[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE ARGONNE NATIONAL LABORATORY]

The Reaction of Uranium Oxides with Liquid Dinitrogen Tetroxide. Anhydrous Uranyl Nitrate[1]

BY GEORGE GIBSON[2] AND JOSEPH J. KATZ

The hydrated peroxide, $UO_4 \cdot 2H_2O$, and the hydrated oxide, $UO_3 \cdot 2H_2O$, react completely with liquid dinitrogen tetroxide within a few hours at 25° and 1.1 atm. pressure to yield a product with the empirical composition $UO_2(NO_3)_2 \cdot NO_2 \cdot 2H_2O$. Under comparable experimental conditions, $UO_3 \cdot H_2O$ yields $UO_2(NO_3)_2 \cdot 2NO_2 \cdot H_2O$. These compounds are unstable in dry air and readily lose dinitrogen tetroxide, yielding, respectively, $UO_2(NO_2)_2 \cdot 2H_2O$, and $UO_2(NO_3)_2 \cdot NO_2 \cdot H_2O$. The anhydrous oxides, UO_3, U_3O_8 and $UO_{2.2}$ react partially with liquid dinitrogen tetroxide at 25° in one to four days. "Active" uranium trioxide reacts in seven to eight hours at 90° and 14.5 atm. dinitrogen tetroxide pressure. The product obtained from all of the anhydrous uranium oxides is $UO_2(NO_3)_2 \cdot 2NO_2$. This compound, in agreement with Späth, undergoes thermal decomposition to yield anhydrous uranyl nitrate, $UO_2(NO_3)_2$. A possible reaction mechanism for the liquid phase N_2O_4 reaction is noted and some properties of anhydrous uranyl nitrate are described.

Sabatier and Senderens[3] have shown that higher oxides of certain metals may be prepared by oxidation of the metal or a lower oxide by means of gaseous, anhydrous dinitrogen tetroxide at 200 to 400° and atmospheric pressure. Katz and Gruen[4] have employed this procedure in the preparation of Np_3O_8 and also report that U_3O_8 is oxidized to a brick red form of uranium trioxide rather than the usual yellow form. As a result of these gas phase studies, it appeared of interest to examine analogous reactions in the liquid phase. It was found that the oxides of uranium react smoothly with liquid N_2O_4 to yield a variety of products, one of which, $UO_2(NO_3)_2 \cdot 2NO_2$, can be readily converted to anhydrous uranyl nitrate, $UO_2(NO_3)_2$ in agreement with the earlier observation of Späth.[5]

Liquid Phase Nitrogen Tetroxide Reactions.—There has been considerable interest in recent years in liquid phase N_2O_4 reactions, and Addison and Thompson[6] have suggested an hypothesis which appears to account qualitatively for the reactions described here. In brief, these workers suggest that liquid dinitrogen tetroxide undergoes self-ionization

$$N_2O_4 \rightleftarrows NO^+ = NO_3^-$$

and attribute the oxidation reactions observed in liquid N_2O_4 to small concentrations of the nitrosonium ion NO^+ which are present as a result of the ionic equilibrium. (Goulden and Miller[7] have given evidence which indicates that NO^+ is solvated by NO_2 to produce the nitrosonium nitrogen dioxide ion $N_2O_3^+$, quite analogous to the hydronium ion H_3O^+.) The reaction of liquid N_2O_4 with UO_3, for example, can then be compared formally with the corresponding reaction in aqueous acid solution

$$UO_3 + 2NO^+ \longrightarrow UO_2^{++} + N_2O_3$$
$$UO_3 + 2H^+ \longrightarrow UO_2^{++} + H_2O$$

Since all metal nitrates are essentially insoluble in liquid N_2O_4, solid uranyl nitrate forms by precipitation with NO_3^- ion. The UO_3 reaction is then in essence a solvolytic reaction. For UO_2, the oxidation–reduction reaction can be written

$$UO_2 + 2NO^+ \longrightarrow UO_2^{++} + 2NO$$

Nitric oxide, of course, immediately undergoes reaction with excess N_2O_4 to give N_2O_3. In both cases, then, N_2O_3 is a reaction product. This agrees the observation that all of the final reaction mixtures observed during the course of this work were colored an intense blue-green, indicating the formation of N_2O_3.

Experimental

Materials.—Where possible the lower uranium oxides were prepared from uranium peroxide. Because of the extremely finely divided state of precipitated uranium peroxide, oxides of small particle size are obtained and are referred to here as "active" oxides.

The following preparations were made for this study:

(a) $UO_4 \cdot 2H_2O$.—From spectroscopically pure uranyl nitrate hexahydrate dissolved in water by precipitation at 75° with 30% hydrogen peroxide. The product was first dried at 40° and then for 30 min. at 100°.

(b) U_3O_8.—Uranium peroxide dihydrate was heated in air for five hours at 600–650°. The ignition was carried out at 650° rather than the more usual 900 to 1000° temperature since such an oxide was found to be more reactive with liquid dinitrogen tetroxide.

(c) UO_3(active).—Uranium peroxide dihydrate was heated in air for 48 to 96 hours at 340°.

(d) $UO_3 \cdot 2H_2O$ and $UO_3 \cdot H_2O$.—UO_3(active) was equilibrated with water vapor at 25 and 100°, respectively.

(e) UO_3(anhydrous).—This material was a sample prepared by Sheft, Fried and Davidson[8] by the oxidation of U_3O_8 with O_2 under pressure.

(f) $UO_2(UO_{2.2})$.—Prepared by the method of Boullé, *et al.*,[9] by thermal decomposition of uranyl oxalate for three to four hours at 10^{-5} mm. pressure and 350°. X-Ray analysis of this oxide by Professor W. H. Zachariasen indicated a composition $UO_{2.2}$ rather than $UO_{2.0}$. All of the above products were characterized by chemical and X-ray analyses and were in all cases between 99.8 and 99.9% pure.

The **dinitrogen tetroxide** was obtained from commercially available cylinders. Before use the gas was passed through a phosphorus pentoxide drying tower and then condensed in a storage vessel on the vacuum line.

Apparatus and Procedure.—The reactions were carried out in Pyrex tubes consisting of a 12/30 female standard taper joint attached to tube 1.2 × 13 cm. through a capillary construction. Since the reaction products of the hydrated oxides cake badly, glass beads were added through a side arm; these proved effective in breaking up the reaction mass on intermittent shaking.

The reaction tubes containing approximately 0.009 to 0.018 mole of oxide were attached to a vacuum line and

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[2] On leave of absence from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois, for the academic year 1949–1950.

[3] P. Sabatier and J. V. Senderens, *Ann. chim. phys.*, [7] **7**, 356, 384, 396 (1896).

[4] J. J. Katz and D. M. Gruen, THIS JOURNAL, **71**, 2106 (1949).

[5] E. Späth, *Monatsh.*, **33**, 853 (1912).

[6] C. C. Addison and R. Thompson, *J. Chem. Soc.*, S211, S218 (1949).

[7] J. D. S. Goulden and D. J. Miller, *ibid.*, 2620 (1950).

[8] I. Sheft, S. Fried and N. Davidson, THIS JOURNAL, **72**, 2172 (1950).

[9] A. Boullé, R. Jary and M. Dominé-Bergés, *Comptes rend.*, **230**, No. 3, 300 (1950).

TABLE I

REACTION OF ANHYDROUS URANIUM OXIDES WITH LIQUID N_2O_4

Oxide	Temp., °C.	Pressure, atm. of N_2O_4	Reaction time	Oxide[a] reacted, %	Analytical results, % (corrected for unreacted oxide) U	NO$_2$
UO_3 (anhydrous)	25	1.1	25 da.	69.8	47.5	15.9
UO_3 "active"	25	1.1	12 da.	96.9	49.1	18.05 ± 0.19
UO_3 "active"	90	14.5	4.5 hr.	99.8	49.1	15.98 ± 0.93
UO_3 "active"	90	14.5	7 hr.	100	48.9	16.48 ± 0.04
UO_3 "active"	90	14.5	7 hr.	100	49.2	16.63
U_3O_8	25	1.1	20 da.	88.3	48.9	18.54
U_3O_8	90	14.5	7 hr.	85.6	48.6	18.22
$UO_{2.2}$	90	14.5	7 hr.	96.1	50.0	16.51 ± 0.29
Calculated for $UO_2(NO_3)_2 \cdot 2NO_2$					48.99	18.93

[a] Based on ether extraction of the product. Similar results are obtained when solubility in water is used to determine the degree of reaction.

pumped down to 10^{-5} mm. pressure. (In the case of the hydrated oxides the tube contents were cooled with a Dry Ice–trichloroethylene-bath to prevent dehydration of the oxide). After five to six cc. of liquid dinitrogen tetroxide had been condensed into the reaction tube by means of liquid nitrogen, the tubes were sealed off at the capillary and allowed to warm up to room temperature. For those runs conducted at elevated pressures, a nickel bomb tube which could be pressurized was employed. This apparatus made it feasible to use glass vessels at elevated pressures by application of external pressure to the glass reaction vessel. The vapor pressure of N_2O_4 at 90° is 14.5 atm., and an external pressure of 16.5 atm. was maintained in the nickel bomb tube. A sleeve furnace placed around the nickel tube served as a heat source. The temperature of the furnace was controlled by means of a Variac to ±1°.

At the end of the reaction period the tube contents were frozen with liquid nitrogen; the tube was opened at the capillary tip and rapidly attached to a phosphorus pentoxide tower through which excess dinitrogen tetroxide was evaporated off at room temperature. All subsequent transfers or operations on the solid products were carried out in a good dry box.

Analyses.—Dinitrogen tetroxide content (as NO_2) in the reaction products was determined by cerate oxidation. The sample in a glass-stoppered capsule was added to an excess of 0.1 *N* cerate plus 10 ml. of 6 *N* sulfuric acid in an iodine flask. After five minutes of intermittent shaking, the excess cerate was back-titrated with 0.1 *N* ferrous ammonium sulfate. Results on a given sample could be reproduced to ±0.03% or better. Uranium was determined by ignition of the sample to U_3O_8 at 900°. Water was determined by the Karl Fischer method. Total nitrogen was determined by Devarda's method, as described by Hillebrand and Lundell.[10]

Results and Discussion

Results

Reaction of Anhydrous Oxides.—The experimental conditions and results of a number of experiments are given in Table I. The sole product of all of these reactions is $UO_2(NO_3)_2 \cdot 2NO_2$. Under ordinary conditions, when the excess N_2O_4 is removed at room temperature the nitrogen dioxide content of the product is often low to the extent of approximately 2%. By removing excess N_2O_4 from the reaction mixtures at 0–10° and immediately analyzing, it is possible to obtain a product with the calculated NO_2 content. All of the reaction products obtained in this work are more or less unstable with respect to loss of nitrogen dioxide even in a dry atmosphere at room temperature. Our observation on the loss of small amounts of NO_2 at room temperature from $UO_2(NO_3)_2 \cdot 2NO_2$ is identical with that observed by Späth[5] for his product. When about 15% of the NO_2 sites are vacant, corresponding to an NO_2 content of 16–17% the substance appears to be then quite stable at room temperature since free N_2O_4 is not observed to be liberated when this substance is stored in dry air, and the composition remains constant over periods of months.

Reactions of Hydrated Oxides.—The hydrated uranium oxides react considerably more rapidly than the anhydrous oxides with liquid N_2O_4. Nevertheless, these reaction mixtures were permitted to stand for long periods of time to ensure complete reaction.

The much more rapid reaction observed for the hydrated oxides as compared to the anhydrous oxides may be explained in two ways. It is possible that the crystal structure of the anhydrous oxides is less conducive to reaction, as is generally observed with anhydrous *vs.* hydrated oxides. Alternatively, the greater rate may result from the formation of nitrous and nitric acids from the interaction of the water of hydration and N_2O_4; the reaction of UO_3 and HNO_3, for example, is known to be rapid. Since all of the water introduced with the hydrated oxides is quantitatively accounted for in the final product, we prefer the first interpretation.

The results of a few experiments are given in Table II. The degree of hydration of the original oxide determines the composition of the product, all of the water of hydration being found in the product of the reaction. Uranium trioxide monohydrate yields $UO_2(NO_3)_2 \cdot 2NO_2 \cdot H_2O$ as a lemon-yellow crystalline product. It is the least stable of the hydrated uranyl nitrate–NO_2 addition compounds we have observed. When exposed to sulfuric acid in a desiccator at atmospheric pressure, NO_2 is lost and the composition $UO_2(NO_3)_2 \cdot NO_2 \cdot H_2O$ is approached.

TABLE II

REACTION OF HYDRATED URANIUM OXIDES WITH LIQUID N_2O_4

Reactions all at 25° and 1.1 atm. N_2O_4 Pressure.

Oxide	Reaction time, days	Composition of product, % U	NO$_2$	H$_2$O
$UO_3 \cdot H_2O$	11	48.1	12.37	3.51 ± 0.7
$UO_3 \cdot H_2O$	14	48.3	12.94	..
Calculated for $UO_2(NO_3)_2 \cdot 2NO_2 \cdot H_2O$		47.22	12.30	3.57
$UO_3 \cdot 2H_2O$	23	50.2	7.62 ± 0.03	7.99
$UO_4 \cdot 2H_2O$	47	52.0	9.12	..
$UO_4 \cdot 2H_2O$	7	52.1	9.04 ± 0.11	..
Calculated for $UO_2(NO_3)_2 \cdot NO_2 \cdot 2H_2O$		50.00	9.66	7.56

Both uranium peroxide dihydrate and uranium trioxide dihydrate yield $UO_2(NO_3)_2 \cdot 2H_2O$. By pumping on this compound at 25° in a vacuum of 10^{-5} mm., NO_2 is lost preferentially and uranyl nitrate dihydrate is obtained. The identity of the uranyl nitrate dihydrate was determined by X-ray crystal analysis through the courtesy of Dr. W. H. Zachariasen, and by chemical analysis for U and H_2O. This material had a NO_2 content of 0.23%. In general we have found that the last traces of NO_2 are removed only with difficulty from these addition compounds.

All of the hydrated uranium oxide–nitrogen dioxide products were readily soluble in water and diethyl ether at 25°, with vigorous evolution of any contained NO_2. Spectrophotometric curves for the ether solution of $UO_2(NO_3)_2 \cdot NO_2 \cdot 2H_2O$ were identical with uranyl nitrate dihydrate solutions in ether.

We may qualitatively conclude from the decomposition data that uranyl nitrate addition compounds with a combined total of three nitrogen dioxide and water groups will be relatively unstable. Such compounds preferentially lose

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[10] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 639.

NO_2 to acquire a more stable grouping with either NO_2 and H_2O, or $2H_2O$.

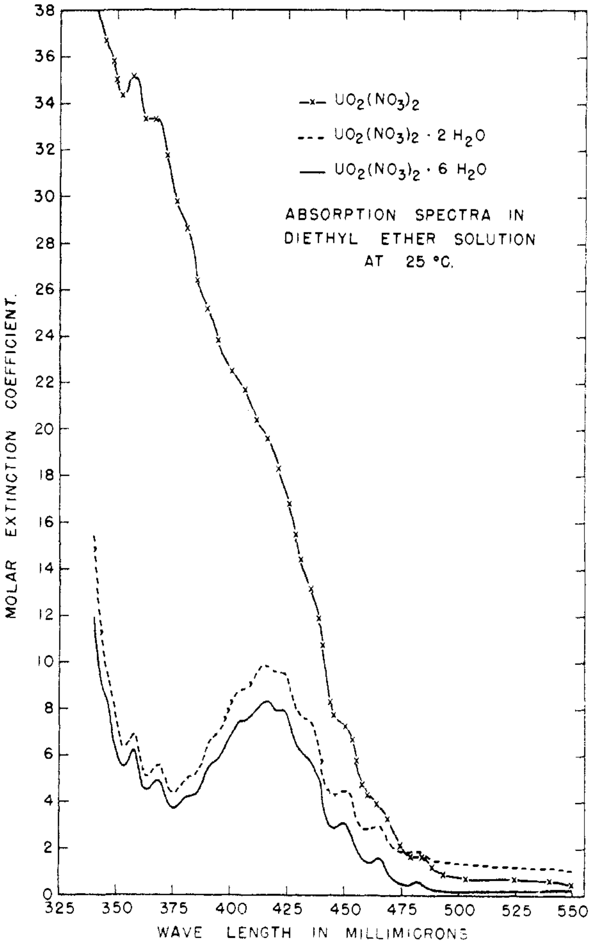

Fig. 1.

Thermal Decomposition of $UO_2(NO_3)_2 \cdot 2NO_2$. Preparation of $UO_2(NO_3)_2$.—Following Späth's[5] general procedure, one- to two-gram samples of $UO_2(NO_3)_2 \cdot 2NO_2$ 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 $UO_2(NO_3)_2$. Calcd. for $UO_2(NO_3)_2$: U, 60.41; N, 7.11. Found: U, 60.12, 60.47; NO_2, 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 $UO_2(NO_3)_2 \cdot 2NO_2$ 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.

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NOTES

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

BY NOEL F. ALBERTSON

The report by Holly, Cahill and Folkers[1] on the unexpected synthesis of *sym*-bis-(N-carbobenzoxy-L-alanyl)-hydrazine from N-carbobenzoxy-DL-alanine 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-carbobenzoxy-DL-methionine 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 attempt[1] 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 *p*H 5 was added 14.5 g. of N-carbobenzoxy-DL-methionine 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°. Recrystallization from 235 ml. of acetic acid gave 8.4 g. of white solid, m.p. 246.7–248.5° cor., $[\alpha]^{25}D$ −3.1° (1% in pyridine).

Anal. Calcd. for $C_{26}H_{34}H_4O_6S_2$: 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).