

of the acetonitrile, was fractionated through a spinning band column (18-inch by 6-mm. I.D.), and a cut of 17 grams (61% yield) was taken at 151° C. (n_D^{20} 1.3340) (lit. (4) b.p. 157–159° C., n_D^{20} 1.3350). This cut gave a single sharp peak on gas-liquid chromatography (25% LAC on Chromosorb W, 6 feet by 1/4 inch, 85° C., 37.2 ml. per min. of helium, retention time 19.0 minute). An additional fraction (2.2 grams) was found to be 90% pure (total yield of product 68%). I.R. $\lambda_{\text{max}}^{\text{film}}$ strong CF_2 absorption between 8 and 9 μ , no OH absorption.

Because of the discrepancy between the reported boiling point (4) and that found in this work, and because of the difficulties encountered in obtaining reproducible elemental analyses, the NMR and mass spectra are reported.

NMR (τ) (in CDCl_3 on a Varian HR60 spectrometer). 6.24 (2 protons, triplet, J_{HF} 15 cps, CH_2Br), 3.96 (1 proton, 3 triplets, J_{HF} gem. 51.9 cps, J_{HF} vic. 5.00 cps, CHF_2). Mass spectrum (on a CEC 21-103C). Calcd. for $\text{C}_7\text{H}_3\text{F}_{12}\text{Br}$: parent mass 394; parent + 1, 7.61% of parent; parent + 2, 98.0% of parent. Found: parent mass 394; parent + 1, 7.36% of parent; parent + 2, 96.5% of parent. Principal peaks at mass 143 ($\text{CF}_2\text{CH}_2^{79}\text{Br}^+$), 145 ($\text{CF}_2\text{CH}_2^{81}\text{Br}^+$), 93 ($\text{CH}_2^{79}\text{Br}^+$), 95 ($\text{CH}_2^{81}\text{Br}^+$), 51 (CHF_2^+).

Anal. Calcd. for $\text{C}_7\text{H}_3\text{F}_{12}\text{Br}$: C, 21.30; H, 0.77; F 57.75; Br, 20.21. Found: C, 21.0 (average of 4 analyses); H, 1.16 (average of 4 analyses); Br, 20.56.

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LITERATURE CITED

- (1) Baer, D.R., *Ind. Eng. Chem.* **51**, 829 (1959).
- (2) Dannley, R.L., Weschler, J.R., Jackson, G.R., Jr., *J. Am. Chem. Soc.* **77**, 3643 (1955).
- (3) Faurote, P.D., Henderson, C.M., Murphy, C.M., O'Rear, J.G., Ravner, H., *Ind. Eng. Chem.* **48**, 445 (1956).
- (4) Faurote, P.D., O'Rear, J.G., *J. Am. Chem. Soc.* **78**, 4999 (1956).
- (5) Knunyants, I.L., Chen, Tsin-Yun, Gambaryan, N.P., Rokhlin, E.M., *Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva* **5**, 114 (1960); *CA* **54**, 20962i (1960).
- (6) Krogh, L.C., Reid, T.S., Brown, H.A., *J. Org. Chem.* **19**, 1124 (1954).
- (7) Tiers, G.V.D., Brown, H.A., Reid, T.S., *J. Am. Chem. Soc.* **75**, 5978 (1953).
- (8) Wiley, G.A., Hershkowitz, R.L., Rein, B.M., Chung, B.C., *Ibid.*, **86**, 964 (1964).

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Thermal Denitration of Uranyl Nitrate Hexahydrate

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The thermal decomposition of uranyl nitrate hexahydrate was studied in the temperature range of 250° to 400° C. at atmospheric and at <0.1-mm. pressure. The intermediate and final products of the decomposition were determined. The denitration follows a zero-order reaction until less than half of the uranyl nitrate remains. The specific reaction rate constants were measured for denitration, and from these data the heats and entropies of activation were calculated.

THE THERMAL DECOMPOSITION of uranyl nitrate hexahydrate (UNH) is an important process in the nuclear energy industry. This material, isolated as an intermediate from spent reactor fuel, is thermally decomposed to uranium trioxide. The trioxide is reduced by hydrogen to the dioxide, which is subsequently hydrofluorinated. Although uranyl nitrate hexahydrate has been processed for years in this manner, the over-all operation has presented various difficulties. One of the problems is the wide range of reactivity toward hydrofluorination of different batches of uranium trioxide.

Lack of information about the decomposition of uranyl nitrate hexahydrate gave rise to a number of uncertainties about process performance. Therefore, a program was initiated to elucidate the mechanism of the decomposition, identify the intermediate products, and determine the kinetics of denitration at temperatures up to 400° C.

Early in the century, uranyl nitrate prepared by the dehydration of the hexahydrate was reported to contain the di- and trihydrate (11, 15). These findings were later verified by several methods including phase relationships (12) and vapor pressure measurements (8). The presence of anhydrous uranyl nitrate has been reported in thermolysis measurements of uranyl nitrate hexahydrate (16) and in the thermal decomposition of uranyl nitrate dihydrate (13). Methods of preparation for the hexa-, tri-, and dihydrates (10) as well as anhydrous uranyl nitrate (5) are readily available.

Five crystalline polymorphs of UO_3 (α - ϵ) and one amorphous form are known and have been prepared (7). There are also four monohydrates (α - δ), two dihydrates (α - β), and a hemihydrate (9). All of these would not be expected to be final products in the thermal decomposition of UNH, because of their thermal instability (3). Industrially, γ - UO_3 is the usual product of the

thermal decomposition of uranyl nitrate hexahydrate. The desired product is a form of UO_3 that reacts at a consistent rate during hydrogen reduction and subsequent hydrofluorination.

DISCUSSION

Experimental. An analysis of the reagent grade uranyl nitrate hexahydrate was performed by ignition of this salt to U_3O_8 . This method gave a value of 47.49 wt. % uranium *vs.* the theoretical value of 47.41 wt. %.

Ten grams of UNH were decomposed in each experiment. Crystals of UNH were ground to produce a homogeneous system with respect to crystalline size; this grinding process eliminated the necessity of choosing well-defined crystals and provided a consistent starting material. The salt was heated in an all-glass system with a bath of Woods metal. Samples were heated both under vacuum (<0.1-mm. pressure) and at atmospheric pressure at temperatures ranging from 250° to 400° C. The decompositions at atmospheric pressure were made with nitrogen flowing through the system at a rate of 30 cc. per minute. The pressure was maintained within 5 mm. of ambient pressure in order to simulate plant conditions for the production of uranium trioxide.

Volatile products of decomposition were collected in a closed all-glass system. A trap cooled with liquid nitrogen was used to collect condensable products. At the end of each decomposition the gaseous products were transferred through a drying tube of magnesium perchlorate to calibrated storage bulbs for analysis by infrared and mass spectroscopy. The transfer was made under conditions that prevented HNO_3 volatilization. Pressure in the bulbs was measured with a Bourdon gage (6).

The water that was released during thermal decomposition was determined by adding the gain in weight of the drying tube and the weight of water remaining in the trap. The amount of water in the trap was obtained by subtracting the weight of nitric acid, as determined by titration, from the total weight of the contents of the trap.

The intermediate and the final products are tabulated in Table I. The intermediates were identified by infrared and x-ray diffraction spectra. The final products obtained by the thermal decomposition of uranyl nitrate hexahydrate were identified primarily by two methods—x-ray diffraction and ignition. Other data (14) show the formation of $\text{UO}_3 \cdot 0.5\text{H}_2\text{O}$ as a product in the decomposition of uranyl nitrate trihydrate at 210° C.

Spectral data for the compounds are available in the literature (1, 2, 13).

Results. The amounts of water and uranyl nitrate remaining in the reaction vessel at the designated times during the decompositions are shown in Figure 1. Water was determined as described in the previous section. The quantity of nitrogen-containing compounds, expressed as anhydrous uranyl nitrate, was derived as the difference between the original amount of uranyl nitrate and the sum of the quantities of nitrogen compounds in the storage bulbs and in the cold trap.

The data for the thermal denitration under vacuum and at atmospheric pressure do not follow simple kinetics. Under vacuum at 250° and 300° C., the first half of the denitration follows a zero-order reaction. At 350° and 400° C. the first three fourths of the denitration follows a zero-order reaction. Plots of these data are shown in Figure 1A and B. A comparison of the curves of data taken under vacuum (Figure 1A and B) and at ambient pressure (Figure 1C and D) shows that, over the temperature range studied, the reactions are pressure-dependent. The rates generally increase with increasing temperature, and under isothermal conditions, the rate at atmospheric pressure is always greater than the rate under vacuum.

The data in Figure 1 show α (fraction decomposed) *vs.* t (time).

$$\text{Since } \alpha = \frac{C_0 - C}{C_0}$$

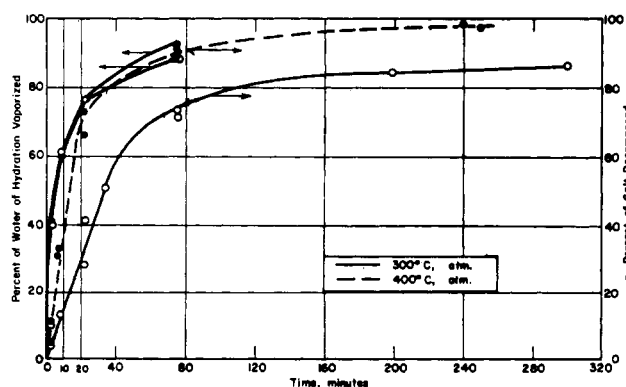
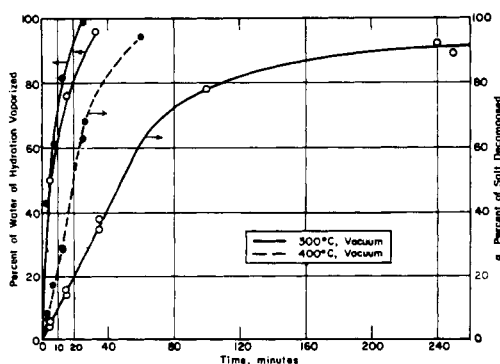
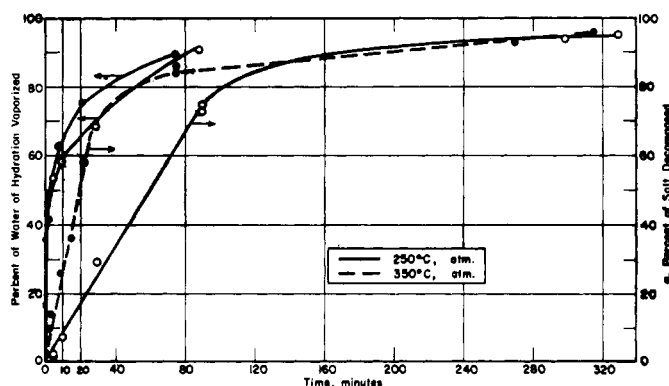
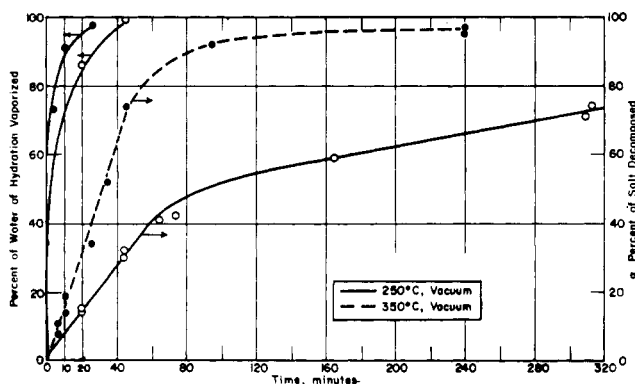


Figure 1. Thermal denitration of uranyl nitrate hexahydrate

- A. 250° and 350° C., vacuum (upper left)
 B. 300° and 400° C., vacuum (lower left)

- C. 250° and 350° C., atm. (upper right)
 D. 300° and 400° C., atm. (lower right)

Table I. Thermal Decomposition Intermediate and Final Products

Temp., ° C.	Pressure	Intermediates	Final Products
250	Vac.	UO ₂ (NO ₃) ₂ ·3H ₂ O, UO ₂ (NO ₃) ₂ ·2H ₂ O, UO ₂ (NO ₃) ₂ , UO ₂ (OH)NO ₃	UO ₃ (amorphous)
400	Vac.	UO ₂ (NO ₃) ₂ ·2H ₂ O, UO ₂ (NO ₃) ₂ , UO ₂ (OH)NO ₃	UO ₃ (amorphous)
250	Atm.	UO ₂ (NO ₃) ₂ ·3H ₂ O, UO ₂ (NO ₃) ₂ ·2H ₂ O, UO ₂ (OH)NO ₃ , UO ₂ (NO ₃) ₂	γ - UO ₃
400	Atm.	UO ₂ (NO ₃) ₂ ·3H ₂ O, UO ₂ (NO ₃) ₂ ·2H ₂ O, UO ₂ (NO ₃) ₂ , UO ₂ (OH)NO ₃	UO ₃ ·0.5H ₂ O β + γ - UO ₃

and for a zero-order reaction $-\frac{dC}{dt} = k$, or $C = -kt + c$

where C_0 = original concentration
 C = concentration at a given time
 k = specific reaction rate

$$\text{then } \alpha = 1 - \frac{C}{C_0}$$

$$= 1 - \frac{1}{C_0}(-kt + c)$$

$$= \frac{kt}{C_0} + c'$$

and slope = $\frac{\alpha}{t}$ or $\frac{k}{C_0}$

Therefore $k = \text{slope} (C_0)$

The values of k calculated from Figure 1 are shown in Table II.

The reaction must be catalyzed by one of the volatile products of the reaction; however, there should be some sigmoid character to the denitration curve when the fraction decomposed is plotted against time. The sigmoid character was not observed until crystals of random size larger than 50 mesh were decomposed. Then a definite but short induction period was observed (Figure 2). A shortened period of induction is typical when crystal size is reduced. Apparently grinding the crystals changed the induction period to less than 3 minutes at any given temperature; samples were not taken before the reaction had progressed 3 minutes to allow thermal equilibrium to become established. The induction period and the difference in rates at different pressures showed that the reaction is autocatalytic.

At the initiation of decomposition of a solid, Garner and Pike reported nucleation mainly at the surface, as shown by photographs in studies of the decomposition of copper sulfate pentahydrate (4). The portions of data that follow zero order are in agreement with this information. The nucleation should occur at some type of crystal lattice imperfection and should produce a new surface layer with a different structural formation which has a higher energy at the phase boundary. This situation results in a less stable molecule, so that the amount of energy that must be added to the molecule to reach the activated state is decreased. The decomposition then changes from a surface nucleation reaction to an expansion of the nuclei into the crystal by a phase-boundary reaction. Ideally, the phase-boundary reaction should spread uniformly into an isotropic medium and must follow zero-order kinetics.

The point at which the denitration reaction stops following zero-order kinetics (50 to 75% denitration) also corresponds to the point at which 99% of the water initially present during vacuum denitration and about 90% of the water initially present during denitration at atmospheric pressure are vaporized. At this point the reaction rate rapidly decreases, showing that the first part of the reaction is autocatalytic with respect to water or nitric acid but not oxides of nitrogen.

Table II. Specific Reaction Rates

Initial 50 to 75% of reaction

Temp., ° C.	Vacuum Rate, Min. ⁻¹	Atm. Pressure Rate, Min. ⁻¹
250	0.0135	0.0171
300	0.0212	0.0312
350	0.0322	0.0543
400	0.0520	0.0788

Table III. Heats and Entropies of Activation

Pressure	ΔH*	ΔS*
Vacuum	5.1	-32
Atmospheric	6.2	-29

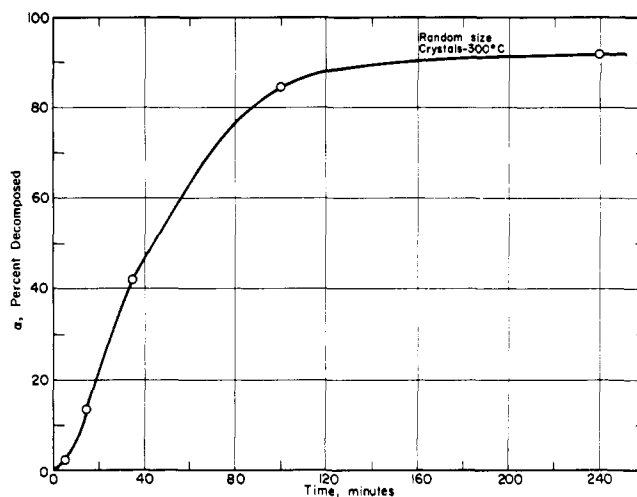


Figure 2. Denitration of uranyl nitrate hexahydrate under vacuum

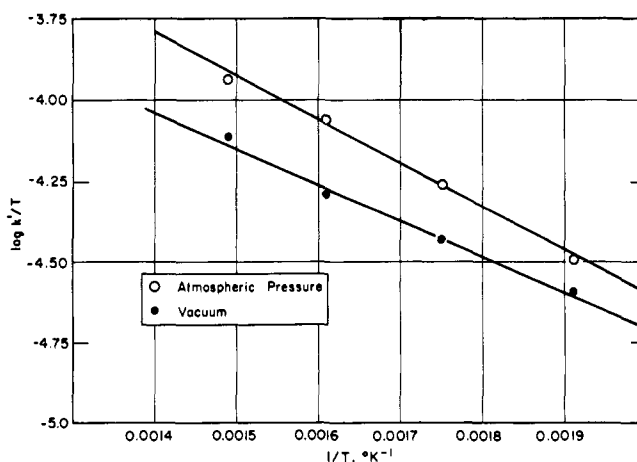


Figure 3. Thermal denitration of uranyl nitrate hexahydrate Initial 50 to 75% of reaction

The mechanism of the thermal denitration of UNH differs from that observed during the denitration of uranyl nitrate dihydrate (13). The presence of the additional water of hydration not only changes the mechanism to an autocatalytic phase boundary reaction, but also modifies the intermediate products. At atmospheric pressure the salt melted and stayed molten for a maximum of 10 minutes (250° C.) and then solidified. Under vacuum the salt remained solid but gave up its water of hydration much more rapidly at a given temperature. Estimates by x-ray diffraction of the quantity of intermediate material present during any given portion of the denitration were always low, never more than 20 %. This small quantity of intermediate products lends support to the interpretation of a phase-boundary reaction.

Beyond the zero-order portion of the curve, the data do not follow any simple kinetic interpretation. The problem is complicated by the decomposition of the intermediates, which are present at different concentrations depending upon the temperature. The final portion of each curve is therefore a composite of several contributing reactions.

The reaction rate at 400° C. under vacuum did not decrease after the zero-order portion of the reaction (Figure 2) as rapidly as expected from observations at lower temperatures. A decomposition at 1- μ pressure for 24 hours at 350° C. produced a mixture containing 0.18 wt. % as nitrogen. After 6 hours, at 400° C. a similar sample contained only 0.04 wt. % as nitrogen. Residual nitrogen after 6 hours at 300° to 350° C. normally is 0.2 to 0.3 wt. % nitrogen. The low nitrogen content can be explained on the basis of the creation of more deformations in the intermediate substrate near the end of the decomposition at 400° C., as compared to 350° C., and these deformations lower the activation energy of the second portion of the higher temperature reaction. A consequence of the lowered activation energy is that less nitrate nitrogen is trapped in the crystal lattice of the product.

The same final products are obtained by vacuum denitration of anhydrous uranyl nitrate and uranyl nitrate di- and hexahydrate. At atmospheric pressure, β - UO_3 is formed at a lower temperature (400° C.) with the hexahydrate than with the dihydrate (500° C.), although the final products are identical. The presence of similar intermediates through the temperature range studied in the decomposition of uranyl nitrate hexahydrate shows that the primary variable affecting the phase of UO_3 formed during the reaction is final temperature, assuming other factors are held constant.

The specific reaction rates were plotted according to absolute reaction rate theory on the basis of Equation 1 rather than the empirical Arrhenius equation.

$$k' = \frac{kt}{h} e^{-(\Delta H^* - T\Delta S^*)/RT} \quad (1)$$

where k' = specific reaction rate constant

k = Boltzmann constant

T = absolute temperature

h = Planck's constant
 ΔH^* = heat of activation
 ΔS^* = entropy of activation
 R = gas constant

With $\log k'/T$ plotted against $1/T$, as shown in Figure 3, the slopes of the lines are $-\Delta H^*/2.303R$ and the intercepts are equal to $\Delta S^*/2.303R + 4.48$. The equations of the lines in the figure were calculated by the least-squares method, and the heats and entropies of activation calculated from them. The values determined are shown in Table III.

The small differences in the heats of activation indicate that there is a marked similarity in the structure of the activated complex.

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LITERATURE CITED

- (1) Am. Soc. Testing Materials, ASTM X-Ray Power Data' File Card No. 2-0276.
- (2) Bridge, J.R., Melton, C.W., Schwartz, C.M., Vaughan, D.A., Battelle Memorial Institute, **BMI-1110** (July 12, 1956).
- (3) Cornman, W.R., "The Polymorphs of UO_3 : Conversion to UF_4 ," USAEC Rept. **DP-750** (1962).
- (4) Garner, W.E., Pike, H.V., *J. Chem. Soc.* **1937**, p. 1565.
- (5) Gibons, G., Katz, J.J., *J. Am. Chem. Soc.* **73**, 5436 (1951).
- (6) Hill, R.A.W., Hamilton, R.A., *Research* **7**, 555 (1954).
- (7) Hoekstra, H.R., Siegel, S., *Proc. U. N. Intern. Conf. Peaceful Uses of Atomic Energy, 2nd Geneva* **28**, 231 (1958).
- (8) Kapustinskii, A.F., Baranova, L.I., "Soviet Research on the Lanthanide and Actinide Elements," 1949-1957, Part I, *Basic Chemistry*, New York Consultants Bureau, p. 18 (1959).
- (9) Katz, J.J., Rabinowitz, E., "The Chemistry of Uranium," *Nat'l Nuclear Energy Ser. Div. VIII Vol. 7*, p. 287, McGraw-Hill, New York 1951.
- (10) Katzin, L.I., Simon, D.M., Ferraro, J.R., *J. Am. Chem. Soc.* **74**, 1191 (1952).
- (11) Lebeau, P., *Bull. Soc. Chim.* **9**, 298 (1911).
- (12) Marshall, W.L., Gill, J.S., Secoy, C.H., *J. Am. Chem. Soc.* **73**, 1867 (1951).
- (13) Ondrejcin, R.S., Garrett, T.P., *J. Phys. Chem.* **65**, 470 (1961).
- (14) Tridot, G., *Ann. Chim.* **10**, 225 (1955).
- (15) Vasilev, A.M., *Zh. Russ. Fiz-Khim Obshch.* **42**, 570 (1910).
- (16) Wendlandt, W.W., *Anal. Chem. Acta* **15**, 435 (1956).

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CORRECTION

In the article "Heats of Combustion, Formation, and Isomerization of Nineteen Alkanols," [*J. CHEM. ENG. DATA* **10**, 374 (1965)], there is an error in line 2 of the abstract on p. 375. The first sentence should read, "Measurements were made of the heats of combustion of 19 alkanols in the liquid state at 25° C."