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 anyhdrous 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.

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

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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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."