Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, MERCURY

1. Mercury(I) Fluoride

Mercury(I) fluoride [13967-25-4], Hg_2F_2, also known as mercurous fluoride, is a light-sensitive golden yellow material decomposing in water at 15°C. Some of the physical properties are listed in Table 1. Hg_2F_2 resembles AgF in activity with the exception that the former does not form complex compounds or mixed halogen fluoride salts. Consequently, almost an equivalent amount of Hg_2F_2 is sufficient for halogen exchange reactions (1). A mixture of Hg_2F_2 and I_2 (1:1 molar ratio) is much more effective than Hg_2F_2 alone (2). Mercury(I) fluoride is classified as a soft fluorinating reagent (3). Reactions of Hg_2F_2 with monobromides and monoiodides produce fairly good yields, but in polybromides and polyiodides only one halogen is replaced at 120–140°C. Loss of hydrogen halide gives the corresponding olefins (4).

Several preparatory methods for the manufacture of Hg_2F_2 have been reported (5). Whereas no commercial applications for Hg_2F_2 have been reported, it is available from Advance Research Chemicals and Aldrich Chemicals in the United States. As of 1993, the U.S. market was a few kilograms per year at a price of $1500/kg.

2. Mercury(II) Fluoride

Mercury(II) fluoride [7783-39-3], HgF_2, also known as mercuric fluoride, is a white, hygroscopic solid which turns yellow instantly on exposure to moist air. It must be handled in a dry box or under an atmosphere of dry nitrogen. Some of its physical properties are listed in Table 1. Whereas HgF_2, classified as a moderate fluorinating reagent (3), is superior to both AgF and Hg_2F_2, it has been replaced by anhydrous potassium fluoride [7789-23-3], KF, owing to the toxicity of mercury and the disposal regulations issued by the EPA (see MERCURY COMPOUNDS). HgF_2 is an excellent reagent for the addition of fluorine to olefins (1).

Mercury(II) fluoride is easily prepared by passing pure elemental fluorine over predried $HgCl_2$ at 100–150°C until all the chloride ions have been replaced. It is also produced *in situ* by condensing anhydrous HF over HgO (6) or over $HgCl_2$ (10).

Mercury(II) fluoride has been used in the process for manufacture of fluoride glass (qv) for fiber optics(qv) applications (11) and in photochemical selective fluorination of organic substrates (12). It is available from Advance Research Chemicals, Aldrich Chemicals, Johnson/Matthey, Aesar, Cerac, Strem, and PCR in the United States. The 1993 annual consumption was less than 50 kg; the price was $800–1000/kg.

Mercury salts are highly toxic and must be handled carefully. It is necessary to consult the material safety data sheet prior to handling. Strict adherence to OSHA/EPA regulations is essential. The ACGIH adopted (1991–1992) TLV for mercury as inorganic compounds is TWA 0.1 mg/m^3 and for fluorides as F^- 2.5 mg/m^3.

Table 1. Properties of Mercury Fluorides

Property	Hg_2F_2	HgF_2
mol wt	439.22	238.61
density, g/cm^3	8.73	8.95
melting point, °C	>570 (dec)	645
ΔH_f, kJ/mol[a]	−485	−405
ΔG_f, kJ/mol[a]	−469	−362
C_p, J/(mol·K)[a]	+100.4	+74.86
S, J/(mol·K)[a]	161	134.3

[a] To convert J to cal, divide by 4.184.

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