarks |
|---|---|---|---|---|---|---|---|
| $y$<br>$\Delta y$ | $n$ | $c$ | OH/U | $H_2O/U$ | $(N/U)_s$ | $(C/U)_s$ | |
| $y_0$ | 4.00 | 3.00 | 0 | 0 | 16/4 = 4 | 12/4 = 3 | Starting point |
| same (%) | 100 | 100 | 0 | 0 | | | |
| $y_{A/B}$ | 2.78 | 2.06 | 0.66 | ~ 0.56 [b] | 11/4 = 2.75 | 8/4 = 2.00 | Stage A (181 days) |
| $\Delta y_{0-A/B}$ | 1.22 | 0.94 | 0.66 [c] | ~ 0.56 [c] | | | |
| same (%) | 30.5 | 31.3 | – | – | | | |
| $y_{B/C}$ | 0.70 | 0.42 | ~ 1.8 [d] | ~ 0.8 [e] | 3/4 = 0.75 | 2/4 = 0.50 | Stage B (134 days) |
| $\Delta y_{A/B-B/C}$ | 2.08 | 1.64 | ~ 1.1 [c] | ~ 0.2 [c] | | | |
| same (%) | 52.0 | 54.7 | – | – | | | |
| $\Delta y_{0-B/C}$ | 3.30 | 2.58 | ~ 1.8 [c] | 0.8 [c] | 13/4 = 3.25 | 10/4 = 2.50 | Stages A + B (315 days) |
| same (%) | 82.5 | 86.0 | – | – | | | |
| $y_{15}$ | 0.52 | 0.40 | 1.72 | 0.64 | 2.1/4 = 0.52 | 1.6/4 = 0.40 | Stage C (values for W15 represent the final composition, i.e. the end of stage C), 205 days |
| $\Delta y_{B/C-y_{15}}$ | 0.18 | 0.02 | ~ 0.1 | ~ 0.2 | | | |
| $\Delta y_{0-y_{15}}$ | 3.48 | 2.60 | 1.72 [c] | 0.64 [c] | 13.9/4 = 3.48 | 10.4/4 = 2.60 | Stages A + B + C (520 days) |
| same (%) | 87.0 | 86.7 | – | – | | | |

[a] Four AUC molecules (i.e. 16, 4, or 12 atoms of N, U, or C respectively) within one structural unit.

[b] Determined by graphic extrapolation for period B; for period A no extrapolation could be made because of large experimental error of the respective points.

[c] Formally this value should be negative.

[d] By graphic extrapolation (1.76 from stage B, 1.83 from stage C).

[e] By graphic extrapolation (0.74 from stage B, 0.85 from stage C).

181 days). More than one half of the above components were decomposed.

The changes during the third period of decomposition are the least apparent (during 205 days only $< 5\%$ of ammonia and $< 1\%$ of the carbonate component were evolved). The final product of the decomposition is probably a hydroxy carbonate of approximate formula $(NH_4)_{0.52}[UO_2(CO_3)_{0.40}(OH)_{1.72}](H_2O)_{0.64}$ whereas the completely decomposed product should be, under our experimental conditions, so called dihydrate $UO_3 \cdot 2H_2O$ (or, more exactly [6] $UO_2(OH)_2 \cdot H_2O$). The composition of our (meta)stable decomposition product is really rather close to it.

Though the values of OH/U and $H_2O/U$ found during stage A are rather scattered (see Table 2), they are considered to be real, not fictional. For example, the initial values of the OH/U ratio are calculated as small differences between two large numbers with the experimental error comparable to the difference itself. A certain increasing trend with the proceeding decomposition is probably valid for the OH/U changes, which is presented in Fig. 2. For the $H_2O/U$ ratio some small non-zero values ($< 0.5$) should exist. All these estimates will be confronted later with results of IR spectroscopy.

The structural unit of the initial AUC consists of four uranyl complexes [7,8], i.e. of 16 nitrogen, 4 uranium and 12 carbon atoms. The ammonium groups are located in two different crystallographic positions (eight by eight). The first type of ammonium group is bound to the anionic complexes $[UO_2(CO_3)_3]^{4-}$ by four, the second one by six hydrogen bonds (two hydrogen atoms of these groups form two bridges each, the other two hydrogens only one bridge) [8]. The calculated boundary value of $n_{A/B} = 2.78$ agrees well with the composition of a solid phase with five of the sixteen ammonium groups decomposed (here the calculated value of $n = 11/4 = 2.75$, see Table 7).

It can thus be concluded that four ammonium groups are decomposed during stage A, and that while the fifth ammonium group is being decomposed a change in the reaction kinetics occurs. Period B comprises the splitting of another seven ammonium groups, and the value of $n = 1.00$ corresponds to the solid phase with twelve decomposed groups. By the decomposition of the thirteenth ammonium group ($n = 3/4 = 0.75$) another kinetic change is started, corresponding to the experimental value of $n_{B/C} = 0.70$. A numerical illustration of these considerations is given in Table 7. The carbonate decomposition is considered to be secondary and controlled by the ammonium content of the solid phase.

Any coordination of water molecules to uranium atoms is very improbable (see below). On the other hand, the coordination of hydroxyl groups is quite possible. Hydroxyl groups are formed in close proximity to uranium atoms by the decomposition of the unstable coordinated hydrogen carbonate according to the equation

$$U\text{–}(HCO_3^-) \rightarrow U\text{–}(OH^-) + CO_2$$

The facility of this decomposition may be the main reason for which no hydrogencarbonate uranium complexes have yet been identified (although the carbonate complexes are fairly stable) [5].

The hydroxyl group is incapable of any bidentate coordination and in the particular case of AUC it cannot even form a bridge because the distance between the uranium atoms of neighbouring complexes is too large (nearly 1500 pm in the carbonate ligands plane) [8]. The decomposition of a carbonate ligand must therefore lead (at least during the initial stages of the decomposition) to a decrease in average coordination number of uranyl. In the final stages of the decomposition, however, the possibility of hydroxyl bridge formation cannot be excluded as the distances amongst modified uranyl complex particles are considerably shorter.

As to the molecular structure of the investigated complex, bidentate carbonate ligands in AUC are coordinated to the equator of the uranium atom, the coordination number being six for uranyl (or eight for the uranium atom). The uranium atom lays in the centre of a hexagonal bipyramid formed by two axial oxygen atoms of uranyl and six equatorial carbonate oxygens.

Ammonium groups are in no immediate contact with uranium atoms and are bound in the lattice by strong hydrogen bonds [7,8]. The coordination number of uranyl $cN(UO_2)$ must be decreased by a decomposition of carbonate ligands unless the vacant coordination positions are reoccupied by decomposition products (i.e. hydroxyls or water molecules).

Any further considerations about the coordination number of uranyl groups are influenced by the following facts: If the decomposition were complete, the resulting solid phase should be formed (in view of the room temperature and the presence of air humidity during the experiment) by the so called dihydrate $UO_2(OH)_2 \cdot H_2O$, the molecular water of which is (as in precipitated sodium uranates [9]) bound between the layers of $UO_2(OH)_2$ and is not coordinated to uranium atoms [6,10]. (It is, in fact, zeolitic and not crystalline water.) Any coordination of water to the vacant coordination sites of uranium atoms during the AUC decomposition is therefore highly unlikely. The same should apply in the case of hydroxo carbonate final products (observed in our experiments) as the hydroxo uranyl phases are built on the same principles [10].

A detailed molecular structure of $UO_3 \cdot 2H_2O$ has not been reliably determined [10]. On the other hand the monohydrates were investigated thoroughly and they were shown to consist of octahedric units (uranyl oxygens in the apices, four hydroxyls in the square base, see e.g. Ref. 11 and the works cited there) with $cN(UO_2) = 4$. Because of the close relation [10] of the $UO_3$ phases containing water, the change of the uranyl coordination number from six to four during the later stages of decomposition cannot be excluded.

A numerical basis for similar considerations is given in Table 8. The

TABLE 8

Hypothetical coordination data of AUC samples

| Sample | $cN(UO_2) = 2c$ | $6-2c$ | $4-2c$ | $\frac{6-2c}{OH/U}$ | $\frac{4-2c}{OH/U}$ | Stage |
|---|---|---|---|---|---|---|
| W-0 | 6.04 | −0.04 | [a] | – | – | A |
| W-1 | 5.74 | 0.26 | [a] | – | – | |
| W-2 | 5.44 | 0.56 | [a] | 5.09 | – | |
| W-3 | 5.06 | 0.94 | [a] | 4.94 | – | |
| W-4 | 4.64 | 1.36 | [a] | 4.00 | – | |
| W-5 | 3.46 | 2.54 | 0.54 | 2.85 [b] | 0.61 | B |
| W-6 | 2.68 | 3.32 | 1.32 | 2.91 | 1.16 | |
| W-7 | 2.06 | 3.94 | 1.94 | 2.81 | 1.39 | |
| W-8 | 1.26 | 4.74 | 2.74 | 2.91 | 1.68 | |
| W-9 | 0.84 | 5.16 | 3.16 | 2.82 | 1.73 [c] | C |
| W-10 | 0.82 | 5.18 | 3.18 | 2.82 | 1.73 | |
| W-11 | 0.82 | 5.18 | 3.18 | 2.88 | 1.77 | |
| W-12 | 0.80 | 5.20 | 3.20 | 2.89 | 1.78 | |
| W-13 | 0.82 | 5.18 | 3.18 | 2.99 | 1.84 | |
| W-15 | 0.80 | 5.20 | 3.20 | 3.02 | 1.86 | |

[a] The results are negative.

[b] The average of all samples of stages B and C is 2.89 ± 0.07, i.e. ± 2.3%.

[c] The average of samples of stage C is 1.79 ± 0.05, i.e. ± 2.8%.

hypothetical uranyl coordination numbers equal to $2c$ (that should apply provided no recoordination occurred after some carbonate decomposition) are shown to become unjustifiably low for highly converted samples. Some bonding of hydroxyl ligands to the loose positions together with a certain tendency towards decreasing the uranyl coordination number can be expected.

For the sake of illustration, the number of vacant coordination positions $(6-2c)$ or $(4-2c)$, respectively, is also given in Table 8 for various AUC samples. The respective values are divided then by the OH/U ratio to learn the average number of contacts for each hydroxyl to keep the uranyl coordination number constant (and equal to its original value). It can be shown that $cN(UO_2)$ falls below six during stage A, but the value of four cannot be reached. More exactly, the coordination number of six is most probably preserved with a certain number of sites not saturated.

For stages B and C a possibility of decreased coordination numbers cannot be excluded. A constant value of $(6-c)/(OH/U)$ equal to $2.89 \pm 0.07$ (i.e. ± 2.3%) is characteristic for both kinetic periods, whereas the constant value of $(4-c)/(OH/U) = 1.79 \pm 0.05$ (i.e. 2.8%) applies only for period C. From the point of view of a chemist, the former case would represent prevailing triple bonding of the coordinated hydroxyls; the latter one, prevailing double bridges. Of course, even a complete numerical accordance could not be considered proof of the real arrangement in the complex solid phase. We tried only to set up the limits within which our concepts should remain.

## CONCLUSIONS

Chemical analysis confirms that dry AUC is not stable under laboratory conditions when stored in the air. Certain visual changes (colour, transparency of the crystals) are accompanied by a decrease in ammonium and carbonate content. Three different kinetic stages of decomposition were observed during about 520 days, characterized by their own constant decomposition rate, and about 87% of ammonia and carbonate present in the initial sample were lost at the end of the decomposition. It was concluded from the mass balance that two new solid phase components (one ionic and one non-ionic), most likely hydroxyl ion and molecular water, were formed during the decomposition.

About 30% of the unstable components were decomposed during the first stage lasting 181 days. During this period the coordination-deficient AUC solid phase probably arises, in which the number of bonds of the uranyl as the central ion is lower than the original value of six, the freed coordination places not being completely occupied by other ligands, e.g. by the hydroxyls formed.

More than one half of the unstable components were evolved during the second stage of the decomposition. This period took 134 days and was characterized by a maximum rate of decomposition and by a considerable increase in the hydroxyl and water content. In addition to the formation of a coordination deficit (without replacing the remaining ligands from their original positions), there is also a possibility of lowering the uranyl coordination number below six (forming a new coordination polyhedron of the remaining ligands). The reaction rate was strongly decreased (especially the carbonate decomposition one) during the third stage of the AUC decomposition, the end of which was determined only approximately due to the insufficient amount of the sample. The (meta)stable final product was uranyl hydroxo carbonate with a low carbonate content. Its chemical composition corresponds to the formula $(NH_4)_{0.52}[UO_2(CO_3)_{0.4}(OH)_{1.72}](H_2O)_{0.64}$ and is close to the compound $UO_2(OH)_2 \cdot H_2O$, the oxide phase stable under the given experimental conditions.

These conclusions from the chemical analysis will be confronted with the results of some physico-chemical measurements in further communications.

## REFERENCES

1 I.I. Chernyaev: Kompleksnye soedineniya urana, Nauka, Moscow, 1964.
2 L. Hälldahl and O.T. Sörensen, Thermochim. Acta, 29 (1979) 253.

3 F. Giollitti and V. Viacchiarelli, Gazz. Chim. Ital., 35 (1905) 170.
4 Č. Barta and V. Baran, unpublished results.
5 V. Baran, F. Škvor and V. Voseček, Inorg. Chim. Acta, 81 (1984) 83.
6 V.J. Wheeler, R.M. Dell and E. Wait, J. Inorg. Nucl. Chem., 26 (1964) 1829.
7 R. Graziani, G. Bombieri and E. Forsellini, J. Chem. Soc. Dalton Trans., (1972) 2959.
8 V.N. Serezhkin, M.A. Soldatkina and N.V. Boyko, Zh. Strukt. Khim., 24 (1983) 138.
9 V. Baran, J. Spalová and L. Šourková, J. Radioanal. Nucl. Chem. Lett., 95 (1985) 331.
10 H.R. Hoekstra and S. Siegel, J. Inorg. Nucl. Chem., 35 (1973) 761.
11 J.C. Taylor, J.W. Kelly and B. Downer, J. Solid State Chem., 5 (1972) 291.