SYNTHESIS OF THE FIRST ORGANOFLUORINE COMPOUND:

150TH ANNIVERSARY OF THE HISTORIC EXPERIMENT OF DUMAS AND PELIGOT

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The year 1986 has had special commemorative significance in fluorine chemistry, for it marks the 100th anniversary of the isolation of elemental fluorine on 26th June 1886 by the celebrated French chemist Henri Moissan. An international symposium was held in Paris during August 1986, to celebrate the centenary of that important event. However, what has gone unmarked is the 150th anniversary of a seminal discovery in organofluorine chemistry, namely the first definitive synthesis of a C–F bond.

J. Dumas and E. Péligot were the pioneering chemists involved in this demonstration [1] that a stable bond could be formed between carbon and fluorine (an element only postulated to exist at that time) and they were, like Moissan, French. The organofluorine compound concerned was the simplest possible - methyl fluoride. However, the reaction they discovered signposted future developments, and would nowadays be called a typical S_N2 displacement on carbon by fluoride ion.

Amongst his pioneering researches, the great chemist J. Dumas[a] carried out extensive investigations on reactions of wood spirit (methanol) [2]; his co-worker in this study was E. Péligot.[b] By treatment with concentrated sulphuric acid, dimethyl sulphate had been obtained. In 1835, this ester was heated with dry potassium fluoride, methyl fluoride being generated [1]:

$$(CH_3O)_2SO_2 \quad + \quad 2\ KF \quad \longrightarrow \quad 2\ CH_3F \quad + \quad K_2SO_4$$

We have presented elsewhere [3] some observations on this historic experiment, and also listed the other reports of successful syntheses of organofluorine compounds in the discipline's earliest days; the next two were in 1854 and 1863, and few appeared before the late 1880 s.

The reaction of Dumas and Péligot certainly broke fresh ground, and it is, of course, the primeval example of a group of processes, all of which conform to a general mechanistic pathway, and which, as the subject has developed, have been used widely in the controlled synthesis of aliphatic C-F bonds:

$$RX + MF \longrightarrow RF + MX \qquad (X = \text{a nucleofugal entity}).$$

The halogen exchange process is perhaps the most important example; after early work by Moissan and Meslans, it was developed brilliantly by Swarts, and was central to his establishment of aliphatic fluorine chemistry as a coherent sub-discipline. Later, it was adapted for the commercial production of chlorofluorocarbons, and later still for the synthesis of C-F bonds in arenes [4].

The Dumas-Péligot reaction has also been extended directly in modern synthetic practice. An important development utilized the reaction of an arenesulphonyl ester of an alcohol with potassium fluoride to give an alkyl fluoride [5]. Subsequently, further and more sophisticated extensions have been introduced, including the use of 'super' leaving groups (e.g. trifluoromethanesulphonate), and a range of fluoride sources, leading to syntheses of many types of organofluorides [6].

Dumas and Péligot were the true originators of organic fluorine chemistry, and deserve to be well remembered as such.

a. Jean Baptiste André Dumas (1800-1884) began his scientific career as an apprentice to an apothecary in Alais, moved to Geneva (1816) and thence to Paris (1823). He subsequently exercised great influence on the development of organic chemistry. His name is attached to methods for the determination of vapour density and of organically-bound nitrogen. He became Minister of Education.

b. E. M. Péligot (1811-1890) became Professor of Chemistry at the Conservatoire des Arts et Métiers in Paris, doing good work in inorganic, organic and technical chemistry (beet sugar industry).

REFERENCES.

1 J. Dumas and E. Péligot, *Ann. Pharm.*, *15* (1835) 246; *Ann. Chim. Phys.*, *61* (1836) 193.

2 J. Dumas, *Traité de Chimie appliquée aux Arts*, Béchet Jeune, Paris, Tome V, 1835, p. 417-450.

3 R. E. Banks and J. C. Tatlow, in R. E. Banks, D. W. A. Sharp and J. C. Tatlow (eds), *Fluorine: The First Hundred Years (1886-1986)*, Elsevier Sequoia, Lausanne, 1986, pp. 72-76.

4 A summary of these developments is given in Ref. 3, pp. 92-103; 255-7.

5 W. F. Edgell and L. Parts, *J. Am. Chem. Soc.*, *77* (1955) 4899.

6 For a few examples, see Ref. 3, pp. 231, 232.