SOME RECENT DEVELOPMENTS IN THE CHEMISTRY OF HYPOFLUORITES*

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In this paper we shall discuss a new and convenient method for the preparation of hypofluorous acid, HOF, and we shall describe the synthesis and characterization of the hitherto unknown methyl hypofluorite, CH_3OF. The archetypal hypofluorite HOF is known to have remarkable oxygenating properties. Its investigation and application have been inhibited, however, by the difficulty of its synthesis, which has heretofore involved passage of elemental fluorine over ice in a complex recirculating system, and by the fact that the neat material can be explosively unstable. It has recently been found that passage of fluorine through acetonitrile containing 5-20% water generates strongly oxidizing solutions, and we have subsequently shown that these solutions contain HOF. Characterization of the solutions by NMR and molecular spectrometry indicates that a 1:1 hydrogen-bonded complex between the HOF and acetonitrile is present. The complex appears to be significantly more stable than neat HOF, and this interaction therefore serves as a means of "taming" hypofluorous acid and making the compound more accessible to researchers interested in working with it.

Methyl hypofluorite has widely been assumed to be unmakeable because of the ease with which it could decompose to HF and formaldehyde. In fact, the compound can be readily prepared by fluorination of a cooled solution of methanol in acetonitrile or propionitrile, and even by fluorination of neat methanol at Dry Ice temperature. The extremely volatile compound (m.p. –142 °C, b.p. –33 °C) can be distilled from the reaction mixture, and it has been isolated and characterized by mass, NMR, and infrared spectrometry. Photoionization mass spectrometric measurements of fragment thresholds yield values of ca. –94 and 196 kJ/mol respectively for the enthalpy of formation of CH_3OF and the dissociation energy of its oxygen-fluorine bond. This makes the oxygen-fluorine bond in CH_3OF very slightly weaker than that in HOF, but stronger than that in any other known hypofluorite. Neat liquid CH_3OF can decompose explosively, but the compound is well-behaved and relatively long-lived in the gas phase and as a solution in acetonitrile or propionitrile. It adds the elements of CH_3O and F to olefins; with unsymmetrical olefins the addition takes place in the direction of electrophilic methoxylation rather than electrophilic fluorination.

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