Review

Overview on the history of organofluorine chemistry from the viewpoint of material industry

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Abstract: Fluorine (from "*le fluor*", meaning "to flow") is a second row element of Group 17 in the periodic table. When bound to carbon it forms the strongest bond in organic chemistry to give organofluorine compounds. The scientific field treating them, organofluorine chemistry, started before elemental fluorine itself was isolated. Applying the fruits in academia, industrial organofluorine chemistry has developed over 80 years via dramatic changes during World War II. Nowadays, it provides various materials essential for our society. Recently, it utilizes elemental fluorine itself as a reagent for the introduction of fluorine atoms to organic molecules in leading-edge industries. This paper overviews the historical development of organofluorine chemistry especially from the viewpoint of material industry.

Keywords: organofluorine chemistry, fluorine, fluorination

Introduction—Incunabula of organofluorine chemistry

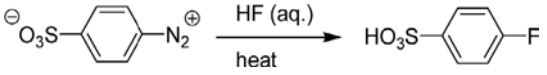
Alexander Borodin (1833–1887), who is well-known as a composer in classical music, is said to have made the first organofluorine compound.[1] More precisely, he carried out the first nucleophilic replacement of a different halogen atom by fluoride (Eq. 1) and reported the results in 1862.[2)–4)] This was the first example of synthesis of an organofluorine compound by halogen exchange, which is now broadly used in fluorine chemistry and especially in fluorochemical industry for the introduction of fluorine atoms into organic molecules. Borodin was a promising young chemist, and became a professor of chemistry in 1864.

[1]

Actual first synthesis of an organofluorine compound was reported by Dumas *et al.* in 1835,[4] who prepared methyl fluoride from dimethyl sulfate (Eq. 2).

$$(CH_3O)_2SO_2 + 2\ KF \rightarrow 2\ CH_3F + K_2SO_4 \qquad [2]$$

Formation of an aryl carbon–fluorine (C-F) bond was first carried out through diazofluorination by Schmitt *et al.* in 1870 (though the characterization was wrong), then by Lenz in 1877 (Eq. 3).[4]



[3]

Mineral fluorides were recognized and used as early as 16th century. In 17th century, it was already known that glass was etched when it was exposed to a new acid generated from fluorspar and sulfuric acid.[5] The generated acid was called hydrofluoric acid and was characterized by Scheele in 1771.[5),6)] Then it was eventually realized that hydrofluoric acid contained a previously unknown element, fluorine. Although organofluorine compounds were prepared in mid 19th century, elemental fluorine itself was not isolated at that time.

After continuous efforts by a great number of chemists, elemental fluorine was finally isolated in 1886 by Moissan, who electrolyzed a melt mixture

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