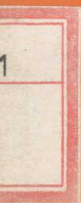


**Miloš Hudlický**

# **Organic Fluorine Chemistry**



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## Preface

The present book is essentially based on the lectures on the chemistry of organic compounds of fluorine that I gave in 1969 at Virginia Polytechnic Institute in Blacksburg, Virginia, as a graduate course. References to material published to the end of 1969 are included. The book is primarily meant to provide the background for such a course, and, at the same time, to be a brief survey of recent knowledge in, and an introduction to deeper study of, this area of chemistry, which has been treated in a number of comprehensive monographs.

I would like to thank Professor S. C. Cohen, Syracuse University, for the compilation of the data on mass spectra and nuclear magnetic resonance spectra, and my son, Tomáš Hudlický, and my daughter, Eva Hudlická, for their help with the indexes.

February 13, 1970

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## Chapter 1

# Introduction

### DEVELOPMENT OF FLUORINE CHEMISTRY

The chemistry of fluorine has been marked with a certain delay in development as compared with the chemistry of other halogens. Hydrofluoric acid was not prepared until 1771, by K. W. Scheele, and elemental fluorine not until 1886, when H. Moissan subjected a solution of potassium fluoride in anhydrous hydrogen fluoride to electrolysis in a platinum apparatus. This delay is reflected in the chemistry of fluorine compounds. The early development of inorganic fluorine chemistry is mainly due to H. Moissan and O. Ruff. The foundations of organic fluorine chemistry were laid by F. Swarts in the late 19th and early 20th century. It was not, however, until 1930 that Freons, fluorinated refrigerants, were discovered by T. Midgley, Jr., and A. L. Henne, and thus organic fluorine compounds entered the field of large-scale technology. This important discovery started a kind of a chain reaction which led to the development of the technology of elemental fluorine, of many methods of preparation of inorganic and especially organic fluorine compounds, and to the discovery of important and peculiar compounds such as Teflon and other fluorocarbons. Fluorine chemistry played an important role in atomic energy projects (isotopic uranium hexafluorides were separated by thermodiffusion in the medium of fluorocarbons), and plays a part even in space research.

Fluorine chemistry caused an "explosion" not only in the number of prepared compounds, which increased over a period of 30 years (1930–1960) from several hundreds to over 14,000, but also in the number of publications on this subject, which is ever increasing. There were three monographs on fluorine prior to 1930, whereas there are more than 30 today.

In order to facilitate the exchange of views and information, international symposia have been established: 1959, Birmingham, England; 1962, Estes Park, USA; 1965, Munich, Germany; 1967, Estes Park, USA; 1969, Moscow, USSR; 1971, Durham, England.

Table 1 lists the most essential monographs now available to the fluorine

Table 1. Selected Monographs on Fluorine Chemistry

Author or Editor	Title	Publisher	Place	Year
Haszeldine, R. N., and Sharpe, A. G.	Fluorine and Its Compounds	Methuen and Co.	London	1951
Lovelace, A. M., Rausch, D. A., and Postelnek, W.	Aliphatic Fluorine Compounds	Reinhold Pub. Corp.	New York	1958
Pavlath, A. E., and Leffler, A. L.	Aromatic Fluorine Compounds	Reinhold Pub. Corp.	New York	1962
Forche, E., Hahn, W., and Stroh, R.	Fluorverbindungen: Herstellung, Reak- tivität und Unwandlungen (Houben-Weyl, Methoden der Organischen Chemie, 5/3)	G. Thieme Verlag	Stuttgart	1962
Sheppard, W. A., and Sharts, C. M.	Organic Fluorine Chemistry	W. A. Benjamin	New York	1969
Simons, J. H.	Fluorine Chemistry, I-V	Academic Press	New York	1950 1954 1963 1965 1964
Stacey, M., Tatlow, J. C., and Sharpe, A. G.	Advances in Fluorine Chemistry, 1-5	Butterworths	London	1960 1961 1963 1965 1965
Tarrant, P.	Fluorine Chemistry Reviews, 1-4	Marcel Dekker	New York	1967 1968 1969
Pattison, F. L. M.	Toxic Aliphatic Fluorine Compounds	Elsevier	Amsterdam	1959
Banks, R. E.	Fluorocarbons and Their Derivatives	Oldbourne Press	London	1963

**Table 2. Topics Covered in the Main Series on Fluorine Chemistry****Fluorine Chemistry, J. H. Simons, editor***Volume I*

Nonvolatile Inorganic Fluorides. Emeleus, H. J.

Volatile Inorganic Fluorides. Burg, A. B.

The Chemistry of the Fluoro Acids of Fourth, Fifth, and Sixth Group Elements. Lange, W.

The Halogen Fluorides. Booth, H. S.

Boron Trifluoride. Booth, H. S.

Hydrogen Fluoride. Simons, J. H.

Hydrogen Fluoride Catalysis. Simons, J. H.

Preparation of Fluorine. Cady, G. H.

Physical Properties of Fluorine. Cady, G. H.

The Theoretical Aspects of Fluorine Chemistry. Glockler, G.

The Action of Elementary Fluorine upon Organic Compounds. Bigelow, L. A.

Fluorocarbons and Their Production. Simons, J. H.

Fluorocarbons—Their Properties and Wartime Development. Brice, T. J.

Fluorocarbon Derivatives. Pearlson, W. H.

Aliphatic Chlorofluoro Compounds. Park, J. D.

Fluorine Compounds in Glass Technology and Ceramics. Weyl, W. A.

*Volume II*

Fluorine-Containing Complex Salts and Acids. Sharpe, A. G.

Halogen Fluorides—Recent Advances. Emeleus, H. J.

Analytical Chemistry of Fluorine and Fluorine-Containing Compounds. Elving, P. J.

Organic Compounds Containing Fluorine. Tarrant, P.

Metallic Compounds Containing Fluorocarbon Radicals and Organometallic Compounds Containing Fluorine. Emeleus, H. J.

Fluorocarbon Chemistry. Simons, J. H.

The Infrared Spectra of Fluorocarbons and Related Compounds. Weiblen, D. G.

*Volume III*

Biological Effects of Fluorine Compounds. Hodge, H. C., Smith, F. A., and Chen, P. S.

*Volume IV*

Biological Properties of Inorganic Fluorides. Hodge, H. C., and Smith, F. A.

Effect of Fluorides on Bones and Teeth. Hodge, H. C., and Smith, F. A.

*Volume V*

General Chemistry of Fluorine-Containing Compounds. Simons, J. H.

Physical Chemistry of Fluorocarbons. Reed, T. M., III

Radiochemistry and Radiation Chemistry of Fluorine. Wethington, J. A., Jr.

Industrial and Utilitarian Aspects of Fluorine Chemistry. Brice, H. G.

**Advances in Fluorine Chemistry, Stacey, M., Tatlow, J. C., and Sharpe, A. B., editors***Volume I*

The Halogen Fluorides—Their Preparation and Uses in Organic Chemistry. Musgrave, W. K. R.

Transition-Metal Fluorides and Their Complexes. Sharpe, A. G.

The Electrochemical Process for the Synthesis of Fluoro-Organic Compounds. Burdon, J.

Table 2 (Continued)

Fluoroboric Acids and Their Derivatives. Sharp, D. W. A.  
Exhaustive Fluorinations of Organic Compounds with High-Valency Metallic Fluorides. Stacey, M., and Tatlow, J. C.

*Volume 2*

The Thermochemistry of Organic Fluorine Compounds. Patrick, C. R.  
Fluorine Resources and Fluorine Utilization. Finger, G. C.  
Mass Spectrometry of Fluorine Compounds. Majer, J. R.  
The Fluorides of the Actinide Elements. Hodge, N.  
The Physiological Action of Organic Compounds Containing Fluorine. Saunders, B. C.  
The Fluorination of Organic Compounds Using Elementary Fluorine. Tedder, J. M.

*Volume 3*

Effects of Adjacent Perfluoroalkyl Groups on Carbonyl Reactivity. Braendlin, H. P., and McBee, E. T.  
Perfluoroalkyl Derivatives of the Elements. Clark, H. C.  
Mechanisms of Fluorine Displacement. Parker, R. E.  
Nitrogen Fluorides and Their Inorganic Derivatives. Colburn, C. B.  
The Organic Fluorochemicals Industry. Hamilton, J. M., Jr.  
The Preparation of Organic Fluorine Compounds by Halogen Exchange. Barbour, A. K.

*Volume 4*

The Balz-Schiemann Reaction. Suschitzky, H.  
Some Techniques and Methods of Inorganic Fluorine Chemistry. Peacock, R. D.  
Ionic Reactions of Fluoro-Olefins. Chambers, R. D.  
Structural Aspects of Monofluorosteroids. Taylor, N. F., and Kent, P. W.  
Fluorides of the Main Group Elements. Kemmitt, R. D. W., and Sharp, D. W. A.  
The Vibrational Spectra of Organic Fluorine Compounds. Brown, J. K., and Morgan, K. J.

*Volume 5*

Oxyfluorides of Nitrogen. Woolf, C.  
Fluorides of Phosphorus. Schmutzler, R.

**Fluorine Chemistry Reviews**, Tarrant, P., Richardson, R. D., and Lagowski, J. J., editors

*Volume 1*

Synthesis, Compounding, and Properties of Nitroso Rubbers. Henry, M. C., Griffis, C. B., and Stump, E. C.  
Electrochemical Fluorination. Nagase, Shunhi  
The Fluoroketenes. Cheburkov, Y. A., and Knunyants, I. L.  
Hexafluoroacetone. Krespan, C. G., and Middleton, W. J.  
Fluorocarbon Toxicity and Biological Action. Clayton, J. W.  
Diels-Alder Reactions of Organic Fluorine Compounds. Perry, D. R. A.  
Methods of the Introduction of Hydrogen into Fluorinated Compounds. Mettillie, F. J., and Burton, D. J.  
Reactions Involving Fluoride Ion and Polyfluoroalkyl Anions. Young, J. A.

*Volume 2*

The Cycloaddition Reactions of Fluoroolefins. Sharkey, W. H.

Table 2 (Continued)

- 
- The Reactions of Halogenated Cycloalkenes with Nucleophiles. Park, J. D., Murtry, R. J., and Adams, J. H.  
Ionization Potentials and Molecule-Ion Dissociation Energies for Diatomic Metal Halides. Hastie, J. W., and Margrave, J. L.  
Nuclear Magnetic Resonance Spectra of M-F Compounds. Brey, W. L., and Hynes, J. L.  
The F<sup>19</sup> Chemical Shifts and Coupling Constants of Fluoroxy Compounds. Hoffman, C. J.

*Volume 3*

- Fluorine Compounds in Anesthesiology. Larsen, E. R.  
Reactions of Fluoroolefins with Electrophilic Reagents. Dyatkin, B. L., Mochalina, E. P., and Knunyants, I. L.  
Fluoroalicyclic Derivatives of Metals and Metalloids. Cullen, W. R.  
Phosphorus, Arsenic, and Antimony Pentafluorophenyl Compounds. Fild, M., and Glemser, O.

*Volume 4*

- Polyhaloalkyl Derivatives of Sulfur. Dresdner, R. D., and Hooper, T. R.  
The Chemistry of Fluorinated Acetylenes. Bruce, M. I., and Cullen, W. R.  
The Chemistry of Aliphatic Fluoronitrocarbons. Bissell, E. R.
- 

chemist, and Table 2 titles of the chapters in the collections *Fluorine Chemistry*, Volumes I-V, *Advances in Fluorine Chemistry*, Volumes 1-5, and *Fluorine Chemistry Reviews*, Volumes 1-4.

## HANDLING OF FLUORINE, HYDROGEN FLUORIDE, AND FLUORINE COMPOUNDS

Fluorine, hydrogen fluoride, and some inorganic and organic fluorides are poisonous, highly corrosive, and generally dangerous, and require special precautions in work with them.

One of the most hazardous substances is *elemental fluorine*, which may cause explosions in contact with organic material. It is imperative to use eye protection (plastic shield), rubber gloves, and a plastic apron when working with fluorine. Breathing even small concentrations of fluorine should be avoided.

Another dangerous compound requiring the same precautions is *anhydrous hydrogen fluoride*, especially as a liquid. Its action on skin is immediate and causes painful and slowly healing wounds. Even aqueous hydrofluoric (and also fluoroboric) acid injures skin readily, and any contact with fingers and nails should be carefully avoided.

Burns caused by fluorine or hydrogen fluoride must be immediately taken care of. The burnt area must be washed free of acid by tap water, if

possible, immersed in ice-cold 70% ethyl alcohol for up to 30 min, and finally covered by a paste made from magnesium oxide and glycerol. With large and deep burns, subcutaneous injections of calcium gluconate in the injured area are recommended. When hydrogen fluoride gets into the eye, the eye is to be flushed with lukewarm water and finally with 2% solution of sodium bicarbonate. With serious injuries of the eye, 0.5% pantocain solution is to be applied to relieve the pain [1].

Other fluorine compounds are much less dangerous, although handling them requires precautions usual for common poisonous and corrosive substances. This applies to most of the inorganic fluorides, especially to arsenic and antimony fluorides, and to strong acids such as fluoro-, difluoro-, and trifluoroacetic acid, fluoroboric acid, etc.

*Fluoroacetic acid* is dangerous not only by token of its acidity but also as an enzymic poison of high toxicity. For the same reason, its derivatives and homologs having an even number of carbon atoms in their chains and a single fluorine atom in the  $\omega$ -positions must also be handled with proper care [2].

Another group of compounds, *alkyl fluorophosphates*, known as "nerve gases," are very poisonous because of their action on the enzyme cholinesterase [3].

Although some of the fluorinated organic compounds such as *perfluoroisobutylene* are extremely toxic (of the order of phosgene), there is usually little chance of their being encountered. The only common source of perfluoroisobutylene is pyrolysis of polytetrafluoroethylene (Teflon), but this is serious only at very high temperatures, usually not encountered under the operating conditions of Teflon-coated tools [4].

## EQUIPMENT AND APPARATUS

Common *glass equipment* can be used for working with most fluorides and even fluorine provided no hydrogen fluoride is generated during the reaction. Hydrogen fluoride, especially highly concentrated or anhydrous, eats up glass very rapidly, and its contact with glass must be limited to a very short time. Since silicon tetrafluoride is formed from glass and hydrogen fluoride, glass cannot be used in cases where such contamination is undesirable. For safety reasons, work with elemental fluorine or highly corrosive fluorides such as halogen fluorides and antimony pentafluoride is preferably done in plastics or metals. Thus, the use of glass apparatus is practically limited to work with alkaline fluorides, silver fluoride, mercury fluorides, antimony trifluoride, and a few others.

For work with all fluorides, including anhydrous hydrogen fluoride, at atmospheric or not very elevated pressure, *plastics* are very suitable provided not too high a temperature is used. The temperature limits for plastics are

**Table 3. Corrosion of Materials by Fluorine and Hydrogen Fluoride  
(Penetration in inches per year) [5]**

Material	Dry fluorine	Anhydrous hydrogen fluoride		Hydrofluoric acid 40–65 %, up to 50°C
		up to 50°C	100–150°C	
Fe	<0.004	<0.02	>0.05	>0.05
Hastelloy (55% Ni, 17% Mo, 16% Cr) 6% Fe, 4% W	—	<0.02	<0.02	<0.02
Ni	<0.004	<0.02	—	0.02
Monel (67% Ni, 30% Cu, 3% Al)	0.004	0.02	<0.02	<0.02
Ag, Au, Pt	<0.004	—	—	—
Cu	<0.004	<0.02	<0.05	>0.05
Pb	<0.04	>0.05	>0.05	<0.004
Bronze	—	<0.02	>0.05	>0.05
Al	>0.1	—	—	>0.05
Glass	<0.004	—	—	>0.05
Plastics:				
Epoxy resins	—	—	—	Stable
Polyester, polyamide	—	Unstable	—	Unstable
Polyvinyl chloride	—	Limited use	—	—
Polyethylene	Stable	Stable	—	Stable
Polychlorotrifluoroethylene	Stable	Stable	—	Stable
Polytetrafluoroethylene	Stable	Stable	—	Stable

up to 100°C for polyethylene, about 200°C for polychlorotrifluoroethylene, and about 250–280°C for polytetrafluoroethylene or copolymers of tetrafluoroethylene with hexafluoropropylene.

Any kind of reaction of fluorides and fluorine, including reactions much above atmospheric pressure, can be carried out in *metallic equipment or autoclaves*. For most purposes, mild steel is satisfactory, although its corrosion may sometimes be very high, particularly in the presence of water in the reaction medium. Special stainless steel such as Hastelloy is much more resistant and more suitable, especially for work of high accuracy. Hydrogen fluoride, fluorine, and corrosive fluorides can be successfully handled in copper, and some fluorides even in aluminum equipment. The most suitable metals for work with hydrogen fluoride and fluorine are nickel and Monel metal, whose corrosion is very low even at high temperatures.

Numerical data in Table 3 show corrosion of various materials and can be a guide for the choice of material for equipment in any particular case [5].

In addition to apparatus fitted for any particular reaction, some special apparatus was developed for the preparation of organic fluorine compounds. Noncatalytic fluorinations with elemental fluorine require a special type of a



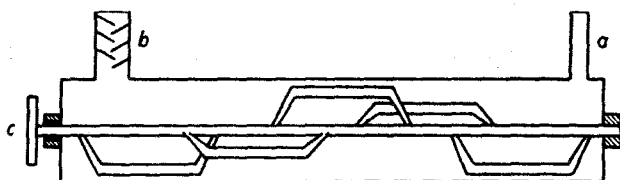


Fig. 1. Rotary apparatus for fluorination by means of silver difluoride or cobalt trifluoride: (a) inlet tube, (b) outlet tube with baffle plates, (c) rotating shaft with paddles.

cold-flame burner allowing fast mixing of the reaction components [6]. Catalytic fluorinations with elemental fluorine are carried out in vertical reactors filled with the appropriate substrate coated with the metal catalyst [7]. Reactions of organic compounds with high-valency metal fluorides such as cobalt trifluoride are carried out in rotary horizontal tubes fitted with paddle stirrers (Fig. 1) [8]. Electrochemical fluorinations achieved by electrolysis of organic compounds in liquid anhydrous hydrogen fluoride are performed in electrolytic cells similar to those used for the production of fluorine (Fig. 2) [9].

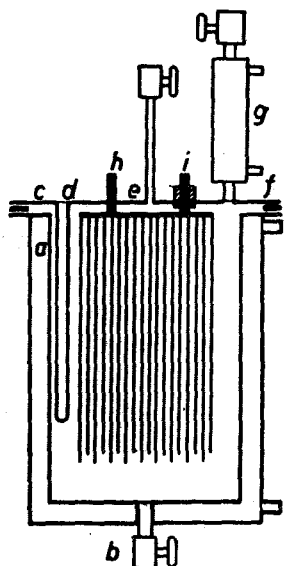


Fig. 2. Apparatus for electrolytic fluorination: (a) electrolytic cell with water jacket, (b) liquid product outlet, (c) cell lid, (d) thermometer well, (e) electrolyte inlet, (f) gaseous product outlet, (g) reflux condenser, (h) cathode, (i) anode.