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NASA TECH BRIEF

Lewis Research Center

Radiochemical Synthesis of Pure Anhydrous Metal Halides

Pure anhydrous lower valence metal halides have been produced using radiation chemistry. The method is an extension of the process described in a previous Tech Brief (Reference B72-10439) on the use of radiation chemistry as a practical tool for inorganic preparations and in particular the deposition of metals by irradiation of their aqueous metal salt solutions with high energy (2MeV) electrons.

Higher valence metal halides can, in general, be easily produced in the anhydrous state by conventional chemical methods. Production of lower valence metal halides by conventional chemical methods, however, involves difficulties in isolating the reaction product, contamination of the product by container materials due to the high temperatures required, formation of oxygen-containing materials in the product, and contamination of the product by the reducing agent.

This method allows the preparation and isolation of pure anhydrous lower valence metal halides. A higher valence metal halide is dissolved in an organic liquid and exposed to high energy (2MeV) electrons. This causes the metal halide in solution to be reduced to a lower valence metal halide. The product deposits as a precipitate which is easily removed from other reaction products and excess reactants which remain in solution. The higher valence metal halides are usually more covalent or less ionic in character than the reduced lower valence metal halides; therefore, the higher valence metal halides are soluble in certain organic liquids and the more ionic reduced halides are relatively insoluble in the same liquid.

Irradiation of certain organic liquids generates reducing species. These reducing species include hydrogen atoms, solvated electrons and possibly organic radicals. Some organic liquids that are radiolytically reducing include hydrocarbons (heptane and toluene), heterocyclic ethers (tetrahydrofuran), primary alcohols (ethanol) and secondary alcohols (2-propanol). Solutions of higher valence metal halides in hydrocarbons provide an oxygen and water free system. Hydrolysis of the metal halide with any water present forms insoluble oxyhalides and hydrated oxides which can be readily removed; thus the anhydrous system is maintained. Many higher valence metal halides are not soluble in hydrocarbons; therefore, more polar organic liquids must be employed such as tetrahydrofuran. The organic solvent selected is one in which the higher valence metal halide starting material is soluble but in which the reduced lower valence metal halide is insoluble.

Notes:

1. Examples of reactions which have been performed by this method are as follows:
   a. Solution: Tin IV chloride in heptane
      Product: Tin II chloride
   b. Solution: Tin IV iodide in heptane
      Product: Tin II iodide
   c. Solution: Titanium IV chloride in heptane
      Product: Titanium III chloride and Titanium II chloride
   d. Solution: Iron III chloride in tetrahydrofuran
      Product: Iron II chloride
   e. Solution: Copper II bromide in n-butonol
      Product: Copper I bromide
2. There are numerous practical applications for pure anhydrous lower valence metal halides. For applications where the metal halide is to be vapor deposited, it is important that it be anhydrous or it will tend to decompose. Low valence titanium halides are used as catalysts to promote certain organic reactions. Stannous chloride is of interest for use in vapor lamps because it produces a continuous spectrum of visible light.
3. Further information is available in the following report:
   NASA TN-D-7285 (N73-24156), Survey of Application of Radiation to Preparative Chemistry
   Copies may be obtained at cost from:
   Aerospace Research Applications Center
   Indiana University
   400 East Seventh Street
   Bloomington, Indiana 47401
   Telephone: 812-337-7833
   Reference: B73-10407

(continued overleaf)

4. Specific technical questions may be directed to:
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Patent Status:

Inquiries concerning rights for the commercial use of this invention should be addressed to:
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