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(13) Structure III for alkyldibromogold complexes also explains their ready reducibility in contrast to the dialkylbromogold analogues (see ref 6b and 6d).
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(15) (a) V is written as an ion pair in analogy to $Br^- BrPPh_3^+$ [see ref 9]. (b) Stable salts of dimethyldihaloaurate(III) [^1H NMR of Ph_4As^+-$(CH_3)_2AuBr_2^-$: δ 1.21]. W. M. Scovell and R. S. Tobias, *Inorg. Chem.*, **9**, 945 (1970); see also G. C. Stocco and R. S. Tobias, *J. Am. Chem. Soc.*, **93**, 5057 (1971).
(16) Compound IV may be formed from I in eq 2 directly by brominolysis of two methyl groups on the same gold atom. Alternatively, cleavage of two methyl groups on separate gold atoms in I could afford a metastable monomethyldibromogold dimer (i.e., II cis or trans) which then rearranges to IV.
(17) (a) The ^1H NMR spectrum of $Ph_4As^+(CH_3)_2AuI_2^-$ shows the methyl singlet at δ 1.45 ppm [see ref 15b]. (b) A methylgold(III) species presented in eq 4 may be an intermediate in the formation of dimethylgold(III) complexes since methyl transfer from CH_3AuPPh_3 can be facile,[18] e.g., $CH_3I_2AuPPh_3 + CH_3AuPPh_3 \rightarrow (CH_3)_2IAuPPh_3 + IAuPPh_3$, etc.
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Uranium(IV) Sulfite and Uranium(IV) Oxysulfite

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Efforts to prepare sulfites of uranium have led to products of indefinite composition or have employed conditions that prevented the isolation of sulfites of uranium(IV). Rosenheim and Kelmy[1] reported the isolation of $(NH_4)_4[U(SO_3)_4]$ but this could not be confirmed during the present studies. Other early efforts to isolate sulfites of uranium(VI) demonstrated their existence in solutions from which only products of irreproducible composition could be isolated.[2,3] Both Aloy and Auber[4] and Yevteev and Petrzhak[5] reduced uranyl salts with sodium dithionite and sodium formaldehyde sulfoxylate, respectively, but reoxidized the products to sulfates by recrystallization from sulfuric acid.

There are several cases in connection with the processing of uranium ores in which uranium(IV) sulfite was probably formed but not isolated because of the conditions employed.[6-8] In a similar context precipitation of uranium(IV) sulfite was precluded by the presence of fluoride ion[9,10] and the preferential separation of $(NH_4)UF_5$. Other related actinide chemistry is concerned with sulfite complexes of neptunium(V)[11] and with the use of sodium dithionite for the reduction of higher oxidation states of plutonium to plutonium(III).[12]

We report here the synthesis of uranium(IV) sulfite as the tetrahydrate, its characterization, and pyrolysis to high purity uranium(IV) oxide. Also included is a closely related product, uranium(IV) oxysulfite–4-water.

Experimental Section

All experimental methods and physical measurements were made as described earlier.[13] For cases in which, for example, x-ray diffraction, spectral, DTA, or TGA data are given here only in part, the complete data are available elsewhere.[14]

Uranium(IV) Sulfate–4-Water. In a typical experiment, a solution of 3.3780 g of $Na_2S_2O_4$ (2.5-fold in excess of a 1:1 mol ratio) in 100 ml of water was added with stirring to 3.7816 g of $UO_2(NO_3)_2 \cdot 6H_2O$ in 100 ml of water. From the resulting deep red solution, a pale green precipitate separated immediately. After 10 min of stirring, the precipitate was filtered in an atmosphere of nitrogen and washed with six 50-ml portions of water. The product was then washed with three 25-ml portions of ethanol and dried by drawing dry nitrogen through the filter cake. Anal. Calcd for $U(SO_3)_2 \cdot 4H_2O$: U, 50.64; S, 13.62; H, 1.70. Found: U, 50.73; S, 13.66; H, 1.76. X-ray diffraction data (*d* spacings in Å; relative intensities in parentheses): 6.60 (1.0), 4.10 (0.8), 3.99 (0.8), 3.83 (0.7), 3.31 (0.5), 2.18 (0.5). Crystallite size, 0.0400 μm. The yield was essentially quantitative.

A 0.0024-g sample of $U(SO_3)_2 \cdot 4H_2O$ was placed in a furnace preheated to 650 °C in a dry nitrogen atmosphere and heated for 75 min. After cooling to 25 °C, the sample was found to have lost 0.0475 g or 42.26% of the original weight. The weight loss calculated for the elimination of $4H_2O$ and $2SO_2$ is 42.55%. Anal. Calcd for UO_2: U, 88.15. Found: U, 88.36; S, 0.02; Na, 0.07. X-ray diffraction data: 3.13 (1.0), 2.71 (0.5), 1.92 (0.6), 1.64 (0.5). Crystallite size, 0.4270 μm.

Uranium(IV) Oxysulfite–4-Water. When the foregoing procedure for the synthesis of $U(SO_3)_2 \cdot 4H_2O$ was changed *only* to the extent of conducting the filtration without protection from exposure to the atmosphere, the color of the precipitate changed from pale green to dark gray; this product was washed and dried as described above. The yield was quantitative; the product did not give an x-ray diffraction pattern. Anal. Calcd for $UO(SO_3) \cdot 4H_2O$: U, 58.62. Found: U, 58.36. When this product was dried at 10^{-2} Torr over P_2O_5 for 12 h, the color changed from dark gray to light gray. Anal. Calcd for $UO(SO_3) \cdot 2H_2O$: U, 64.32; S, 8.65; H, 1.08. Found: U, 64.16; S, 8.65; H, 1.15; Na, 0.36 ppm. This product also did not give an x-ray diffraction pattern.

A 7.394-mg sample of the tetrahydrate was heated to 218 °C under dry nitrogen in a DTA sample holder. After cooling to 25 °C the weight loss was found to be 1.317 mg or 17.81%; that required for the loss of $4H_2O$ is 17.73%. A larger sample (0.7292 g) was heated in a furnace at 600 °C for 90 min; the weight loss found was 0.2451 g or 33.61% as compared with 33.50% calculated for the loss of $4H_2O$ and SO_2. Anal. Calcd for UO_2: U, 88.15. Found: U, 87.96; S, 0.01; Na, 0.13. X-ray diffraction data: 3.10 (1.0), 2.69 (0.5), 1.91 (0.5), 1.63 (0.5). Crystallite size, >0.5000 μm. When the decomposition was carried out at temperatures below 600 °C (e.g., at 550°) the x-ray diffraction pattern included *d* spacings attributable to UO_2 but also the following ones which are characteristic of UOS: 2.70 (0.4), 1.94 (1.0), 1.65 (0.8), 1.57 (0.4), 1.37 (0.2), 1.22 (0.3). Slower initial heating rates appeared to favor the formation of UOS.

Discussion

It should be emphasized at the outset that the synthesis of essentially pure $U(SO_3)_2 \cdot 4H_2O$ is accomplished only by rigorous exclusion of atmospheric oxygen during both filtration and washing. Thereafter it can be stored indefinitely without decomposition in an inert atmosphere. As shown by DTA and TGA data,[14] this salt is decomposed to UO_2 as follows. An endotherm at 75 °C corresponds to the loss of 3.08 mol of H_2O followed by a broad endotherm beginning at ca. 110 °C which coincides with the loss of 1.02 mol of H_2O. The decomposition of the anhydrous salt is characterized by three endotherms: 550 °C (–0.50 mol of SO_2), 590–680 °C (–0.98 mol of SO_2), and 690 °C (–0.52 mol of SO_2).

The pyrolysis of the product formulated above as $UO(SO_3) \cdot 4H_2O$ proceeded essentially the same as described above except for a sharp endotherm at 460 °C that corresponds to the loss of 0.93 mol of SO_2. In the case of the dihydrate, an endotherm at 90 °C corresponds to loss of 2.03 mol of H_2O; at higher temperatures the data were less conclusive. An endotherm at 690 °C corresponds to the loss of 2.03 mol of H_2O and correlates with a loss of 48 amu from the TGA data. Both results are compatible with the formation of UOS which, as noted above, was detected by x-ray diffraction data. Experiments conducted on a much larger scale, however, led to analytical data which showed that the oxysulfide was a minor component in all cases.

It should also be pointed out that the analytical data for $UO(SO_3) \cdot 2H_2O$ are equally compatible with the formulation $U(OH)_2(SO_3) \cdot H_2O$. The latter seems untenable, however, since it could arise only by hydrolysis of a dried salt that was formed in an aqueous medium. The product in question can be explained only on the basis of oxidation of the normal sulfite. It is unfortunate that the spectral data, with but few exceptions, were not of sufficient quality to permit even tentative assignments; in general, the bands were broad and diffuse. In support of the oxysulfite formulation, however, it may be noted that bands at 460 and 505 cm^{-1} were observed and that these bands have been assigned by earlier workers[15] to $\nu(U{=}O)$.

With regard to the UO_2 formed by the decomposition of both of the sulfites described above, all initial products contained low levels of sodium. It has been shown earlier[13,16] that this impurity can be eliminated by ignition for longer times at higher temperatures.

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Registry No. $U(SO_3)_2{\cdot}4H_2O$, 61931-01-9; $UO(SO_3){\cdot}4H_2O$, 61966-62-9; $UO(SO_3){\cdot}2H_2O$, 61966-63-0; $UO_2(NO_3)_2$, 10102-06-4; $Na_2S_2O_4$, 7775-14-6.

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On the Reduction of Nitrate by Diammonium Oxopentachloromolybdate(V) in Dimethylformamide

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Sir:

In a recent paper, we reported the results of a kinetic study of the reduction of nitrate by $(NH_4)_2MoOCl_5$ in DMF.[1] More recently, our mechanistic interpretation of these results has been questioned and an alternative mechanism, making use of our kinetic data, proposed by Garner et al.[2] We find it necessary, therefore, to point out the mechanism of Garner et al. is, in fact, not in agreement with our results.

In our original work, we proposed the Cl^- trans to the oxo group of $MoOCl_5^{2-}$ dissociates essentially completely in DMF, giving $MoOCl_4^-$:

$$MoOCl_5^{2-} \rightleftharpoons MoOCl_4^- + Cl^- \qquad (1)$$

In our mechanism, nitrate then displaces a second Cl^-, producing an intermediate $MoOCl_3(NO_3)^-$ complex, which subsequently undergoes electron transfer to give products:

$$MoOCl_4^- + NO_3^- \rightleftharpoons MoOCl_3(NO_3)^- + Cl^- \qquad (2)$$

$$MoOCl_3(NO_3)^- \rightarrow MoO_2Cl_2 + NO_2 + Cl^- \qquad (3)$$

Using ESR, Garner et al. have provided good evidence that the initial reaction 1 produces a six-coordinate species, with a molecule of DMF displacing a Cl^-, again the displacement being essentially complete under the conditions used in our work:[2]

$$MoOCl_5^{2-} + DMF \rightleftharpoons MoOCl_4(DMF)^- + Cl^- \qquad (4)$$

In view of the donor ability of DMF,[3] this is not surprising; it is also easily accommodated in our mechanism, by replacement of the coordinated DMF by NO_3^- in a reaction analogous to (2):

$$MoOCl_4(DMF)^- + NO_3^- \rightleftharpoons MoOCl_3(NO_3)^- + Cl^- + DMF \qquad (5)$$

This in no way affects our kinetic arguments, although, as pointed out by Garner et al.,[2] it may account for the relative slowness of the reaction.

Garner et al., however, have proposed another mechanism to explain our results:

$$MoOCl_4(DMF)^- \rightleftharpoons MoOCl_4^- + DMF \qquad (6)$$

$$MoOCl_4^- + NO_3^- \rightleftharpoons MoOCl_4(NO_3)^{2-} \qquad (7)$$

$$MoOCl_4(NO_3)^{2-} \rightarrow MoO_2Cl_4^{2-} + NO_2 \quad \text{(fast)} \qquad (8)$$

$$MoOCl_4^- + Cl^- \rightleftharpoons MoOCl_5^{2-} \qquad (9)$$

By application of the steady state condition to $MoOCl_4^-$, they obtained the rate expression (P = products):

$$dP/dt = \frac{k_6k_7[MoOCl_4(DMF)^-][NO_3^-]}{k_6[DMF] + k_7[NO_3^-] + k_9[Cl^-]} \qquad (10)$$

Unfortunately, these authors state the integrated form of this expression is consistent with our data, when in fact, it is not. Clearly, in their mechanism, since the only source of Cl^- is the initial displacement of a coordinated Cl^- of $MoOCl_5^{2-}$ by DMF (reaction 4), which is very rapid and essentially complete,[2] Cl^- concentration must be constant during the reaction, even when no additional Cl^- has been added. In the presence of excess NO_3^-, this leads to a simple first-order rate expression, which must hold at all Cl^- concentrations:

$$dP/dt = k_{obsd}\,[MoOCl_4(DMF)^-]$$

$$k_{obsd} = \frac{k_6k_7[NO_3^-]}{k_6[DMF] + k_7[NO_3^-] + k_9[Cl^-]} \qquad (11)$$

As is clearly stated in our paper, however, first-order plots are linear only to ~50% reaction in the absence of added Cl^-, deviating after that in a negative direction.[1] This was shown by us to be due to inhibition by Cl^- released during the reaction. By using a rate expression of the form

$$-d[Mo(V)]/dt = k_{obsd}\,[Mo(V)]/[Cl^-] = k_{obsd}\,[Mo(V)]/(3[Mo(V)]_0 - 2[Mo(V)]) \qquad (12)$$

$$Mo(V) = MoOCl_4^- \text{ or } MoOCl_4(DMF)^-$$

$$[Mo(V)]_0 = [MoOCl_5^{2-}]_0$$

in which Cl^- is a variable, an integrated rate expression was obtained by us which gives linear plots to >90% reaction and consistent rate constants:

$$2[Mo(V)] - 3[Mo(V)]_0 \ln[Mo(V)] = k_{obsd}\,t + I \qquad (13)$$