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Hydridic Nature of the "Lower Oxide of Thorium"[1]

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It has been known since the early work with thorium metal that it will dissolve readily on treatment with HCl, but that a voluminous black residue is left. In a recent paper[3] one of us showed that decomposition of the residue in HCl containing small amounts of fluoride or fluorosilicate gave 1 mole of hydrogen gas per g.-atom of Th^{4+} produced in the solution. The analytical data were consistent with a composition ThO, with an apparent oxidation state of 2 for the thorium, but there was no obvious explanation for the apparent strong retention of water and HCl by the solid (2 atoms of hydrogen per thorium).

Some time later, we became aware of a paper by Karabash[4] on the same topic. From the tendency of the residue material to oxidize explosively,[3] Karabash assumed it to be hydridic; elemental analyses and gas evolution data led him to the formulation HTh(OH)O. Although the evidence on which he postulates formation of a complex hydride of thorium(IV) is not convincing,[5] there is ample precedent[6] for the formation of metallic hydrides by the reaction of metals with strong acids. Furthermore, Karabash's formulation is consistent with the results presented in our earlier paper.[3] The catalytic evolution of hydrogen[3] could be explained by the displacement of hydride anion from Th(IV) by fluoride or fluorosilicate anion; combination of the hydride ion with a proton in the acid solution would yield a molecule of H_2, in 1:1 ratio to the Th(IV) liberated. In addition, an explanation would be ready-made for the difficulty in removing hydrogenous material excess to the formula ThO.

We now have performed an experiment which demonstrates unequivocally that the thorium residue contains hydridic hydrogen.

A sample of thorium metal was treated with $DCl-D_2O$. The black residue was washed repeatedly with $HCl-H_2O$ to remove hydroxylic or other readily exchangeable deuterium. The resultant solid, upon decomposition in HCl with catalytic fluorosilicic acid, yielded hydrogen gas containing 87% HD, 12% H_2, and 1% D_2. Hydrogen formed by reaction of solvent protons would contain only H_2. Hydrogen produced by the thermal decomposition of the residue would be an approximately statistical mixture of the hydrogen isotopic species H_2, HD, and D_2, corresponding to its deuterium content. The very high HD content of the gas actually evolved on dissolution of the residue, together with the very low D_2 content, can be explained if it is formed by combination of a deuteride ion from the residue with a proton from the reacting solution. The rate of exchange of the deuteride with protons in acid solution must be very low. This is consistent with our earlier observations on the insensitivity of the neutron diffraction pattern of the residue prepared in ordinary HCl to washing with $DCl-D_2O$. Consideration of the implications of this observation led to design of the experiment described above.

Taken together with our earlier analytical data,[3] therefore, the residue is a compound of Th(IV) which may be formulated ThO(X)H. The group X is largely hydroxyl (corresponding to Karabash's formulation) but also may be chloride.

Our earlier experiments with the corresponding uranium residue[3] showed that at the end of the catalytic solution process all the uranium was present as U(IV), but that not more than 1 and most often about 0.65 mole of hydrogen was evolved per mole of U(IV) dissolved. This gave an apparent oxidation state generally greater than 2. In terms of the hydride formulation, these observations would correspond to U(IV) in the form UO(X)H, but with variable proportions of the hydride anion displaced by hydroxyl or chloride. The data cannot be reconciled with Karabash's hypothesis of a hydride derivative of U(III).

The black thorium residue is turned yellow by the action of air, particularly in ammoniacal environment,[3] by hydrogen peroxide,[3] nitric acid,[3] the elemental halogens (Cl_2, Br_2, I_2), and by Ce^{4+}

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Student aide (Lawrence College), Argonne-A.C.M. program, Fall, 1961.

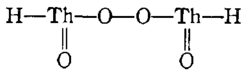
[3] L. I. Katzin, *J. Am. Chem. Soc.*, **80**, 5908 (1958).

[4] A. G. Karabash, *Zh. Neorgan. Khim.*, **3**, 986 (1958).

[5] Neither the elemental analyses nor the gas evolution on heating necessarily imply hydridic structure. The gas evolution by action of permanganate (*e.g.*, in 4 *N* sulfuric acid), used to "prove" the hydridic nature of the uranium residue, and hence by inference, that of the thorium residue, has been shown by us to be faulty evidence: copious amounts of gas (oxygen!) are evolved even in the total absence of one of the residues.

[6] *E.g.*, G. Brauer and H. Muller, *J. Inorg. Nucl. Chem.*, **17**, 102 (1961).

oxidizing agent. Permanganate also yellows the residue, but the color becomes obscured by deposition of (probably) MnO_2. Even with boiling, Ce^{4+} evolves no gas from the residue. The yellow material formed with nitric acid oxidation was found to retain no nitrogen. Karabash[4] also found yellowing with hydrogen peroxide, and on the basis of this reaction postulated that the yellow form corresponds to the species



$$\mathrm{H{-}\underset{\underset{O}{\|}}{Th}{-}O{-}O{-}\underset{\underset{O}{\|}}{Th}{-}H}$$

To form this peroxide by oxidation from HTh(O)-OH requires one equivalent of oxidizing agent per thorium. With the stable oxidizing agent Ce^{4+}, reaction at room temperature or with slight warming produced yellow residue with the consumption of only 10–20% of the expected amount of oxidant. More cerium could be consumed by prolonged boiling, but this further consumption might be due to residual chloride, etc. Only small volumes of permanent gas (in many cases, none) could be evolved under these conditions, in contrast with the claims of Karabash for permanganate oxidation. As noted above, permanganate in our hands could give the yellowing reaction. It may be that the yellowing reaction is limited primarily to surface layers, but the nature of the reaction and its product must still be classed as uncertain.

Experimental

One g. of cast thorium metal was dissolved in 5 *N* DCl. The mixture was heated under reflux to complete reaction. After cooling, the residue was separated by centrifugation. This residue then was washed four times with 2 *N* HCl, separating each wash liquid by centrifugation.

The washed residue was transferred to a two-neck flask. To one neck was attached a bent-necked flask containing 6 *N* HCl with the usual catalytic amounts of fluorosilicic acid. The second neck of the reaction vessel was attached to a vacuum line. The solution was frozen down and degassed, and the stopcock to the vacuum line was closed. The solution was added to the thorium residue by rotating the flask about its joint, and the mixture was heated until reaction was complete and the residue dissolved. The gas was transferred to a gas sample tube by means of a Toepler pump, and analyzed mass spectrometrically. (The instrument used was a Consolidated Engineering Corp. Model 21-620. We thank C. E. Plucinski for the analysis.) The gas contained only hydrogen, the isotopic composition of which was HD, 87%; H_2 12%; and D_2, 1%.

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A Novel Synthesis of the Hexafluorophosphate of the Cyclopentadienyliron Tricarbonyl Cation

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The cation $[C_5H_5Fe(CO)_3]^+$, a member of the isoelectronic series which includes the species $C_5H_5Mn(CO)_3$,[1] $[C_5H_5Cr(CO)_3]^-$,[2] and $[C_5H_5V(CO)_3]^{-2}$,[3] was unknown until recently when two syntheses of this cation were reported. One method was based on the reaction of a cyclopentadienyliron dicarbonyl halide with carbon monoxide in an inert solvent in the presence of an aluminum halide as a catalyst.[4] The other method was based on the reaction of a cyclopentadienyliron dicarbonyl halide with carbon monoxide in acetone solution[5] in the presence of sodium tetraphenylborate. A substituted cyclopentadienyliron tricarbonyl cation also has been prepared by the protonation of fulveneiron tricarbonyl derivatives.[6]

This note describes a new method for the synthesis of the hexafluorophosphate of this cation involving the carbonylation of cyclopentadienyliron dicarbonyl iodide in the presence of a mixture of aqueous 65% hexafluorophosphoric acid and propionic anhydride. This method has the advantage that analytically pure $[C_5H_5Fe(CO)_3][PF_6]$ may be isolated directly from the reaction mixture and is suited for the convenient preparation of this salt in quantities of 20 g. and greater.

This hexafluorophosphoric acid–propionic anhydride mixture is also of use in the synthesis of stable salts of other substituted iron tricarbonyl cations. Treatment of cycloheptatrieneiron tricarbonyl and cyclooötatetraeneiron tricarbonyl with a hexafluorophosphoric acid–propionic anhydride mixture at room temperature yields the stable salts $[C_7H_9Fe(CO)_3][PF_6]$ and $[C_8H_9Fe(CO)_3][PF_6]$, respectively. Other salts of these

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(1) E. O. Fischer and R. Jira, *Z. Naturforsch.*, **9b**, 618 (1954).

(2) E. O. Fischer and W. Hafner, *ibid.*, **10b**, 140 (1955).

(3) E. O. Fischer and S. Vigoureux, *Ber.*, **91**, 2205 (1958).

(4) E. O. Fischer and K. Fichtel, *ibid.*, **94**, 1200 (1961).

(5) A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961).

(6) E. Weiss and W. Hübel, *Angew. Chem.*, **73**, 298 (1961).