

Recent Advances in Fluorine Chemistry

A. A. ALBERTS, Z. D. WELCH and E. T. MCBEE, Purdue University

In 1931, Freon 12 was introduced to the refrigeration industry as the "ideal" refrigerant (1). This refrigerant—a fluorine-containing organic compound, dichlorodifluoromethane—is characterized by its chemical inertness, thermal stability, and nontoxicity. In the decade which followed, the demand for this material increased rapidly. Also, in the same period there was an increase in interest in fluorine-containing organic compounds. This increase in interest can be attributed to the many unusual properties possessed by fluorine-containing compounds, e.g. the fluorine atoms in organic compounds containing two fluorine atoms attached to a carbon atom are very firmly held. This enhanced stability is transmitted to a lesser degree to substituents on adjacent carbon atoms. Hence, it is not surprising to find that fluorine compounds have potential uses as plastics, lubricants, tanning agents, heat-transfer agents, hydraulic fluids, dielectrics, and pharmaceuticals (2).

A symposium on fluorine chemistry was a part of the 110th meeting of the American Chemical Society held at Chicago, September, 1946. Many of the topics discussed in this paper were presented at this symposium.

Three general methods have been used for the preparation of fluorine-containing compounds; namely, (1) direct fluorination, (2) replacement of halogen in an organic compound by the use of inorganic fluorides, and (3) addition of hydrogen fluoride to carbon-carbon multiple bonds. However, with a few exceptions these procedures are not generally applicable to the preparation of fluorocarbons, i.e. compounds containing only fluorine and carbon. Consequently, new methods for the preparation of such compounds were sought when it was demonstrated that fluorocarbons were needed in large quantities by the Manhattan Project. As a result of this research, a fourth method was made available for the preparation of fluorine compounds. This method is the reaction of an organic compound with certain metal fluorides, e.g., cobalt (III) fluoride, silver (II) fluoride, manganese (III) fluoride, cerium (IV) fluoride, and lead (IV) fluoride. These metal fluorides are most conveniently prepared by reaction of the lower valent fluoride with elemental fluorine. As a matter of fact, with the exception of lead (IV) fluoride, the only known method of preparation involves the use of elemental fluorine.

The large-scale production of fluorine can be acclaimed as a real achievement inasmuch as the production of fluorine, prior to 1942, was costly and the amount produced insignificant, less than 25 pounds per day. This development is particularly noteworthy when one considers the chemical reactivity and the corrosiveness of fluorine. The production of

fluorine depends upon the electrolytic decomposition of hydrogen fluoride. One type of cell uses 2000 amperes at about 10 volts (3) to which a small amount of lithium fluoride, less than 1%, is added to the electrolyte, $\text{KF} \cdot 2\text{HF}$. The anode may be of carbon or nickel and the cathode of iron. By maintaining the hydrogen fluoride concentration at 38 to 38.5% the cells have run up to 1½ years with no major shut down.

The development of cells for large-scale production was carried out by the Harshaw Chemical Company, E. I. duPont de Nemours and Co., and the Hooker Electrochemical Company. Laboratory cells were also developed by Johns Hopkins University, Massachusetts Institute of Technology and Pennsylvania Salt Mfg. Company.

Fluorine has been successfully delivered into storage tanks at 30 pounds per square inch by oil-operated, diaphragm pumps transmitting pulsations hydraulically to a second pumping head containing a fluoro-hydrocarbon (3). It has also been successfully compressed and stored in cylinders of copper, nickel or steel at pressures as high as 300 pounds per square inch (4, 5).

A process for the production of an equally satisfactory coolant was developed by McBee and his associates at Purdue University (9). *n*-Heptane was chlorinated photochemically in the liquid phase to a chlorine content of about 83%. This mixture of polychloroheptanes was converted to polychloropolyfluoroheptenes by fluorination with hydrogen fluoride at 125° C. in the presence of an equal weight of antimony (V) chloride. The product was removed from the reactor by distillation leaving the antimony residues which can be reused effectively in subsequent fluorination if anhydrous conditions are maintained.

The polychloropolyfluoroheptene (average formula $\text{C}_7\text{H}_x\text{Cl}_3\text{F}_9$) was further fluorinated in the vapor phase by either cobalt (III) fluoride or silver (II) fluoride to perfluoroheptane and monochloroperfluoroheptane. It was found that silver (II) fluoride is more effective in the replacement of chlorine atoms by fluorine than cobalt (III) fluoride. Perfluoroheptane prepared in this manner was contaminated with chlorine containing substances. These contaminants could be removed by azeotropic distillation with methyl ethyl ketone producing pure perfluoroheptane (10).

In addition to the coolant mentioned previously, other fluorine-containing materials were needed for the Manhattan project. These materials were characterized by their low vapor pressure as well as their chemical inertness.

Terphenyls and open chain hydrocarbons containing from sixteen to twenty-one carbon atoms per molecule were fluorinated in the vapor-phase with cobalt (III) fluoride at 300° C. Compounds whose general formula may be represented by the formula $-(\text{CF}_2)_n-$ were formed. Silver (II) fluoride also proved satisfactory in this fluorination. However, when silver (II) fluoride was used, the reaction was conducted in the liquid phase. (11, 12, 13).

A tetrafluoroethylene polymer, known as Teflon and marketed by DuPont, has many uses owing to its nonreactivity to chemicals, including fluorine (14). Tetrafluoroethylene is prepared by the thermal decomposition of chlorodifluoromethane (15). In addition to the desired

tetrafluoroethylene, a series of new compounds having the general formula $H(CF_2)_nCl$ is obtained, accompanied by a small quantity of highly toxic substances. The identity of these latter materials has not been established.

Another fluorine containing polymer was prepared by the polymerization of perfluorovinyl chloride (16, 17). The products isolated ranged from colorless, stable oils to solid resins. By further fluorination of these oils with cobalt (III) fluoride the thermal stability of the oils was increased.

Simons and McArthur (18) have reported that hydrogen fluoride is a suitable media for the liquid-phase oxidation with molecular oxygen. The products formed are not those usually expected. Benzene is converted to phenol; toluene, to cresol. In the complete combustion of certain compounds, carbon is formed rather than carbon monoxide and carbon dioxide.

Fluorine containing organic acids can be prepared by the permanganate oxidation of fluorine containing olefins (19, 20). For example, trifluoroacetic acid is prepared by the oxidation of 3,3,3-trifluoro-1,1,2-trichloropropene. Perfluoroglutaric and perfluoroadipic acids are prepared by the oxidation of 1,2-dichloroperfluorocyclopentene and 1,2-dichlorocyclohexene respectively. These fluorine containing acids are relatively strong and water soluble.

The use of hexafluoroacetylacetonates as a reagent for the separation of the rare earth elements by distillation has been reported by Quill (21).

The action of fluorine on molten sulfur results in the formation of sulfur (VI) fluoride. This material is arousing much interest and finds use as a gaseous dielectric in high voltage generators (22).

The energy released in the exothermic reaction of hydrogen and fluorine has been utilized in a torch that is capable of producing a temperature over 6000° F. By the use of Hydrogen-Fluorine torch, copper can be welded with ease. Nickel, Monel, and steel were welded with equal facility, but aluminum resisted efforts of being welded (23).

Undoubtedly a great many discoveries of the recent years are as yet unreported because of censorship regulations, either for national security or because of patent security. Nonetheless, the importance of fluorine containing substances has been established and the future of fluorine chemistry is most promising.

References

1. Morse, Refrigerating Eng. **32**:17 (1936).
2. McBee—Paper 27, Abstracts of Papers Presented at American Chemical Society, Division of Industrial and Engineering Chemistry, September 1946.
3. Osborne, Paper No. 33., id.
4. Priest and Grosse, Paper No. 35, id.
5. Turnbull, Froning, and Stricklin, Paper No. 39, id.
6. Chem. Eng. News, **24**:2462 (1946).
7. McBee et al—Paper No. 53, Abstracts of Papers Presented at American Chemical Society, Division of Industrial and Engineering Chemistry, September 1946.

8. Parmalee, et al—Paper No. 55, id.
9. McBee et al—Paper No. 58, id.
10. McBee et al—Paper No. 59, id.
11. Irwin et al—Paper No. 87, id.
12. Struve et al—Paper No. 88, id.
13. Stilmar et al—Paper No. 89, id.
14. Renfren and Lewis, *Ind. Eng. Chem.*, **38**:870 (1946).
15. Benning et al—Paper No. 75, Abstracts of Papers Presented at American Chemical Society, Division of Industrial and Engineering Chemistry, September 1946.
16. Miller et al—Paper No. 76, id.
17. Belmore, Ewalt, and Wojcik—Paper No. 86, id.
18. Simons and McArthur—Paper No. 78, id.
19. McBee, Wiseman, and Bachman, Paper No. 70, id.
20. Henne and Zimmerschied, Paper No. 71, id.
21. Quill and Staniforth, Paper No. 91, id.
22. Gall and Church, Paper No. 92, id.
23. Priest and Grosse, Paper No. 93, id.

Papers 2-5, 7-13, 15-20, and 23 were published in the March (1947) issue of *Ind. Eng. Chem.*