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Reaction of Bis(tetraethylammonium) Tetrabromodioxouranium(VI) with Liquid Ammonia

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To supplement the somewhat fragmentary information available concerning the ammoniates, amides, and imides of the uranyl ion,[1-3] we have investigated the interaction of $[(C_2H_5)_4N]_2UO_2Br_4$ and anhydrous liquid ammonia. Numerous reactions of the resulting primary and secondary reaction products are also described.

Experimental Section

Unless otherwise indicated, all experimental methods were the same as those reported in recent publications.[4]

Synthesis of $[(C_2H_5)_4N]_2UO_2Br_4$.—This bright yellow salt was prepared in substantially quantitative yield by treatment of a solution of 2.98 g of UO_2Br_2 in 20 ml of 95% ethanol with 3.20 g of $(C_2H_5)_4NBr$ at 25° for 15 min and recrystallized from acetonitrile. *Anal.* Calcd for $[(C_2H_5)_4N]_2UO_2Br_4$: U, 28.0; Br, 37.6. Found: U, 27.8; Br, 37.5.

Interaction of $[(C_2H_5)_4N]_2UO_2Br_4$ and NH_3.—In a typical experiment, 6.01 g of the bromide was treated with 50 ml of liquid ammonia at either -35 or $-78°$ for 15 min. The pale yellow insoluble product was filtered and washed six times[5] with 30 ml portions of ammonia. After drying under reduced pressure for 12 hr, the yield of insoluble product was 3.02 g or 83% based on $[(C_2H_5)_4N]_2UO_2Br_4$. *Anal.* Calcd for $[UO_2(NH_2)_2\cdot NH_3](NH_4Br)_2$: U, 46.2; Br, 31.0; N, 13.6. Found: U, 45.7; Br, 30.9; N, 13.4. Ir data (4000–600 cm^{-1} in all cases): 3270 s, 3215 s, 3160 s, ~1725 br, sh, 1609 ms, ~1595 sh, 1461 w, 1404 ms, 1387 m, 1293 m, 1264 m, 1241 ms, ~1234 sh, 1125 m, ~952 sh, 932 vs, 892 ms, 858 m, 662 m, ~630 sh. Evaporation of the combined supernatant solution and washings provided a pale yellow residue which contained uranium; X-ray diffraction data confirmed the presence of NH_4Br and $(C_2H_5)_4NBr$.

Deammoniation of $[UO_2(NH_2)_2\cdot NH_3](NH_4Br)_2$.—A 2.31 g sample of this product was maintained at 10^{-2} Torr for 3 days, whereupon NH_3 gas was evolved and the intensity of the color of the solid increased. *Anal.* Calcd for $UO_2NH(NH_4Br)_2$: U, 49.5; Br, 33.2; N, 8.7. Found: U, 49.3; Br, 33.2; N, 8.5. Ir data: 3150 ms, 1655 vw, 1599 vw, 1400 ms, 891 ms. An X-ray diffraction pattern showed only lines attributable to NH_4Br.

Uranium(VI) Dioxyimide 2-Ammoniate.—A 2.85 g sample of $UO_2NH(NH_4Br)_2$ was washed 15 times with 20 ml portions of NH_3 at $-78°$ to provide a quantitative yield of a bright orange colored ammonia-insoluble solid. *Anal.* Calcd for $UO_2NH\cdot 2NH_3$: U, 74.6; N, 13.2. Found: U, 74.2; N, 12.9. Ir data: 3325 m, 3200 m, br, 1597 m, 1420 m, br, 1217 m, br, 877 s, br, ~825 sh. This product was amorphous to X-rays. For the white ammonia-soluble product, ir and X-ray diffraction data showed only the presence of NH_4Br.

Pyrolysis of $UO_2NH\cdot 2NH_3$.—Heating a 0.6 g sample at 10^{-2} Torr to and at 200° for 12 hr formed a brown powder that was amorphous to X-rays. *Anal.* Calcd for $UO_2NH\cdot NH_3$: U, 78.8; N, 9.3. Found: U, 78.3; N, 9.2. Ir data: 3330 m, 3200 m, br, 1595 w, 1420 m, br, 890 s, br. Further heating at 330° for 12 hr gave a brown-black powder that did not absorb in the ir. *Anal.* Calcd for U_3O_8: U, 84.8. Found: U, 81.9; N, 0.5. An X-ray diffraction photograph showed only the presence of U_3O_8.

Reactions Using $[UO_2(NH_2)_2\cdot NH_3](NH_4Br)_2$.—Although it was our intention to study certain reactions of uranyl amide, all efforts to remove the associated NH_4Br resulted in decomposition, usually resulting in the formation of the imide. Accordingly, the NH_4Br-containing complex was used to study the following reactions.

With Water.—Exhaustive washing with water at 25° gave a colorless filtrate that contained only NH_4Br and a yellow-orange colored solid that was dried over concentrated H_2SO_4 for 3 days. *Anal.* Calcd for $U_3O_{14}NH_{13}$: U, 74.0. Found: U, 73.8. The X-ray diffraction pattern was the same as that reported earlier[6] for a product empirically formulated as "$3UO_3\cdot NH_3\cdot 5H_2O$."

With Methanol.—Similar treatment with anhydrous methanol gave a clear filtrate and washings that contained only NH_4Br and a yellow Br-free insoluble product. *Anal.* Calcd for $UO_2(OCH_3)_2\cdot CH_3OH$: U, 65.2; C, 9.9; H, 3.0. Found: U, 65.0; C, 9.6; H, 3.2. Ir data: 3302 m, 1036 ms, 1027 ms, 1016 s, 1004 ms, 900 s, 876 m, 810 m.

With Benzoic Acid.—A 0.86 g sample of the mixture was added to 2.5 g of benzoic acid in 20 ml of CH_2Cl_2 at 25° without liberation of NH_3 gas. The yellow insoluble product was washed with CH_2Cl_2, then distilled H_2O, and dried *in vacuo* for 3 days. *Anal.* Calcd for $NH_4[UO_2(C_6H_5CO_2)_3]$: U, 36.5; C, 38.7; H, 2.9; N, 2.2. Found: U, 36.6; C, 38.5; H, 3.0; N, 2.4. The ir spectrum was the same as that reported previously.[7]

With Acetylacetone.—A 1.32 g sample was mixed with 3 ml of acetylacetone in 30 ml of CH_2Cl_2 at 25°. Gaseous NH_3 was liberated, white NH_4Br precipitated, and an orange solution formed. Filtration followed by slow evaporation of the solvent yielded yellow crystals that were recrystallized from CH_2Cl_2 and dried *in vacuo* for 12 hr. *Anal.* Calcd for $UO_2(CH_3COCHCOCH_3)_2\cdot CH_3CNH_2CHCOCH_3$: U, 42.0; C, 31.8; H, 4.1; N, 2.5. Found: U, 42.2; C, 32.1; H, 2.9; N, 3.0. The ir spectrum was essentilly identical with that reported earlier.[8]

Discussion

Following reaction between $[(C_2H_5)_4N]_2UO_2Br_4$ and liquid ammonia, retention of NH_4Br in association with $UO_2(NH_2)_2\cdot NH_3$ persisted despite exhaustive washing and the very high solubility of NH_4Br in NH_3. X-ray diffraction and ir data confirmed the presence of NH_4Br and ν(U–Br) was not observed. The possible alternative formulation, $[UO_2NH\cdot 2NH_3](NH_4Br)_2$, is less attractive since the ir spectrum is more complicated than ordinarily observed for a simple ammine.[9] We therefore assign the band at 1125 cm^{-1} to $\omega(NH_2)$ since this mode was not observed in any of the other compounds isolated and corresponds to the spectrum of $Hg(NH_2)Br$.[10,11] The band at 930 cm^{-1} is assigned to the ν_3 mode of the linear uranyl moiety;[12] the frequency of the ν_1 mode is probably 858 cm^{-1} rather than 892 cm^{-1} since an extensive study of solid uranyl com-

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pounds[12] has shown that the difference between the ν_1 and ν_3 modes for the uranyl group is always in the range of 70–80 cm^{-1}. The amorphous amide $UO_2(NH_2)_2 \cdot NH_3$ is presumably polymeric, possibly containing both bridging amide and ammine groups and discrete linear uranyl groups.

The ir spectrum of the deammoniation product $UO_2NH(NH_4Br)_2$ does not show either ν(U–Br) or the presence of coordinated NH_3; the band at 891 cm^{-1} is clearly ν(U–O) and its position and shape suggests the absence of discrete linear uranyl groups in the imide.[13] Ammonium bromide may be washed from this mixture with liquid ammonia; the insoluble product is the amorphous 2-ammoniate, $UO_2NH \cdot 2NH_3$, in the absence of any ammonia-soluble uranium-containing species. This lends further evidence for the formulation given above for $[UO_2(NH_2)_2 \cdot NH_3](NH_4Br)_2$ since if the 2-ammoniate of the imide were present it should be possible to remove NH_4Br by washing. It is reported[3] that UO_2NH does not react with ammonium iodide; this also is in accordance with our observations.

It seems most likely that the $(UO_2Br_4)^{2-}$ ion is ammonolyzed in liquid ammonia to form a complex of the type $(NH_4)_2[UO_2Br_2(NH_2)_2]$ which is sparingly soluble and stable in ammonia but decomposes upon removal of the solvent to form $[UO_2(NH_2)_2 \cdot NH_3](NH_4Br)_2$. An analogous mechanism has been proposed to explain the ammonolysis of hexachlorotitanium(IV) complexes.[14]

The ir spectrum of $UO_2NH \cdot 2NH_3$ confirms the presence of coordinated ammonia and includes ν(U–O) at 877 cm^{-1}. Partial deammoniation occurs *in vacuo* at 200° to give $UO_2NH \cdot NH_3$; again there is ir evidence for coordinated ammonia and a band at 890 cm^{-1} assigned to ν(U–O). The 1-ammoniate undergoes reductive decomposition at 330° to give impure U_3O_8 probably containing minor quantities of other oxides and nitrides.

The ammoniated amide $UO_2(NH_2)_2 \cdot NH_3$ is extremely soluble in and reactive with dilute acids; hydrolysis yields $3UO_3 \cdot NH_3 \cdot 5H_2O$ which was previously isolated from the ternary system UO_3–NH_3–H_2O[15] and by addition of NH_3 to an aqueous solution of a uranyl salt.[16] These products also[6] were characterized by X-ray diffraction data.

The reaction of $[UO_2(NH_2)_2 \cdot NH_3](NH_4Br)_2$ with CH_3OH affords a convenient route to $UO_2(OCH_3)_2 \cdot CH_3OH$ previously formed from UO_2Cl_2 and $LiOCH_3$;[17,18] we report here ir data for this compound. With benzoic acid we obtained a salt $NH_4[UO_2(C_6H_5CO_2)_3]$. The crystalline product obtained from reaction with acetylacetone was identical with a compound previously obtained from uranyl nitrate and acetylacetone in the presence of NH_3.[8,19] There is considerable uncertainty about the nature of this compound; recent studies[8] employing ir and ^1H nmr data suggest that it is a β-ketoimine solvate of dioxobis(acetylacetonato)uranium(VI) and our observations are consistent with this postulate.

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Kinetic Study of the Oxidation of Ferrocene by Chromium(VI)[1a]

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The oxidation–reduction chemistry of ferrocene has received very little previous attention, although studies of Duke[2] and Stranks,[3] as well as earlier work from this group,[4] have been reported. A considerable body of work is now available concerning the kinetics and mechanism of oxidation of metal complexes by chromium(VI); these studies have been reviewed recently.[5]

In the present work we report the results of a kinetic study of the oxidation of ferrocene by Cr(VI), which occurs according to the reaction

$$3Fe(C_5H_5)_2 + HCrO_4^- + 7H^+ = 3Fe(C_5H_5)_2^+ + Cr^{3+} + 4H_2O \quad (1)$$

Experimental Section

Ferrocene from Alfa Inorganics was purified by vacuum sublimation. Potassium dichromate and perchloric acid were reagent grade chemicals used without additional purification. Lithium perchlorate was prepared from the carbonate and was twice recrystallized. Conductance water, prepared by a distillation from alkaline permanganate in a tin-lined still, was used throughout. The ferrocene stock solutions were analyzed by a spectrophotometric titration using a Fe^{3+} solution at the wavelength maximum for $Fe(C_5H_5)_2^+$, 618 nm. This reaction is known to occur with a 1:1 stoichiometry,[4b] and the ferrocene concentrations so determined were within 1% of the concentrations computed based on the weighed amount of ferrocene.

The reaction was studied in a mixed water–acetone solvent, 1:1 by volume, with the mole fraction of acetone in the solvent equal to 0.195. The reaction was studied in perchloric acid solutions with $[H^+] \geq 0.05$ *M*, and ionic strength was maintained at 1.00 *M* by addition of lithium perchlorate.

The kinetic measurements were carried out using a Durrum stopped-flow spectrophotometer equipped with a Kel-F mixing chamber having a 2-cm optical path.

A complication due to certain side reactions had to be considered. First, $HCrO_4^-$ slowly oxidizes acetone if the solution is acidic, so that solutions prepared in this manner decomposed appreciably in the time needed to begin the rate measurements. Also, solutions of ferrocene in aqueous acetone, while stable if neutral, are subject to slow decomposition if acidified. These problems were circumvented by the following procedure. The reaction between $HCrO_4^-$ and $Fe(C_5H_5)_2$, eq 1, requires acid to proceed; in neutral solution these reagents are stable together. The kinetic measurements were carried out by preparing one reservoir solution to contain both $HCrO_4^-$ and $Fe(C_5H_5)_2$, but no perchloric acid. The second solution consisted of perchloric acid, also in aqueous acetone. The reaction in eq 1 which occurs upon mixing is far more rapid than either of the other side re-

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