

JOSEPH H. SIMONS AND HIS WORK IN FLUORINE CHEMISTRY

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Professor Joseph H. Simons was the model of the interdisciplinary scientist. His interests and accomplishments straddled several fields, chemistry, physics and engineering. Nevertheless his most prolific achievements are found in the areas of fluorine and fluorocarbon chemistry. His graduate studies and his early personal research work as a faculty person at Northwestern University and Pennsylvania State College dealt, by and large, with the properties and chemistry of hydrogen fluoride in the liquid and gas states. For example, he was associated, as a principle investigator, with the measurement of eight [1-7] properties of this material. These were the freezing point, vapor pressure, density, surface tension, heat of vaporization, viscosity, the molecular structure of the gas and liquid and the solubility of HF in organic liquids such as benzene and octane. He also was involved in work in which HF was used as a reagent in reactions to prepare fluorides such as a fluorocarbonate [8] and organosilicon fluorides [9]. Some of the data collected in these early studies provided evidence for the phenomenon of hydrogen bonding and its effect on the structure and association manifested by HF.

Another area of chemistry initiated and exploited by Simons at Penn. State was the use of HF as a catalyst in alkylation, condensation and rearrangement reactions. This work resulted in some 20 publications including a new preparation of DDT. However, only ten are listed in the references as being exemplary of the nature of the work [10-19]. A more precise study of the HF catalysis of the alkylation of phenol with t-butyl chloride is recorded in two kinetic studies [20, 21]. The alkylation of toluene with t-butyl chloride was apparently inhibited by HF but enhanced by HCl [22].

Methods for the practical scale preparation of fluorocarbons began with the fluorination of different varieties of carbon, a process usually 'catalyzed' by mercury or one of its salts to inhibit explosions [23, 24] using fluorine generated by the high temperature method [25].

Professor Simons continued his researches in the preparation and chemistry of fluorine-containing compounds through the period of World War II and thereafter. Publications on the preparation of CF_3 derivatives [26, 27], other organic fluorides [28] and the fluorocarbon halides [29, 30] appeared in this period as well as physical chemical papers on the dielectric properties of fluorocarbons [31] and trifluoroacetic acid [32]. Cleavage of a carbon-carbon bond in fluorocarbons by Cl_2 and Br_2 [30] suggested the successful work on the hydrogenolysis of the carbon-carbon bond to form fluorocarbon hydrides [33].

Although the work on the electrochemical process to prepare fluorine-containing compounds using HF as the solvent and source of fluorine was carried out over a period of quite a few years the classic series of five papers on the process did not appear until 1949 [34]. This process opened a Pandora's box for preparing exotic compound containing fluorine many of which entered the chemical literature in the form of patents describing the basic process [35] and the preparation and properties of perfluoropiperidines [36], cyclohexamines [37], ethers [38], acids [39] and amines [40].

The synthetic fluorine work that was initiated at Penn. State terminated in the early 1950s and consisted of the preparation and properties of silver undecafluorocarboxylate [41] and the decomposition of its acid in aqueous solution [42].

Professor Simons moved to the University of Florida and set up his activities in Reed Laboratory, a part of the department of chemical engineering. Much of his work in Fluorine Chemistry was generously supported by 3M. It took a novel turn and reflected a large breadth of new interests, such as fluorocarbon-aromatic ketones, [43] esters [44], ethers [45] the reaction of the esters with PCl_5 [46], the preparation of fluorocarbon acid amide dimers [47] and 'thiocyanates' [48], mercury derivatives of the amides [49] and the acid hydrolysis of the acid dimers [50]. This period of Professor Simons' researches in fluorine and fluorocarbon chemistry terminated with two pieces of work, the first on the preparation of fluorocarbon iodides without the use of solvents or diluents [51] and the silver halide complexes of fluorocarbon acids [52].

Besides his research in fluorine chemistry Joseph Simons wrote reviews on HF and its solutions [53], and on HF [54] in the 5 volume compendium, Fluorine Chemistry, which he also edited. He contributed, too, to Inorganic Syntheses methods or prescriptions for the safe preparation of fluorine [55], anhydrous HF [56], CF_4 [57, 58], SF_6 , SeF_6 , and TeF_6 [59] and BrF_3 [60].

This summary of Joseph Simons' research activities in fluorine chemistry is by no means a complete review of his work nor does it reflect the time, effort and thoughtful deliberation involved. It tends rather to reflect the broad scope of his interests, his dedication to his goals and the productivity of the large number of people who benefited from his mentorship and who, in turn, helped to contribute to his memory.

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