

NO_2 to acquire a more stable grouping with either NO_2 and H_2O , or $2\text{H}_2\text{O}$.

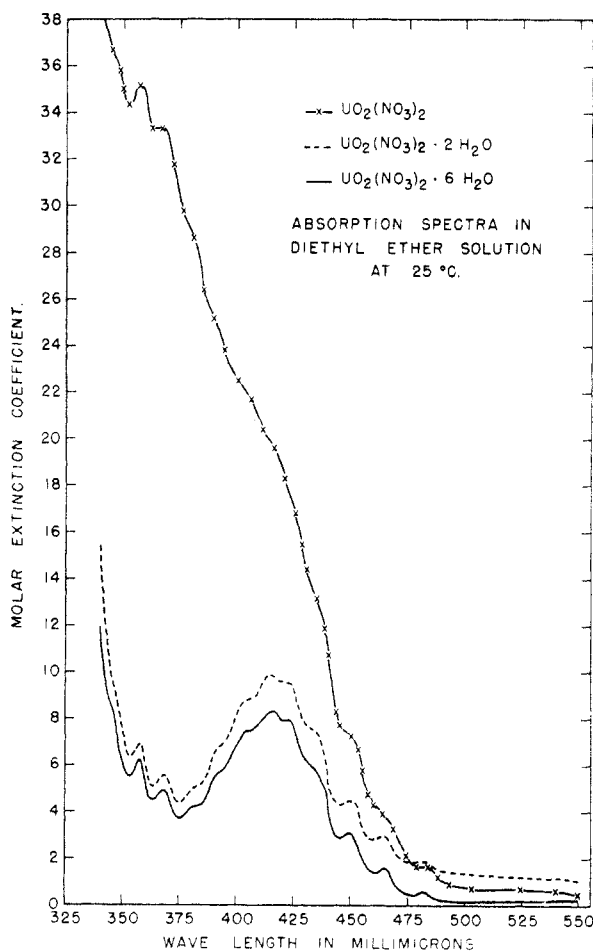


Fig. 1.

Thermal Decomposition of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$. Preparation of $\text{UO}_2(\text{NO}_3)_2$.—Following Späth's⁶ general procedure, one- to two-gram samples of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$ were heated at 163° in an oil-bath at 10^{-5} mm. pressure. The course of the decomposition was followed by frequent weighings. Approximately 90% by weight of the NO_2 of addition was lost in the first 20 minutes of heating at 163° , the remainder in approximately 110 minutes. The original crystalline, lemon-yellow compound gradually changed in color to an orange-yellow powder as dinitrogen tetroxide was pumped off. The product of thermal decomposition has a composition very close to $\text{UO}_2(\text{NO}_3)_2$. Calcd. for $\text{UO}_2(\text{NO}_3)_2$: U, 60.41; N, 7.11. Found: U, 60.12, 60.47; NO_3 , 0.22, 0.14; N, on the sample containing 0.14% NO_2 , 7.09.

The anhydrous salt dissolved rapidly in water to a clear yellow solution, spectrophotometrically identical with solutions of uranyl nitrate hexahydrate. In diethyl ether, uranyl nitrate dissolved partially at room temperature with the evolution of considerable heat and decomposition of approximately one-half of the sample to uranium trioxide. However, dissolution in diethyl ether (in a dry nitrogen atmosphere) at -60° was rapid, yielding a clear solution with no evidence of decomposition. In very intensively dried diethyl ether, however, the solubility of anhydrous uranyl nitrate appears to be low. The absorption spectrum of such a solution is compared with the spectrum of ether solutions of uranyl nitrate dihydrate and hexahydrate in Fig. 1 and clearly shows marked differences. The X-ray powder diffraction pattern of uranyl nitrate is extremely complex, and differs from the known hydrated uranyl nitrates or $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$ itself. The anhydrous uranyl nitrate exhibited a weak ultraviolet fluorescence as compared to uranyl nitrate hexahydrate. The existence of an anhydrous uranyl nitrate seems, therefore, to be reasonably well established. A more detailed examination of its properties is in progress.

Acknowledgment.—We are deeply indebted to Dr. W. H. Zachariasen for the interpretation of the X-ray data given here, to Dr. J. Clark Hindman for his assistance in the preparation of the spectrophotometric curves, to Mr. John Ferraro for the determination of the water content of the various samples cited, to Mrs. Rosanna Hospelhorn for the nitrogen analysis, and to Mr. H. H. Hyman for a number of helpful discussions.

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NOTES

Enzymatic Synthesis of *sym*-Bis-(N-carbobenzoxymethionyl)-hydrazine

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The report by Holly, Cahill and Folkers¹ on the unexpected synthesis of *sym*-bis-(N-carbobenzoxymethionyl)-hydrazine from N-carbobenzoxymethionine and hydrazine in the presence of papain prompts us to record the results of a related experiment. With the expectation of hydrolyzing only the L-isomer, N-carbobenzoxymethionine hydrazide was incubated with papain. However, the product proved to be *sym*-bis-(N-carbobenzoxymethionyl)-hydrazine. In spite of the fairly sharp melting point, the product must be a mixture of the *meso*- and L-forms judging from the yield and

rotation. It is interesting to note that both the attempt¹ to *synthesize* and our attempt to *hydrolyze* an acylamino acid hydrazide led to the formation of a *sym*-bis-(N-substituted)-hydrazine, and that in the experiment reported here enzymatic hydrolysis preceded synthesis.

Experimental

To a solution of 0.5 g. of cysteine hydrochloride in 100 ml. of water, 100 ml. of methanol and 100 ml. of citrate buffer of pH 5 was added 14.5 g. of N-carbobenzoxymethionine hydrazide and an extract of 4 g. of papain in 45 ml. of water. After 3.5 days at 37° the product was filtered, washed with water, aqueous sodium bicarbonate and water and dried at 70° ; yield 11.6 g. melting at $214-222^\circ$. Recrystallization from 235 ml. of acetic acid gave 8.4 g. of white solid, m.p. $246.7-248.5^\circ$ cor., $[\alpha]_D^{25} -3.1^\circ$ (1% in pyridine).

Anal. Calcd. for $\text{C}_{26}\text{H}_{34}\text{H}_4\text{O}_8\text{S}_2$: C, 55.49; H, 6.09; S, 11.40. Found: C, 55.44; H, 5.93; S, 11.80.

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(1) F. W. Holly, J. J. Cahill, Jr., and K. Folkers, *THIS JOURNAL*, **73**, 2944 (1951).