

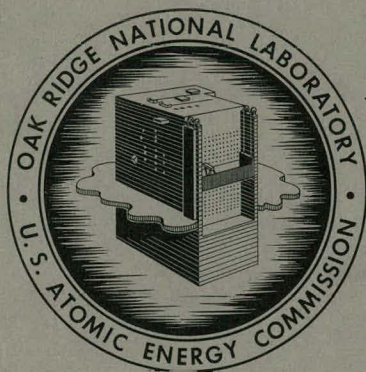
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ORGANIC COMPOUNDS IN FISSION REACTORS.

II. THORIO-ORGANIC COMPOUNDS

W. H. Baldwin



OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

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ABSTRACT

The advantages of the use of organic liquids in fission reactors to minimize corrosion and pressure problems have led to a study of the solution of thorium in such fluids. Thorio-organic compounds were prepared from organic acids, diketones, and other chelating compounds. Salts of carboxylic and phospho-organic acids were insoluble. The chelate with dibenzoylmethane was soluble in molten biphenyl but was decomposed at 300°C. The general low solubility of thorio-organic compounds in nonpolar solvents can be explained by steric effects. The large thorium atom has the ability to form strong coordination complexes with adjacent molecules, leading to coordination polymers. This effect can be minimized by shielding the thorium nucleus with large organic groups such as dibenzoylmethane. The large, branched organic groups needed to impart solubility limit the maximum solubility.

INTRODUCTION

Polycyclic aromatic hydrocarbons have several advantages for use as the liquid medium in fission reactors. Among the advantages, as compared with water, are lower vapor pressure and greater stability toward materials of construction. It was shown in a previous report (1) that thorium dioxide can be dispersed in molten biphenyl with organic compounds. The current report considers the problem of dissolving thorium compounds in molten biphenyl for breeder blankets. Some of these data were reported previously (2).

First consideration has been given to the preparation of thorio-organic compounds and the estimation of solubility. The testing of thermal and radiolytic stabilities was, for the purposes of this report, secondary to the question of solubility.

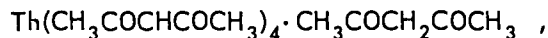
For the most part, the compounds tested were restricted to those that could be considered feasible from the standpoint of neutron economy. This restriction was ignored in the testing of several nitrogen-containing compounds. The nature and the number of nuclei that can be tolerated in the blanket have been presented by Lietzke and Stoughton (3).

EXPERIMENTAL

Thorium Benzoate. — A basic thorium benzoate resulted from adding 50 ml of 2 M sodium benzoate to 5.52 g of thorium nitrate in 200 ml of water.

The pH was adjusted to 6.0; the precipitate was filtered, and washed with water and alcohol. The product weighed 6.1 g; portions, when ashed, yielded 47.4 and 47.0% ThO₂ [the theoretical value for Th(OH)₂(C₆H₅COO)₂ is 52%]. A 4.8-g portion was heated on the steam bath with 4 g of benzoic acid in 200 ml of distilled water for 5 hr, filtered, washed with 0.2% aqueous benzoic acid, and then washed with alcohol; 36.6% ThO₂ was found [the theoretical value for Th(C₆H₅COO)₄ is 36.9%].

Thorium Acetylacetonate. — The method of Young and Kovitz (4) was used to prepare the penta acetylacetonate,



which melted at 150°C; 35.7% ThO₂ was found (theoretical: 36.2%).

Thorium Dibenzoylmethane. — The method of Forsling (5) was used to prepare a product that melted at 190–191°C with no sign of decomposition; the recorded melting point is 196°C.

Thorium Mercaptobenzothiazole. — The procedure of Spacu and Pirtea (6) was used to prepare a product that contained 26.4% ThO₂; the theoretical value for the 1:4 compound is 29.5%, and that for the 1:5 compound is 24.9%.

Thorium 8-Hydroxyquinolate. — The method of Moeller and Ramaniah (7) was used to prepare a compound that contained 31.0% ThO_2 ; the theoretical value for the 1:4 compound is 32.2%, and that for the 1:5 compound is 27.7%.

Thorium Dibutylphosphate. — Dibutylphosphoric acid- P^{32} (38.4 mmoles) in 25 ml of ethanol was added to 25 ml of aqueous thorium nitrate (3.84 mmoles). The pH was adjusted to 1 with 1 M NaOH, and the mixture was allowed to stand at room temperature for 16 hr. The gelatinous precipitate was filtered and then washed with six portions (25 ml each) of ethanol, during which it became granular. The product (3.88 g, 95% yield) was dried at 56°C *in vacuo*. By radioactive assay 11.4 and 11.5% P were found; the theoretical value for $\text{Th}(\text{C}_8\text{H}_{18}\text{PO}_4)_4$ is 11.59%.

Measurement of Solubility. — Samples of thorium compounds and biphenyl (1) were weighed in 10-mm glass tubes sealed at one end. The tubes were then sealed under reduced pressure. The sealed tubes were heated with gentle agitation in an oil bath to temperatures as high as 200°C and in an aluminum block at higher temperatures.

DISCUSSION

Generally, first thought is given to organo-thorium compounds with true carbon-to-metal bonds. So far, no such compounds have been reported for either thorium or uranium. The closest have been the reported (8) π -bonded compounds with cyclopentadiene. The thorium compound was stated to be too unstable for purification.

Many salts of thorium with carboxylic acids have been reported. They range, in composition, from the normal salt that contains four carboxyl groups through a series of basic salts. The structure of the compound obtained will depend upon the degree of reaction between the thorium ion and the anion and the method used in the preparation. For example, the tetrabenzoate can be obtained by careful washing of the salt with aqueous benzoic acid. A mixture of basic benzoates resulted when the salt was washed with water. Wendlandt (9) examined a number of thorium carboxylates on the thermogravimetric balance and found the normal salts to be more stable than the basic. Thorium benzoate was one of the most stable, but it is not soluble in biphenyl (see Table 1).

Thorium carboxylates have been used for decarboxylation to ketones. Thorium azelate was decomposed at 300°C *in vacuo* (10). Thorium

acetate decomposes at 270°C; thorium oxide and water have catalytic effects, so that the reaction begins at lower temperatures (11).

Thorium salts of the hetero-atom acids (phosphorus, sulfur) have been less extensively studied. Banks and Davis (12) obtained the normal salt with benzenephosphonic acid; it is thermally quite stable and suitable for the gravimetric analysis of thorium. The salt was not soluble in biphenyl.

The normal thorium salt was obtained with dibutylphosphoric acid, but it too was not soluble in biphenyl (see Table 1).

The highly charged thorium ion forms many chelates. The chelate with dibenzoylmethane was selected by Comyns (13) as the most likely compound for use in polycyclic hydrocarbons for a breeder blanket. The compound prepared in this laboratory was used to confirm the findings of Comyns: The compound is soluble in the molten biphenyl but lacks the desired thermal stability (see Table 1).

The chelate with 8-hydroxyquinoline reportedly has significant thermal stability on the thermogravimetric balance (14, 15). In molten biphenyl the compound was unstable at 300°C (see Table 1).

The compound formed with mercaptobenzothiazole has been used in the gravimetric analysis of thorium (6). The compound is insoluble in molten biphenyl (see Table 1).

FACTORS AFFECTING SOLUBILITY

The low solubility of many thorium compounds in biphenyl may be, in part, attributed to the degree of association of the thorium compounds. Evidence for this assumption has been presented by Wardlaw and Bradley (16), who studied the alkoxides of thorium and a number of other metals. Each metallic alkoxide exhibits a degree of association that is dependent on the size and configuration of the hydrocarbon chain in the alkoxy group. The observed molecular weight of thorium alkoxide in benzene approached the formula weight only with tertiary alkoxy groups that were of high molecular weight. The hydrocarbon group must be large enough and of the proper configuration to shield the thorium atom from neighboring molecules. The residual coordinating power of the thorium atom tends to be satisfied by oxygen of the alkoxides of neighboring molecules, when possible.

Table 1. Thorium Compounds in Biphenyl

Organic Compound (HA)	Composition	Thorium Concentration (g per kg of mixture)	Behavior in Biphenyl Mixture
Benzoic acid	ThA ₄	31	Insoluble at 200°C
Acetylacetone	ThA ₄ ·HA	150	Soluble at 100°C; solution darkened at 150–160°C
Dibenzoylmethane	ThA ₄	109	Soluble at 175°C; mixture and pure compound decomposed after 3 hr at 290–310°C
Mercaptobenzothiazole	ThA ₄ ·0.5HA	16	Insoluble at 250°C
8-Hydroxyquinoline	ThA ₄ ·HA	0.054	Soluble at 170°C; decomposed after ½ hr at 300°C
Dibutylphosphoric acid	ThA ₄	0.055	Insoluble at 250°C for 3 hr

The thorium salts of acids have second oxygen atoms that can coordinate with neighboring thorium atoms. Thus the phosphorus acids $-P(O)OH$ behave as bidentate ligands for coordination. The phosphinic acids have been shown to be associated as dimers in nonpolar solvents, while the phosphonic acids behave as tridentate ligands showing a higher degree of association.

The compound having the highest solubility in biphenyl (see Table 1) is the chelate of thorium with dibenzoylmethane. The four dibenzoylmethane groups on thorium provide more shielding than any of the other compounds.

The maximum solubility attainable with any compound is a function of the size of the groups. It was shown in the preceding paragraphs that the

organic groups must be large. This limits the amount of thorium in the compound. As an example of this limitation it can be readily calculated that in the compound ThA_4 , when A is methoxide (the simplest), the compound contains 650 g of Th per kg; the tetrabenzoate contains 384 g of Th per kg, and the chelate with dibenzoylmethane contains 205 g of Th per kg.

The factors required to obtain a high solubility of thorium compounds in biphenyl are incompatible with the requirement of high concentrations of thorium.

ACKNOWLEDGMENT

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