Direct Preparation of Partially Fluorinated Methane*

By Shunji NAGASE, Kiyoshi TANAKA and Hajime BABA

(Received September 8, 1964)

Numerous methods are available for the preparation of partially fluorinated methane. Some of them[1,2] use the Swarts reaction which consists of the replacement of the original halogens in an organic molecule with fluorine by halides of antimony. Indirect fluorination of halogenated methane with other inorganic fluorides is frequently used.[3-6] Potassium methyl sulfate[7] and methyl tosylate[8] were shown to be a good source of fluoromethane by their reaction with potassium fluoride. Hydrogenolysis,[9] reduction,[10] disproportionation,[11] or pyrolysis[12] of fluorinated compounds has also been reported. Perhaps the most significant method for direct preparation of partially fluorinated methane was described by Bigelow and his co-worker[13] in one of the important papers on fluorination of organic compounds by elementary fluorine. They obtained, besides the expected C_1 derivatives, hexafluoroethane and octafluoropropane.

In the present paper, accomplishment of partial fluorination of methane by electrochemical fluorination is described. Mono- and di-fluoromethane were obtained directly from methane in a reasonable conversion and current efficiency, using the electrolytic cell equipped with a specially devised "bubbler," one of the important features of the apparatus.

Little attention has been paid to partial fluorination of organic compounds or to fluorination of slightly soluble gases in hydrogen fluoride by an electrochemical process. Simons observed the formation of partially fluorinated methanes as the cleavage products from acetic acid, acetone, trimethylamine, etc., in his

---

* This report will be designated as Part I of a series entitled, "Electrochemical Fluorination of Gases."

1) A. L. Henne, *J. Am. Chem. Soc.*, **59**, 1200, 1400 (1937).

2) W. B. Whalley, *J. Soc. Chem. Ind.* (*London*), **66**, 427 (1947).

3) O. Ruff, O. Bretschneider, W. Luchsinger and G. Miltschitzky, *Chem. Ber.*, **69**, 299 (1936).

4) F. Swarts, *Bull. soc. chim. Belg.*, **46**, 10 (1937); *Chem. Abstr.*, **31**, 7393 (1937).

5) J. H. Simons, R. L. Bond and R. E. McArthur, *J. Am. Chem. Soc.*, **62**, 3477 (1940).

6) C. B. Miller and J. D. Calfee, U. S. Pat. 2676996 (1954).

7) W. H. Bennett, *J. Am. Chem. Soc.*, **51**, 377 (1929).

8) W. F. Edgell and L. Parts, ibid., **77**, 4899 (1955).

9) J. H. Simons, W. H. Pearlson and Wm. R. James, U. S. Pat. 2494064 (1950).

10) A. F. Benning and E. G. Young, U. S. Pat. 2615926 (1952).

11) Wm. S. Murray, U. S. Pat. 2426638 (1947).

12) F. B. Downing, A. F. Benning and R. C. McHarness, U. S. Pat. 2413696 (1947).

13) E. H. Hadley and L. A. Bigelow, *J. Am. Chem. Soc.*, **62**, 3302 (1940).

pioneering work on electrochemical fluorination.[14] Sartori reported a successful attempt at the electrochemical fluorination of gases.[15] Methane, however, was shown to yield tetrafluoromethane and trifluoromethane with very small amounts of di- and mono-fluorinated products.

In the present work, the bubbler type of electrolytic cell afforded as high as 60% (mol.) of monofluoromethane in the fluorinated product, with an anodic current density of 2.2 amp./dm^2 and cell temperature of 5—6°C. This result may be regarded as a significant step in the partial fluorination of organic compounds by an electrochemical process.

The metered methane was introduced, with or without diluent helium, into hydrogen fluoride in the cell through the " bubbler " and fluorinated, after which the products were freed from hydrogen fluoride and oxygen difluoride, condensed, and rectified. The bubbling arrangement was found to be very effective for controlling the fluorination reaction, which is frequently explosive in nature, increase both the conversion and current efficiency during the fluorin ation of methane.

Experimental

Materials.—Methane, from a commercial cylinder, was of over 99.5% pure. Hydrogen fluoride, rated better than 99%, was donated by Daikin Industries Co. The diluent employed was Airco helium (grade for gas chromatograhy use). The other, commonly available, reagents used were either of guaranteed or of first grade.

Apparatus.—The apparatus used for this fluorination reaction consisted essentially of the electrolytic cell, an iron tube for sodium fluoride pellets, three Ichinose gas washing bottles containing a saturated solution of sodium sulfite in which a small amount of potassium iodide and potassium hydroxide had been added, and glass traps immersed in ice and in liquid air. The size and the kind of the materials composing the electrolytic cell were the same as the one fully described earlier,[16,17] except that the cell body was constructed of Monel Metal, and a bubbling arrangement, termed " bubbler", was provided at the bottom of the cell body. The bubbler was placed just below the end of the nickel electrodes (whose effective surface area was 9.2 dm^2) at about 20 mm. distance from them, and standing vertically. The bubbler consisted of $6\phi \times 15$ mm. polyethylene tube, with an internal diameter of 4 mm., whose tip was enlarged to 8 mm. in diameter and capped with a filter paper made of polytetrafluoroethylene (courtesy of Daikin Industries Co.). During operation, the gaseous sample, with or without a metered current of helium, was introduced into hydrogen fluoride, from the bottom of the cell through the drain cock, whose central hole is 4 mm. in diameter, and which is connected directly to this bubbling arrangement. In a preliminary experiment, an attempt was made to produce innumerable minute bubbles in liquid hydrogen fluoride by various methods and materials. Such bubbles should accelerate favorable increase in the concentration of the slightly soluble sample in hydrogen fluoride. Macroscopic observation was made using a semitransparent polyethylene vessel; the bubbler just described above gave the best results.

Other instruments used in this work were low temperature distillation, gas chromatographic, and infrared spectroscopic apparatus. Rectification unit used was substantially the same as the one described by Calfee, Fukuhara and Bigelow.[18] A Podbielniak low temperature distillation column was the essential part. Analytical chromatographic separation was made with a Hitachi KGL-2A model chromatograph.

Infrared absorption spectra were measured on a Perkin-Elmer model 21 double-beam spectrophotometer.

Typical Procedure. — Run 2 is taken as an example. Hydrogen fluoride (1 l.) was placed in the cell and, in order to remove a trace of impurity (mainly water), electrolysis was carried out in a nitrogen atmosphere, prior to the introduction of the sample, with an anodic current density of 2.7 amp./dm^2 and at 5—6°C, until the cell voltage rose to 6.0 V. Then 10 g. of sodium fluoride was added, and the metered sample was introduced from the bottom of the cell into the hydrogen fluoride in the cell, maintained at 5—6°C, through the bubbler at an average flow rate of 0.0029 mol./min. In two experiments, metered helium was admitted simultaneously with the sample into the bubbler.

Then the sample was fluorinated at an anodic current density of 2.2 amp./dm^2.

When the cell voltage became almost steady at 6—6.5 V., traps were placed in ice and liquid air respectively, and electrolysis was carried out for 71 amp. hr.

Fluorinated gas evolved from the cell was passed through a reflux condenser kept at −20°C, and over sodium fluoride, and then bubbled through an aqueous sodium sulfite solution in an Ichinose gas washer to eliminate a trace of explosive oxygen difluoride, passed through a trap immersed in ice, and finally condensed in two consecutive liquid-air traps. Although fluctuation due to a small explosion was sometimes observed on the flow meter of the sample, performance of this electrofluorination unit was very satisfactory for the fluorination of methane.

The product thus obtained was carefully rectified in the low-temperature rectification unit. The molecular weight of each fraction was often measured to aid in identification of the components. The amounts of the rectified products were measured by volume, and subsequently weighed in

---

[14] J. H. Simons, U. S. Pat. 2519983 (1950).

[15] P. Sartori, *Angew. Chem.*, **75**, 417 (1963).

[16] S. Nagase and R. Kojima, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 1397 (1961).

[17] S. Nagase and R. Kojima, This Bulletin, **34**, 1468 (1961).

[18] J. D. Calfee, N. Fukuhara and L. A. Bigelow, *J. Am. Chem. Soc.*, **61**, 3552 (1939).

a glass ampule. The mixture was further separated by gas chromatography, using an activated charcoal column, 2 m. long, maintained at 70°C. Activated charcoal was of 30—60 mesh. The carrier gas was helium and the flow rate was at 147 ml./min. Infrared measurements were frequently carried out on components eluted from the column by transferring the highly diluted components into a 5-cm. cell.

Results and Discussion

The results from the example (run 2) described above and those from a series of similar runs under various operating condition are summarized in the following tabulation.

TABLE I. RECTIFICATION OF FLUORINATED METHANE

Fraction. No.	B. p., °C	Vol. ml.	Wt. g.	Component
1	−162—−159	13	5.6	CH_4
2	−128—−126	3.8	6.7	CF_4[b]
3[a]	−80—−76	4.8	6.1	CH_3F[c], CHF_3[b]
4[a]	−70—hold up	1.5	2.0	CH_3F, CHF_3 CH_2F_2[b]

a) This fraction was further resolved chromatographically.

b), c) The infrared spectra of these products agree with those listed in D. G. Weiblen's "Fluorine Chemistry," Ed. by J. H. Simons, Vol. II, Acadcmic Press. Inc., New York (1954), p. 469, and G. Herzberg's "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Inc., New York (1949), p. 315 respectively.

Table I gives the results obtained by rectifying the product of run 2. In Table II, operating conditions for various runs, conversion and current efficiencies, and composition of the products are presented.

Fractions 1 and 2 usually consisted of essentially pure CH_4, and CF_4, respectively. Fraction 2 in run 6, however, was contaminated with CH_3F, and the boiling range was −130 to −90°C. Fractions 3 and 4 came over as a mixture and were further separated chromatographically. Fraction 3 sometimes showed a wider range of boiling point, −80—−51°C, depending on the proportion of the components. Detectable amounts of other components, such as C_2F_6 or C_3F_8 which are obtained in the reaction of fluorine with methane,[13] were not found in this electrochemical fluorination reaction.

Quantitative analysis of the components separated by chromatography was made on the assumption that the ratio of the peak areas in the chromatogram is a direct measure of the weight per cent of the components.[19,20] The results obtained by this analysis were subsequently converted into mole per cent.

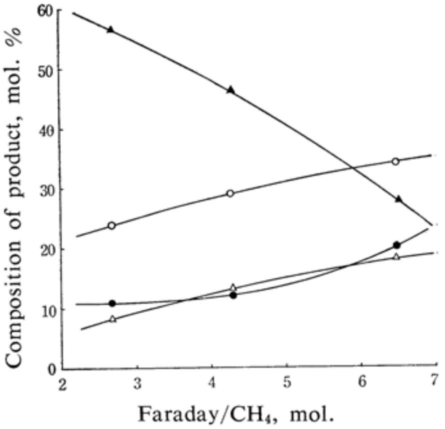

Fig. 1. Relationship between composition of product and Farady/CH_4 (mol.).
-○- CF_4 mol. %
-●- CHF_3 mol. %
-△- CH_2F_2 mol. %
-▲- CH_3F mol. %

Effect of Sample Feed Rate. — Though a definite mechanism for electrochemical fluorination has not yet been established,[21] the products obtained by the present fluorination reaction appeared to be rather close to those expected from a very mild fluorination of methane with elementary fluorine. It appears, that sufficient agitation and effective dispersion of the heat of reaction takes place in this electrochemical process. An increase in the number of sample bubbles should increase the efficiency of this agitation. It is apparent from Table II that the fluorination reaction becomes milder with an increase in the supply of CH_4. This relation is well illustrated in Fig. 1, where the composition of the products obtained in runs 1, 2, and 3 is plotted against the feed factor represented by faraday/CH_4(mol.).

It has been reported that agitation has a profound effect on the milder electrochemical fluorination of chloro-olefins.[22]

Electrochemical fluorination is certainly an anodic reaction, therefore the concentration of the sample near the electrode should play an important role in determining the distribution

---

[19] M. J. Root, "Gas Chromatography," Ed, by V. J. Coates, H. J. Noebels and I. S. Fagerson, Academic Press Inc., New York (1958), p. 99.

[20] R. Amamiya, "Gasu Kuromatogurafiiy," Kyoritsu Shuppan Co., Ltd., Tokyo, (1958), p. 48.

[21] A discussion is presented by J. Burdon and J. C. Tatlow, in "Advances in Fluorine Chemistry," Ed. by M. Stacey, J. C. Tatlow and A. G. Sharpe, Vol. I, Butterworths Scientific Publication Ltd., London (1960), p. 160.

[22] General Electric Co., Brit. Pat. 758492 (1956).

TABLE II. RESULTS OF THE FLUORINATION OF METHANE OPERATED UNDFR VARIOUS CONDITIONS

Run No.	D_A amp./dm^2	Total amt. CH_4 used mol.	Conversion mol. %	Total current eff., %[e)]	Product comp. (mol. %)				Note
					CF_4	CHF_3	CH_2F_2	CH_3F	
1	2.2	0.986	32.2	48.2	24.1	11.0	8.3	56.6	Effect of feed rate
2	2.2	0.613	42.8	44.3	29.0	12.3	12.7	46.0	
3	2.2	0.404	47.7	38.1	34.1	20.2	18.1	27.6	
4[a)]	2.2	0.564	46.3	37.8	17.3	10.5	18.6	53.6	Effect of temp.
5[b)]	2.2	0.635	45.7	41.7	21.9	7.0	10.8	60.3	Effect of helium
6[b)]	2.2	0.479	49.6	33.8	17.2	10.9	13.5	58.4	
7[c)]	2.2	0.536	38.1	33.6	28.9	9.9	11.9	49.3	Effect of bubbler
8[d)]	2.2	0.639	45.1	45.4	13.0	26.5	14.9	45.6	Effect of NaF
9	1.1	0.639	35.5	35.9	25.3	12.4	9.3	53.0	Effect of D_A

a) Cell temperature was kept at 15—16°C.

b) In runs 5 and 6, diluent helium was used at flow rates of 104 ml./min. ($CH_4 : He = 1 : 1.6$ by vol.) and 150 ml./min. ($CH_4 : He = 1 : 3$ by vol.), respectively.

c) The reaction was carried out without using the "bubbler."

d) NaF (50 g.) was used.

e) Calculation of the current efficiency was based on the amount of electricity assumed to be required to liberate fluorine from a discharging fluoride ion which would substitute hydrogen in CH_4 and combine with it to from HF. The total current efficiency shown is the sum of the individual current efficiencies for CF_4, CHF_3, CH_2F_2, and CH_3F.

and yield of the products as well as the efficiency of the reaction. Especially for a gaseous sample sparingly soluble in hydrogen fluoride, it is important to consider the effective concentration of the sample in the reaction zone. A higher feeding rate tends to increase the concentration of the sample. On the other hand, it also increases the amount of escaping sample. These consideration could explain the fact that an increased rate of feeding resulted in a decreased conversion and increased current efficiency.

Effect of Temperature.—The conductivity of hydrogen fluoride solution increases as the temperature rises. Run 4 proceeded at the lower cell voltage of 5.3—5.5 V. at 15—16°C. A decrease in the voltage would lead to milder fluorination. Furthermore, higher temperatures are expected to decrease the solubility of the gases, and hence the products would probably be liberated from the reaction zone at a less fluorinated stage. An opposing factor to the milder reaction might exist due to an increased reaction temperature. The net result was a milder fluorination reaction with a large amount of partially fluorinated products and a small amount of CF_4.

Effect of Dilution.—In vapor phase fluorination of organic compounds with elementary fluorine, the sample or fluorine is often diluted with nitrogen or helium to make the reaction milder. The same technique was applied in the present electrochemical fluorination (runs 5 and 6), with the hope that partial fluorination would proceed favorably. Helium should also help the stripping of the product from hydrogen fluoride at a less fluorinated stage, in addition to creating sufficient agitation in the reaction zone. As expected, runs 5 and 6 gave the highest yield of CH_3F.

Effect of the Bubbler.—Run 7 was carried out without using the bubbler. It was very difficult to control this reaction and frequent explosions were observed. The conversion and current efficiency decreased markedly. Figure 2 is a plot of conversion versus current efficiency and reveals the successful result brought about by the bubbler. It appears that approach of the sample to the electrode is neither steady nor smooth without the bubbler.

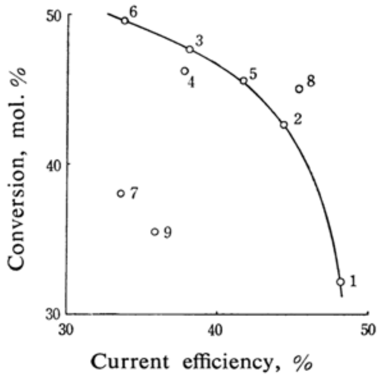

Fig. 2. Relationship between conversion and current efficiency.
The numberals in the diagram indicate run no.

Effect of the Amount of NaF. — Since hydrogen fluoride which contains hydrocarbons is nonconducting, electrolysis of this solution is usually carried out by the use of conductivity additives. In the present experiments, NaF (10 g.) was used as the additive, but for run 8, a larger amount of NaF (50 g.) was used with the expectation that the electrolysis could be carried out at a lower voltage for a milder reaction. Run 8, however, proceeded at the same voltage (6—6.5 V.) as that of the others. However, milder fluorination was accomplished and the smallest yield of CF_4 obtained. This might be attributed to the decreased solubility of partially fluorinated products in hydrogen fluoride.

Effect of the Anodic Current Density. — A smaller current density should make the reaction milder, but run 9, on the contrary, indicates a severe reaction with a smaller conversion and current efficiency.

The lesser degree of agitation may account for this, since the decreased amount of the total gases evolved under this electrolysis condition is not sufficient to cause efficient agitation in the hydrogen fluoride. A similar tendency was observed in the electrochemical fluorination of 2, 2, 3, 3-tetrafluoro-1-propanol.[23]

The overall results seem to demonstrate clearly the usefulness of electrochemical fluorination as a tool for fluorination of gases.

Summary

Partially fluorinated methanes were obtained directly from methane in a reasonable conversion and current efficiency by electrochemical fluorination, using a cell equipped with a bubbling arrangement. This fluorination unit worked satisfactorily for controlling the fluorination reaction of gases slightly soluble in hydrogen fluoride.

Performance and effect of the bubbler, and the effect of sample feed rate, electrolysis temperature, dilution of the sample with helium, the amount of sodium fluoride, and the anodic current density, on the fluorination reaction are described and discussed in detail.

The authors wish to express their sincere thanks to Daikin Industries Co. for supplying some materials, and Dr. Kan Inukai of this Institute for his interest in this work.

Government Industrial Research
Institute, Nagoya
Kita-ku, Nagoya (S. N. & H. B.)

Research Laboratories
Central Glass Co., Ltd.
Ohte-machi, Chiyoda-ku
Tokyo (K. T.)

---

[23] S. Nagase, H. Baba and R. Kojima, This Bulletin, 36, 29 (1963).