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## 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.

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.

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.

**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.

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[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.

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## 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

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

than the previously reported potassium compounds, since by its use 0.68 mole of indole can readily be obtained from 1 mole of *o*-formotoluide.

A further improvement is also described in the experimental part in which the more convenient sodium *o*-toluide is used as the condensing agent. Sodium anilide was also found to be an effective condensing agent. In the previous report[1] sodium amide and alkoxides were found to be quite ineffective.

In the procedures previously reported[1] a mixture of gases was evolved during the reaction period which consisted essentially of carbon monoxide and hydrogen. These gases could have been produced by a decomposition of alkali formate formed in a side reaction during the condensation. Carbon monoxide could have come from the decomposition of an alkali compound of *o*-formotoluide to the alkali metal *o*-toluide and carbon monoxide. The effect of added alkali formate upon the reaction was therefore investigated. It was found that by the addition of potassium formate to a mixture of *o*-formotoluide (1 mole), sodium *o*-toluide and excess *o*-toluidine, 1.07 moles of indole could be obtained based on the *o*-formotoluide. The decomposition of the potassium formate apparently served as a source of carbon monoxide "*in situ*" which combined with the sodium *o*-toluide to increase the yield of indole.

A considerable yield of indole is obtained without the initial addition of *o*-formotoluide to the reaction mixture if instead one adds potassium formate which by pyrolytic decomposition serves as a convenient source of carbon monoxide. This carbon monoxide apparently combined with the alkali metal toluide "*in situ*" to form the alkali metal *o*-formotoluide, which then underwent condensation with the formation of indole. Further, a satisfactory yield of indole is obtained by the use of carbon monoxide at atmospheric pressure upon sodium or potassium *o*-toluide. Using an autoclave at low super atmospheric pressures yields up to 0.82 mole of indole based upon *o*-toluidine actually consumed in the reaction are obtained.

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### Experimental

**Condensation of *o*-Formotoluide by Potassium *o*-Toluide (Procedure A) or Sodium *o*-Toluide (Procedure B): Procedure A.**—To about 300 ml. of liquid ammonia in which was suspended a rusty three-inch nail[2] contained in a one-liter three-necked flask protected from air and moisture by a suitable mineral oil trap was added 11.7 g. (0.3 mole) of potassium. Within twenty minutes the disappearance of the blue color of the potassium solution indicated the complete conversion of the metal to the amide, and 32.1 g. (0.3 mole) of *o*-toluidine was added, followed by 13.5 g. (0.1 mole) of *o*-formotoluide.

The reaction flask was fitted with a thermometer, mechanical stirrer, and a condenser for distillation with provision for final cooling of the reaction mixture under nitrogen. Excess ammonia was then removed by evaporation, the temperature of the reaction mixture was gradually raised, within about fifteen minutes, to about 160° with mechanical stirring, then the temperature was rapidly increased to 270–290° and so maintained for about thirty minutes using a metal-bath heated to about 310°. At the end of the reaction period, reduced pressure (20 mm.) was used to recover, virtually quantitatively, *o*-toluidine from the reaction mixture. After cooling under nitrogen the reaction mixture was treated as previously reported.[1] The indole obtained after removal of ether 8.0 g. (0.068 mole) melted at 51–53° without further purification.

Experiments made with decreased or increased proportions of potassium amide resulted in decreased yields.

**Procedure B.**—For the preparation of sodium *o*-toluide as a condensing agent 14.4 g. (0.6 mole) of sodium hydride was added at room temperature to 77 g. (0.72 mole) of *o*-toluidine in a one-liter three-necked flask set up for distillation and equipped with a mechanical stirrer, thermometer and means of flushing with nitrogen. (When larger scale experiments were carried out, it was best to add the necessary sodium hydride in small portions during the heating period described below, so as to avoid the danger of sudden and uncontrolled release of large volumes of hydrogen.) The temperature was increased gradually with mechanical stirring to about 160° or until hydrogen ceased to be evolved, and 13.5 g. (0.1 mole) of *o*-formotoluide was then added. Further treatment was carried out as described above for the use of potassium *o*-toluide; yield 6.5 g. of indole (0.056 mole).

Experiments made with decreased proportions of sodium *o*-toluide resulted in decreased yields, and an increased proportion of sodium *o*-toluide did not improve yields.

The sodium *o*-toluide can also be prepared by the use of sodium amide upon a solution of *o*-toluidine in liquid ammonia with essentially the same yield. If the use of liquid ammonia is omitted and the sodium amide was added directly to *o*-toluidine under nitrogen, a slight reduction of yield was noted. By the substitution of sodium anilide for the *o*-toluide as the condensing agent yields of indole were lowered about 15%.

**Indole Preparation by the Reaction of Sodium *o*-Toluide upon *o*-Formotoluide with Potassium Formate as a Source of Carbon Monoxide.**—The reaction was carried out on 0.1 mole of *o*-formotoluide exactly as described in procedure B above, except that 17.6 g. (0.4 mole) of freshly fused, cooled and granulated potassium formate was added after all sodium hydride had been converted to the *o*-toluide, and prior to heating to 270–290°; yield 12.5 g. (0.107 mole) of indole.

**Indole Preparation by the Action of Carbon Monoxide upon Sodium *o*-Toluide (Procedure A) or Potassium *o*-Toluide (Procedure B): Procedure A.**—An Aminco autoclave, 1400-ml. capacity, fabricated of 18-8 stainless steel, type 347, with heater and shaker was used for pressure reactions with carbon monoxide. To the *o*-toluidine, 161 g. (1.5 moles) in the autoclave without a liner, was added 28.8 g. (1.2 moles) of sodium hydride. The autoclave was closed and heated with shaking up to approximately 170° until the pressure rose to a constant value of about 500 pounds per square inch. The autoclave was cooled, the hydrogen released and the autoclave filled with carbon monoxide to a pressure of 225 pounds per square inch. The autoclave was then heated with shaking to 300–310° and so maintained for about 0.5 hour; after cooling, the autoclave content was treated with water, steam distilled, and the indole isolated as recorded in earlier work[1]; yield, 30 g. indole (0.25 mole or 56% yield based upon *o*-toluidine not recovered).

The use of lower and higher initial pressures of carbon monoxide decreased the yield of indole. An increase of about 10% in yield of indole was obtained by the use of a Pyrex glass liner in the autoclave.

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[2] Coleman and Maxwell, THIS JOURNAL, **56**, 133 (1934).

For the preparation of indole at atmospheric pressures from sodium *o*-toluide and carbon monoxide, 14.4 g. (0.6 mole) of sodium hydride was treated with 77 g. (0.72 mole) of *o*-toluidine as described above and carbon monoxide was passed into the reaction flask at 200–210° with stirring until absorption ceased (about thirty minutes). The temperature was then increased to 270–290° for a period of about thirty minutes; yield, 10 g. (0.086 mole) of indole.

The passage of gaseous carbon monoxide into the reaction mixture can be avoided, if instead 0.4 mole of potassium or sodium formate is added prior to the 270–290° heating period. The decomposition of the formate provides the necessary carbon monoxide; yield, 6.0 g. (0.051 mole) of indole with potassium formate and 5.0 g. (0.043 mole) with the use of sodium formate.

**Procedure B.**—Potassium (46.8 g., 1.2 moles) in liquid ammonia was converted to the amide as previously described and 154 g. (1.44 moles) of *o*-toluidine was added. The liquid ammonia solution was then transferred from the flask by means of glass tubing to the autoclave, which was cooled by a solution of Dry Ice in acetone. After removal of ammonia by gradual heating of the autoclave to 160° and flushing with nitrogen, the autoclave was cooled to room temperature. Carbon monoxide was then added to a pressure of 170 pounds per square inch (0.6 mole). The autoclave was then heated to 300–310° for thirty minutes and upon cooling the reaction mixture was treated for the isolation of indole as previously described; yield, 36 g. (0.31 mole) indole or a yield of 82% based upon *o*-toluidine not recovered.

This process was also carried out in glass apparatus at atmospheric pressure by passage of carbon monoxide into the stirred mixture of potassium *o*-toluidine and excess *o*-toluidine, first at about 190–200° until carbon monoxide ceased to be absorbed (45 minutes) and continuation of carbon monoxide passage at the reaction temperature of 290–310° for ten minutes. The yields based upon unrecovered *o*-toluidine were less than those obtained by holding the carbon monoxide in contact with the reaction mixture within an autoclave.

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# Unit Cell and Optical Properties of $t,t,\Delta^{9,11}$-Linoleic Acid[1]

BY LEE P. WITNAUER AND FREDERIC R. SENTI

In a previous paper[2] $t,t,\Delta^{9,11}$-linoleic acid was characterized by X-ray diffraction patterns of powdered specimens. Optical and X-ray diffraction data for single crystals provide a more detailed characterization of this acid, and these data are reported below.

**Optical Properties.**—Preparation of $t,t,\Delta^{9,11}$-linoleic acid has been described.[2] Single crystals of the acid were obtained by slow evaporation from xylene at 25°. The crystals were monoclinic and occurred as thin, diamond-shaped plates lying on the orthopinacoid, (100), and bounded by the domes, {011}. Inter-edge angles measured in the plane of the plate were 68° and 112°, both ± 1/2°. Since the X-ray data showed that the monoclinic angle was nearly 90°, the inter-edge angles were nearly equal to the interfacial angles of the dome zone. The axial ratio *b*:*c* computed from these angles is 1:1.47, which is in good agreement with the ratio 1:1.48 determined from the X-ray data.

The crystals gave a positive biaxial interference figure; one optic axis was perpendicular to the plate, and the optic axial plane was parallel to the bisector of the acute angle of the plate. The apparent optic axial angle, $2E$, for NaD light was 54° 18′. The optic angle in the crystal was computed to be 34° 46′. The immersion method with NaD light gave 1.527 as the measured value of B.

**X-Ray Diffraction Data.**—Unit cell dimensions and symmetry elements of $t,t,\Delta^{9,11}$-linoleic acid were determined from diffraction patterns of single crystals taken with a precession camera using copper radiation ($\lambda$ = 1.539 kX.). The plane symmetry of zero and *n*-level patterns placed the crystal in the monoclinic system. Systematic extinction of the general spectra *hkl* occurred when $h + k$ was odd, and *h*0*l* was absent when *l* was odd, permitting either space group *Cc* or *C*2/*c*.

Dimensions of the monoclinic unit cell are $a_0$ = 95.69 kX., $b_0$ = 4.95 kX., $c_0$ = 7.31 kX., and $\beta$ = 90.6°. Crystallographic axis *a* was inclined 0.6° to the plate normal, *b* bisected the obtuse angle, and *c* bisected the acute angle of the plate. The observed density of 1.01 is in reasonable agreement with the density, 1.07, computed with the assumption of eight molecules per unit cell.

**Crystal Structure.**—From the unit cell dimensions and the intensities of the (*h*00) reflections which were observed out to $h = 80$, it is evident that the structure is based on dimeric linoleic acid molecules oriented with their length along the *a* axis. Since the lattice is *C*-centered, $a_0$ (95.69 kX.) corresponds to the projected length of two dimers. The alternation in intensity of the (*h*00) reflections with odd orders strong for $h/2 < 7$ and even orders strong for $7 < h/2 < 20$ is characteristic of the diffraction patterns of all long-chain saturated fatty acids. No reasonable structures based on space group *C*2/*c* were found, and it is likely, therefore, that the structure is based on space group *Cc* with dimers in the general position.

One can estimate the angle of tilt of the linoleic acid dimer with respect to $[d_{001}]$ from the observation that reflection (80.00) is strong. For this reflection to be intense, the contributions of all atoms must be near their maximum values. Considering only the carbon atoms, which must make the major contribution, and assuming the $t,t,\Delta^{9,11}$-linoleic acid dimer to be planar and centrosymmetrical, and to have normal bond angles and lengths, the principal dependence of $F_{h00}$ on $\alpha$ can be expressed by

$$F_{h00} \sim \frac{1}{1 - \cos\,(2\pi ht \cos\alpha)}$$

where $\alpha$ is the angle of tilt measured with respect to $[d_{100}]$ and *t* is the distance between alternate

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[1] Taken in part from a thesis submitted by L. P. Witnauer in partial fulfillment of the requirements for a Master of Arts degree at Temple University, June, 1948.

[2] L. P. Witnauer, P. L. Nichols, Jr., and F. R. Senti, *J. Am. Oil Chem. Soc.*, **26**, 653 (1949).