It is a pleasure to acknowledge the advice and help in some of the experiments of Kenneth Street, Jr., G. H. Higgins and A. Ghiorso. This work was performed under the auspices of the U. S. Atomic Energy Commission.

DEPARTMENT OF CHEMISTRY AND
RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIF.

RECEIVED MARCH 30, 1950

Coördination Compounds of Uranyl Nitrate

BY GEORGE W. WATT AND ALBERT R. MACHEL

A recent paper by Katzin[1] on the formation of mixed solvates of uranyl nitrate with water and a number of organic addenda prompts us to report some of our work relating to similar compounds.[2]

Experimental

Uranyl Nitrate and Methyl Isobutyl Ketone.—In an effort to prepare and isolate anhydrous uranyl nitrate, samples of uranyl nitrate 2-hydrate were dissolved in anhydrous methyl isobutyl ketone ("hexone") and about two-thirds of the solvent was removed by distillation. Water in excess of its solubility in hexone was observed in the distillate and upon dilution of the dark brown still residue with Skellysolve A, a viscous amber oil separated. Since preliminary examination of this product[3] indicated that it was a monohexone solvate of uranyl nitrate, the reaction was studied in more detail.

The nearly quantitative removal of water from the 2-hydrate during the course of the distillation was demonstrated as follows. Uranyl nitrate 2-hydrate (7.014 g.) was dissolved in 70 ml. of hexone and 50 ml. of the solvent was removed by distillation at atmospheric pressure. Samples of the distillate were analyzed for water by a modification of Bryant, Mitchell and Smith's procedure[4] for the determination of water in the presence of carbonyl compounds by means of Karl Fischer reagent.[5] Water found in the distillate amounted to 0.557 g. as compared with 0.586 g. of water present in the weight of 2-hydrate used. In similar experiments, distillates were found to contain 0.277 and 0.511 g. of water as compared with calculated values of 0.291 and 0.586, respectively. The average of these data corresponds to the removal of 1.84 of the 2.00 moles of water present per mole of nitrate.

The dark brown still residue was diluted with 700 ml. of Skellysolve A (boiling range, 28–30°), whereupon a viscous amber oil separated. After the two phases had remained in contact at room temperature for several hours, the pale yellow supernatant solution was removed, concentrated and analyzed for uranium. The oil was transferred to a weighing bottle and dried in a vacuum oven at 58° and a pressure of 3 mm. Data relative to this and other typical experiments are given in Table I; these data amply demonstrate the reproducibility of the solvate having the formula $UO_2(NO_3)_2 \cdot C_6H_{12}O$. Katzin[1] reported a mixed solvate having the composition $UO_2(NO_3)_2 \cdot 2.71H_2O \cdot 0.28C_6H_{12}O$, but this was formed under conditions quite different from those employed in the present work.

During drying, or upon prolonged standing at room temperature, the viscous oil sets to a brittle resinous solid. This product is soluble in hexone, from which the oil is reprecipitated upon dilution with Skellysolve A. The compound is hydrolyzed slowly by water at room temperature, and qualitative tests show that the nitrate ion remains intact. All efforts to crystallize this compound were ineffective.

TABLE I

DATA ON REACTIONS BETWEEN URANYL NITRATE 2-HYDRATE AND HEXONE[a]

$UO_2(NO_3)_2 \cdot$-$2H_2O$, g.	Diluent, ml.	Anal. of insol. prod.[b] U, %	Anal. of insol. prod.[b] C,[c] %	U pptd. as UO_2-$(NO_3)_2 \cdot$-$C_6H_{12}O$, %	U retained in organic solvent, %
3.498	700[d]	49.5	14.4	77.0	17.7
7.069	350	49.8	16.2	76.5	21.4
6.989	700	49.2	15.4	70.9	29.1
7.014	1400	49.8	14.8	63.4	34.6
14.025	700[d]	46.8	16.7	32.5	63.0

[a] All experiments employed 70 ml. of anhydrous hexone, 50 ml. of which was removed by distillation prior to addition of diluent. [b] Calcd. for $UO_2(NO_3)_2 \cdot C_6H_{12}O$: U, 48.2; C, 14.6. [c] Determined by the method of Lindenbaum, Schubert and Armstrong, *Anal. Chem.*, **20**, 1120 (1948). [d] Reaction mixture maintained at 0° for 6 hr. following addition of diluent.

Other Coördination Compounds of Uranyl Nitrate.—Using essentially the procedure of Lloyd and Cleere,[2] treatment of 2.46 g. of uranyl nitrate 2-hydrate in 100 ml. of 95% ethanol at room temperature with 7.60 g. of hexamethylenetetramine in 80 ml. of the same solvent gave a pale yellow precipitate which was washed with ethanol and dried at 105°.

Anal. Calcd. for $UO_2(NO_3)_2 \cdot (CH_2)_6N_4$: U, 44.6; N, 10.5. Found: U, 43.8; N, 11.0.

A similar reaction with excess ethylenediamine yielded a gelatinous yellow precipitate which was dried *in vacuo* over concentrated sulfuric acid.

Anal. Calcd. for $UO_2(NO_3)_2 \cdot [(CH_2NH_2)_2]$: U, 52.5; N, 6.2. Found: U, 50.4; N, 6.1.

When this same reaction was carried out in the presence of phosphate ion at concentrations insufficient to precipitate uranyl hydrogen phosphate, the product consisted of the monoethylenediamine solvate of uranyl hydrogen phosphate. This compound is probably more properly represented as the ethylenediamine analog of ammonium uranyl phosphate, *i. e.*, $[(CH_2NH_3)_2](UO_2PO_4)_2$.

Anal. Calcd. for $UO_2HPO_4 \cdot [(CH_2NH_2)_2]$: N, 3.5; P, 7.8. Found: N, 3.9; P, 7.4.

Efforts were made to prepare coördination compounds of uranyl nitrate with other organic addenda such as urea, thiourea, guanidine, nitrilotriacetic acid and ethylenediamine tetraacetic acid. No evidence of compound formation was observed at room temperature, following refluxing in ethanol, or following dilution with organic solvents including Skellysolve A, diethyl ether, etc.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF TEXAS
AUSTIN 12, TEXAS

RECEIVED JANUARY 6, 1950

---

[1] Katzin, AECD-2213, Aug. 17, 1948.

[2] *Cf.* Lloyd and Cleere, *Science*, **108**, 565 (1948).

[3] These experiments were carried out by Mr. G. L. Sutherland.

[4] Bryant, Mitchell and Smith, THIS JOURNAL, **62**, 3504 (1940).

[5] The authors are indebted to Dr. C. M. Slansky, through whose coöperation these analyses were obtained.

Preparation of Indole

BY FLOYD T. TYSON

In the previously reported[1] preparation of indole by the condensation of *o*-formotoluide, potassium amide of alkoxides were used as condensing agents. The maximum yield reported was 0.40 mole of indole per mole of *o*-formotoluide. It has now been found that potassium *o*-toluide is a more effective condensing agent

---

[1] Tyson, THIS JOURNAL, **63**, 2024 (1941); Marion and Ashford, *Can. J. Research*, **23B**, 26 (1945); Galat and Friedman, THIS JOURNAL, **70**, 1280 (1948).