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Decomposition–reduction stages of ammonium uranyl carbonates under different atmospheres

B.S. Girgis [a] and N.H. Rofail [b]

[a] *Physical Chemistry Department, National Research Centre, Dokki (Egypt)*
[b] *Nuclear Chemistry Department, Nuclear Research Centre, Atomic Energy Authority, Cairo (Egypt)*

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Abstract

Old and freshly-prepared ammonium uranyl carbonates (AUC) have been subjected to DTA–TG analyses, in the presence of H_2 or in air. In H_2 one endothermal and two exothermal effects are observed, whereas in air an endothermal effect only appears. Five kinetic equations (F_1, A_2, R_3, D_3 and SO) are applied to the TG waves and the integrated DTA peaks. In addition, the methods of Borchardt and Daniels (1957), Piloyan et al. (1966, 1967) and Poinsignon et al. (1982) are used with the DTA peaks. A second-order (SO) mechanism is proved by all methods to be the overall apparent endothermal reaction order, yielding the average activation energies of 105 kJ mol^{-1}, 83 kJ mol^{-1} and 102 kJ mol^{-1} for the old (in H_2) and fresh (in H_2 and air) AUC, respectively. Analysis of the TG waves yields much lower activation energies (85, 43 and 52 kJ mol^{-1}). The first (UO_3 to U_3O_8) and second (U_3O_8 to UO_2) reduction stages are associated with exothermic activation energies of 393, 334 kJ mol^{-1} and 379, 422 kJ mol^{-1} (for the fresh and old AUC, respectively). A first-order mechanism is the most probable mechanism controlling the reduction stages.

INTRODUCTION

Uranium carbonate occupies an important position in uranium chemistry. One of its practically stable forms is the complex anion $[UO_2(CO_3)_3]^{4-}$ which appears as a binary ammonium salt. A thermal analysis of tetrammonium uranyl tricarbonate (AUC) showed an endothermal DTA peak in the range 100–280 °C and a TG wave accompanied by a mass loss of 45.6% [1]. This was attributed to the theoretically calculated value due to the evolution of NH_3, CO_2 and H_2O. A small mass loss beyond 570 °C, of 1.35%, was associated with the dissociation of UO_3 to yield U_3O_8. Decomposition of AUC is generally represented by the equations

$$(NH_4)_4[UO_2(CO_3)_3] = 4NH_3 + 2H_2O + 3CO_2 + UO_3 \quad (1)$$

$$UO_3 = \tfrac{1}{3}U_3O_8 + \tfrac{1}{3}O \quad (2)$$

The end product in air/He is U_3O_8, whereas in H_2 it is UO_2 [2]. Hälldahl and Sörensen [2,3] suggested several intermediate hydrated amorphous products ($UO_3(H_2O)_x$; $x = 2.0–0.25$) that undergo stepwise dehydration. Through the reduction stages U_3O_8 was assumed to form between UO_3 and UO_2 in the presence of hydrogen [3,4]. This has been studied by TG, DSC, EM, X-ray and electron diffraction [5,6].

The investigation of AUC decomposition kinetics has not been reported in much detail in the literature. Recently, Qingren and Shifang [8] used a non-isothermal DSC method and solved the curves with a non-linear method. An Avrami–Erofeev equation $[-\ln(1-\alpha)]^{2/3}$ or ($A_{1.5}$) fitted best with an average apparent activation energy of 105 kJ mol^{-1}, under different conditions of particle size and heating rate. From the Kissinger method [9] and the Ozawa plots [10], the apparent activation energies were 98 and 95 kJ mol^{-1}, respectively.

Since decomposition of AUC is an intensely endothermal reaction ($\Delta H = 511$ kJ mol^{-1} [7,8]) this will aggravate the "zero time" effect of the isothermal TG method. Because of this, the non-isothermal TG and DTA methods are used in the present investigation. Two laboratory-prepared AUC samples (old and fresh) were tested for the three thermal effects. Kinetic analysis of the TG and DTA reactions was performed by applying well-established solid-state kinetic equations, to obtain associated activation energies.

This study aims to elucidate the thermal decomposition stages leading to the formation of UO_2 and the accompanying energy changes between the intermediate products.

EXPERIMENTAL

Ammonium uranyl carbonate (AUC) was precipitated in a closed stainless steel vessel attached to a feed system and a mixing chamber, and fitted with gas flowmeters, heater, pH electrode, circulating pump and a gas outlet. The reaction vessel was charged with 0.7 M $(NH_4)_2CO_3$ heated to 60 ° C, then a feed solution composed of 1.6 M uranyl nitrate + 1 M HNO_3 was introduced together with CO_2 in the same inlet to achieve good absorption of CO_2 in the reacting solution. The flow rate of the acidified uranyl nitrate solution was adjusted to 200 ml h^{-1} by the feed pump and CO_2 flow to 35 h^{-1}. After 5 min N_2 and NH_3 were admitted at the respective flow rates of 120 l h^{-1} and 60 l h^{-1}. The pH was adjusted throughout to 7.8–8.2, and fluctuations were regulated by changing the flow rate of NH_3. After addition of all the feed solution the precipitate was left for 20 min under gas flow with the circulating pump on. The flow of NH_3 was then switched off, the solution cooled to 30 ° C, and the gas supplies of CO_2 and N_2 switched off. The suspension was then filtered under reduced pressure, the AUC cake washed twice with 0.5 l of 1.5 M $(NH_4)_2CO_3$, twice with 0.5 l methanol, and was finally left to complete its drying at room temperature.

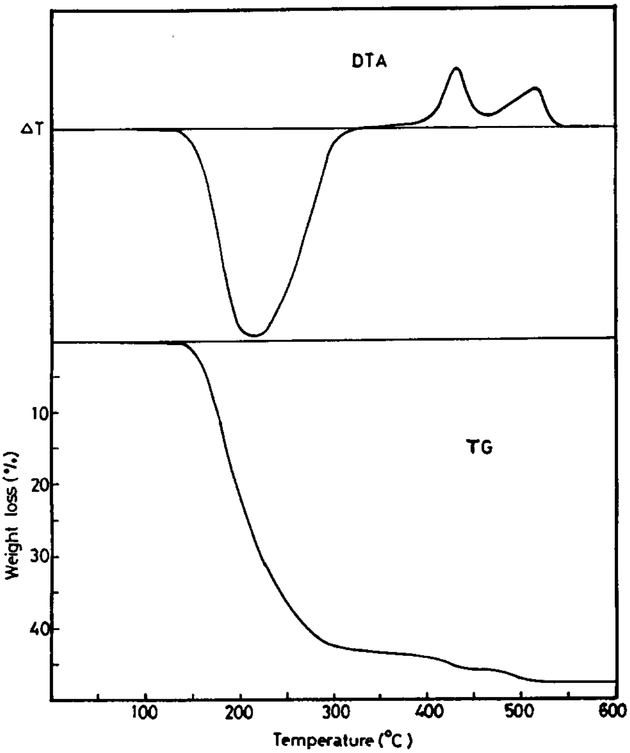

Fig. 1. Thermal analysis curves of stored AUC, under H_2 atmosphere.

Decomposition and reduction of AUC (fresh) was followed by DTA–TG using a Netzsch Thermal Analyzer at a heating rate of 5 deg min^{-1}, in air and H_2 atmospheres. Another sample of AUC, prepared earlier under same conditions and kept in a closed bottle for 2 years (old) was also subjected to thermal analysis in a H_2 atmosphere.

RESULTS AND DISCUSSION

Stages of decomposition

Figures 1–3 illustrate the DTA–TG tracings of AUC (old, H_2 atmosphere) and (fresh, H_2 and air atmospheres). The observed thermal effects and accompanying mass losses are summarized in Table 1.

Only one endothermic effect appears with a DTA peak maximum at 205–215 ° C for both materials, and under the two atmospheres. Under the H_2 atmosphere two exothermic effects appear with peak maxima at 430–445 ° C and 515–525 ° C. The first prominent endotherm is associated with the evolution of NH_3, CO_2 and H_2O to yield UO_3. The first exothermic effect is ascribed to the transformation of UO_3 to U_3O_8 and its crystalliza-

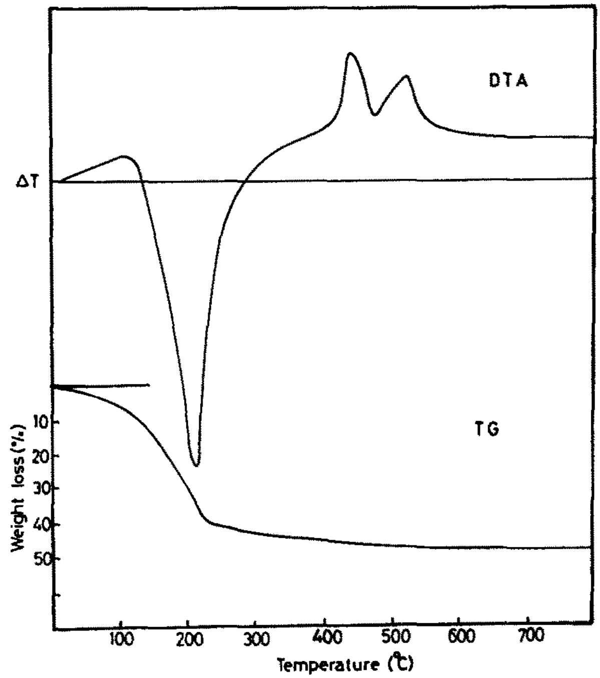

Fig. 2. Thermal analysis curves of fresh AUC, under H_2 atmosphere.

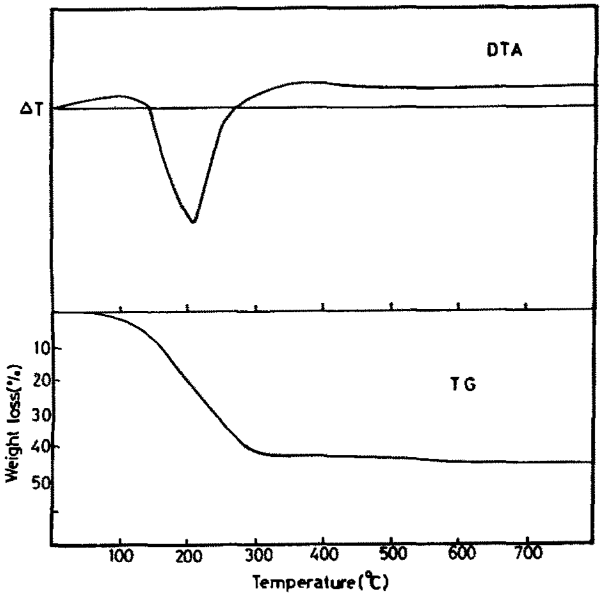

Fig. 3. Thermal analysis curves of fresh AUC, in presence of air.

TABLE 1

Features of the TG and DTA waves

Sample	Analysis	Atmosphere	Description of thermal effects
Old AUC	TG	H_2	≤ 350 °C = 43.8%, ≤ 450 °C = 46.4%, ≤ 700 °C = 48.4%
	DTA	H_2	endo 215 °C, exo 430 °C, exo 515 °C
Fresh AUC	TG	H_2	≤ 350 °C = 43.8%, ≤ 450 °C = 46.4%, ≤ 700 °C = 48.0%
		Air	≤ 350 °C = 42.7%, ≤ 450 °C = 43.4%, ≤ 700 °C = 45.2%
	DTA	H_2	endo 205 °C, exo 445 °C, exo 525 °C
		Air	endo 210 °C

tion, whereas the second exotherm is associated with the reduction of U_3O_8 to UO_2 [2,3]. The end product in air is U_3O_8 but in the presence of H_2 it is UO_2.

The endothermic peak varies to some extent between different investigators, namely 185–210 °C [7,12]. The accompanying mass loss in the range of 100–300 °C also varies between 43.5% and 45.6% [2,7,8,12]. This difference may be ascribed to the assumed formation of intermediate hydrated amorphous products ($UO_3(H_2O)_x$; $x = 1.5–0.25$) suggested by Hälldahl and co-workers [2,3,6,13]. The first exothermal reaction (between 350 and 450 °C) exhibits a mass loss of 2.4–2.6%; the second shows a mass loss of 1.6–2.0%. The former appears to be much higher than the stoichiometric loss in the reaction $UO_3 \rightarrow U_3O_8$ [21], whereas the latter agrees well with the reduction of U_3O_8 to UO_2.

It should be noted that although the primary vigorous decomposition stage shows a DTA peak at 200–210 °C, the complete evolution of NH_3, CO_2 and H_2O needs a long time due to diffusion of the gases [11]. The evolved species are partly adsorbed by the amorphous UO_3 matrix. Besides, the possible formation of the intermediate partially hydrated UO_3 could account for this observation [2,13]. A complete transformation of AUC to UO_3 corresponds to a mass loss of 45.2%. Hälldahl and co-workers [2,13] suggested that at 350 °C a composition corresponding to $UO_3(H_2O)_{0.25}$ exists which accounts for a mass loss of 44%, in addition to some carbonate and ammonia species detected by chemical analysis. They assumed stepwise decomposition, involving various hydrated products, to take place at high temperatures and in a sufficiently reducing atmosphere UO_2 is formed as end product [3].

The decomposition reactions leading to U_3O_8 are generally endothermal. However, the exothermic formation of H_2O from oxygen set free in the dissociation reaction $UO_3 \rightarrow U_3O_8$, in the presence of H_2, leads to the apparent exothermic DTA effect absent in air [2].

TABLE 2

Linear regression parameters of the endothermal effect

Atmosphere	Function	TG			DTA		
		$-r$	S_e	E_a (kJ mol^{-1})	$-r$	S_e	E_a (kJ mol^{-1})
Stored AUC							
H_2	F_1	0.96534	12.6	58.6	0.98209	11.6	70.3
	A_2	0.99566	2.3	30.2	0.98193	4.6	35.1
	R_3	0.94664	14.0	51.8	0.96265	7.4	64.5
	D_3	0.94736	27.9	103.6	0.96857	20.8	125.0
	SO	0.99474	7.4	85.0	0.99679	5.8	100.3
Freshly prepared AUC							
H_2	F_1	0.99121	6.3	31.7	0.97956	9.7	56.1
	A_2	0.991204	3.1	15.8	0.97964	4.9	28.3
	R_3	0.98956	6.2	28.5	0.96705	10.9	49.8
	D_3	0.96581	18.5	57.3	0.96755	22.0	99.8
	SO	0.99018	9.1	43.1	0.99833	4.1	80.4
Air	F_1	0.98030	9.6	37.0	0.97409	11.1	69.4
	A_2	0.98017	4.8	18.5	0.97362	5.5	34.7
	R_3	0.97160	10.7	33.0	0.95952	12.3	61.6
	D_3	0.97823	18.6	66.5	0.95993	24.5	123.3
	SO	0.97385	15.5	51.8	0.99755	8.9	100.1

Kinetics of decomposition / reduction stages

For this purpose, the method outlined by Satava and Skvara [14], which correlates log $g(\alpha)$ functions for different solid state reaction mechanisms with $1/T$, was employed. The best straight line fit indicates the most probable kinetic equation. Testing for data linearization was made by a least squares linear regression analysis. Two parameters are estimated throughout, the correlation coefficient (r) and the standard error of estimate (S_e). Five kinetic equation functions were tested; these are denoted by F_1, A_2, R_3, D_3 and second-order (SO) mechanisms. This choice was based on previous experience with decomposition of various solids [16–19] and suggested by others [3,15]. Every TG wave was transformed into a percentage conversion-temperature curve, and the integrated DTA peaks were likewise transformed [20].

First endothermal decomposition

The obtained data are cited in Table 2, for the old and freshly prepared AUC samples. The integrated DTA peaks always yield higher activation energies, especially so for the thermograms determined in air. Generally, the SO equation seems the best to describe the endothermal decomposition, as judged by the higher r values and lowest data dispersion S_e. The

D_3 mechanism (Jänder equation) claimed previously by Hälldahl and Sörensen [3] to fit decomposition, appears the least suitable in comparison to the other mechanisms.

The activation energies for decomposition in air are invariably higher than those estimated from thermograms in the presence of hydrogen. These are 52 and 100 kJ mol^{-1} in comparison to 43 and 80 kJ mol^{-1}. The difference in absorbed energy was ascribed [2] to a possible decomposition of NH_3 to yield H_2 which is subsequently involved in the formation of H_2O

$$NH_3 \overset{+E}{\rightleftharpoons} \tfrac{3}{2}H_2 + \tfrac{1}{2}N_2$$

and that in the presence of H_2 such a reaction is not favoured. It is noticeable that the old AUC invariably shows higher activation energies in comparison to the fresh AUC. Such aged solid differs from the fresh solid which decomposes more easily. Moreover, the activation energies of the old AUC from both thermal analysis techniques are comparable (15–20%). It is remarkable to note that analysis of the DTA peaks yields identical E_a values for both AUC samples, in the cases of the five tested kinetic equations.

Exothermic reaction stages

Two such stages appear in H_2 atmosphere, and activation energies were estimated only from the integrated DTA peaks due to the very small mass changes associated with these stages in TG curves.

The first exothermic stage, ascribed to the dissociation (or reduction) of UO_3 to U_3O_8 [22], estimates 40% higher E_a by the freshly-prepared AUC in comparison to the old sample (Table 3).

TABLE 3

Linear regression parameters of the exothermic reduction stages estimated from integrated DTA peaks

Reaction	Function	Old AUC			Fresh AUC		
		$-r$	S_e	E_a (kJ mol^{-1})	$-r$	S_e	E_a (kJ mol^{-1})
1st Exothermic	F_1	0.98939	7.5	266	0.97645	10.4	374
	A_2	0.98929	3.5	133	0.97497	5.4	187
	R_3	0.99271	5.1	240	0.96718	11.1	333
	D_3	0.96384	12.7	481	0.97106	21.1	669
	SO	0.98806	7.6	366	0.98070	13.3	528
2nd Exothermic	F_1	0.99593	4.4	405	0.99836	2.8	409
	A_2	0.99489	2.5	202	0.99630	2.1	204
	R_3	0.98883	6.6	362	0.98569	7.3	363
	D_3	0.99110	11.6	725	0.99055	11.8	730
	SO	0.99114	9.1	567	0.99958	5.8	579

TABLE 4

Analysis of the DTA peaks by methods correlating the peak amplitude or peak area with temperature of reaction

Method	Reaction order, n	Parameter	Old AUC (H_2)			Fresh AUC (H_2)			Fresh AUC (air)
			Endo	1st Exo	2nd Exo	Endo	1st Exo	2nd Exo	Endo
Borchardt and Daniels [23]	1	E_a	59	360	434	66	406	365	81
		Range	0.06–0.98	0.08–0.98	0.05–0.95	0.06–0.65	0.05–0.95	0.02–0.98	0.05–0.80
	2	E_a	107			88			103
		Range	0.01–0.98			0.01–0.98			0.01–0.98
Piloyan et al. [24,25]	1	E_a	62	340	423	68	388	363	75
		Range	0.03–0.96	0.08–0.97	0.03–0.95	0.02–0.62	0.01–0.97	0.03–0.97	0.02–0.81
	2	E_a	105			84			100
		Range	0.01–0.97			0.02–0.95			0.01–0.97
Poinsignon et al. [26]	1	E_a	63	330	426	67	405	378	72
		Range	0.03–0.96	0.07–0.97	0.02–0.95	0.02–0.72	0.04–0.97	0.03–0.97	0.04–0.72
	2	E_a	107			78			103
		Range	0.01–0.97			0.02–0.95			0.01–0.95

Confirmation of the predominant reaction order

Three traditional mathematical procedures were applied in order to check the rate-controlling reaction order. These are the methods of Borchardt and Daniels [23], Piloyan et al. [24,25], and that outlined by Poinsignon et al. [26]. The functions $\ln[\Delta T/(A-a)^n]$, $\ln[\Delta T/(1-\alpha)^n]$ and/or $\ln[(d\alpha/dt)/(1-\alpha)^n]$ were plotted versus $1/T$ [27]. Basically all these methods assumed and applied the first-order form with $n = 1.0$; accordingly the evaluated E_a values as well as the range of linear fit are cited in Table 4. The activation energies estimated by the three methods are generally the same within small differences. The outstanding feature is the unsatisfactory range of application of the three mathematical expressions, in case of the endothermal reaction ($\alpha = 0.05$–$0.60/0.80$). This appears in particular with the fresh AUC sample (in air and H_2). Both exothermic reactions exhibit very satisfactory linear relationships covering

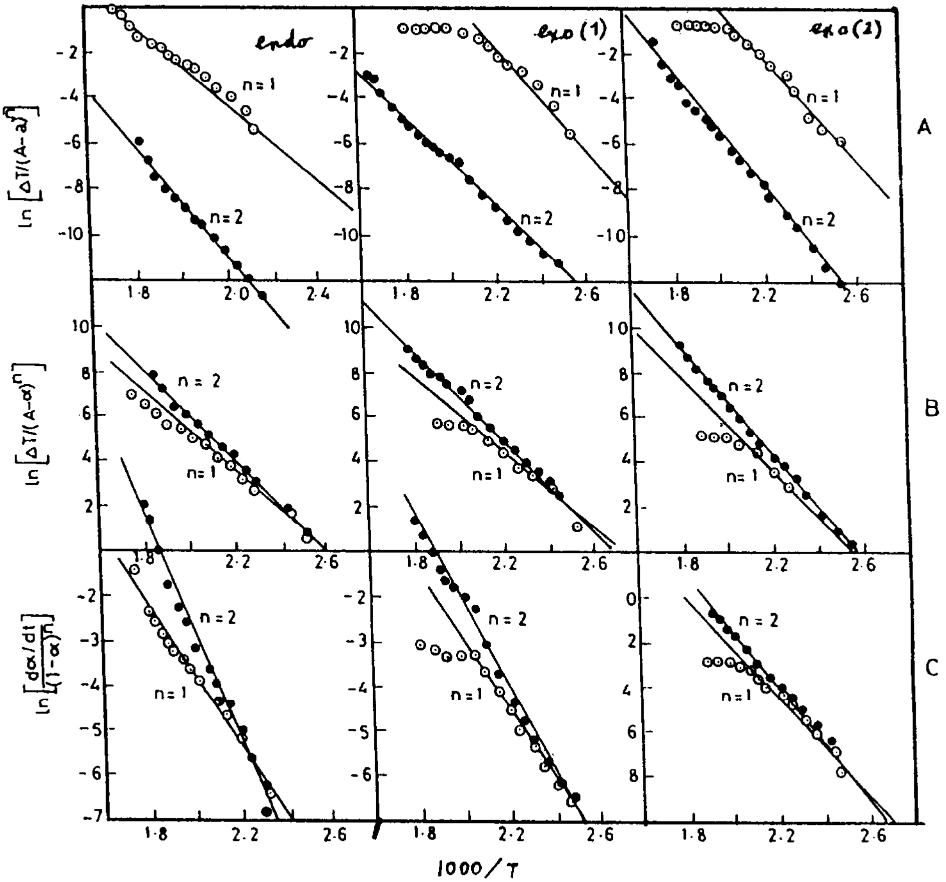

Fig. 4. Linear correlations of the methods of (A) Borchardt and Daniels [23], (B) Piloyan et al. [24,25], and (C) Poinsignon et al. [26], applied to the three DTA peaks.

the whole DTA peaks within $\alpha = 0.03$ and 0.97. This confirms the first-order reaction mechanism that governs these oxide dissociation stages (Table 3).

Referring to Table 2, it appears that the second-order kinetic equation (SO) shows better fit to the endothermal decomposition stage. Accordingly, plotting of the three abovementioned expressions was tried in the second order form with $n = 2$, for this stage (Fig. 4). Very satisfactory straight lines are observed covering the whole decomposition range ($\alpha = 0.02$–0.98) associated with higher activation energies (Table 4). This also confirms the previously suggested order of reaction as apparent from the data in Table 2.

CONCLUSIONS

The principal decomposition reaction of AUC, to yield CO_2, NH_3 and H_2O, is a complex process which involves many simultaneous and consecutive stages. These include evolution of the three gaseous products, with the possible dissociation of $2NH_3 \rightarrow 3H_2 + N_2$ and the stepwise dehydration of the intermediate hydrated UO_3 products. These combine to show an overall apparent second order of reaction. The old AUC exhibits a high mean endothermal energy of 105 kJ mol^{-1} as compared to 83 kJ mol^{-1} needed by the freshly-prepared solid (both in hydrogen). Decomposition of the fresh AUC in air is associated with a higher mean activation energy of 102 kJ mol^{-1}.

Exothermic reduction of fresh AUC releases higher energy in the primary stage (UO_3 to U_3O_8) than the old solid (393 and 334 kJ mol^{-1}). In the second reduction (U_3O_8 to UO_2) the fresh solid shows a lower energy than the old AUC (viz. 379 and 422 kJ mol^{-1}).

It is notable that in all cases the activation energies estimated from the TG wave loss are considerably lower than those evaluated by any of the DTA-peak procedures of analysis (85–105, 43–83, and 52–102 kJ mol^{-1} for the old and fresh samples, respectively).

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