BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 219—222 (1966)

The Fluorination of Ethylene and Ethane*

By Shunji NAGASE,† Kiyoshi TANAKA,†† Hajime BABA† and Takashi ABE†

† *Government Industrial Research Institute, Nagoya, Kita-ku, Nagoya*
†† *Research Laboratories, Central Glass Co., Ltd., Ohte-machi, Chiyoda-ku, Tokyo*

(Received March 15, 1965)

Ethylene and ethane were electrochemically fluorinated in an electrolytic fluorination cell equipped with a bubbler. Several fluorinated ethanes were obtained from these samples in reasonable total-yields with reasonable current efficiencies. The influence of operating conditions on the reaction was investigated. A probable mechanism was described for the formation of the characteristic procucts obtained in the fluorination reaction.

There have been a number of papers dealing with the fluorination of substituted ethylenes by various methods. However, no successful report has yet described the fluorination of ethylene itself by an electrochemical process.1) The present work was carried out in order to examine the possibility of the electrochemical fluorination of ethylene which may undergo polymerization, fragmentation, or simple fluorination. It has been found that ethylene can be fluorinated without difficulty by using an electrolytic fluorination cell equipped with a bubbling arrangement2); fluorinated ethanes are thus produced in a reasonable yield and at a reasonable current efficiency. The electrochemical fluorination of ethane, which has already been reported briefly by Sartori,3) was also carried out in order to compare the results with those of ethylene.

A representative mechanism will be described to account for the formation of the characteristic products obtained in the present electrochemical fluorination.

Experimental

Materials. — The ethylene, obtained from the Ohio Chemical & Surgical Equipment Co., was more than 99.5% pure. The ethane (99.7% pure) was obtained from the Takachiho Chemical Industrial Co. The hydrogen fluoride (more than 99% pure) was supplied by the Daikin Industries Co. The diluent employed was Airco helium gas.

Apparatus and Procedure.—The apparatus used for this fluorination was essentially the same as that used for the fluorination of methane.2) The characteristic part of the fluorination cell was the bubbler. Many minute bubbles of the sample gas were produced in hydrogen fluoride by the use of this bubbler.

The experimental procedure was as follows. Hydrogen fluoride (1 l.) was placed in the cell, and before the introduction of the sample, electrolysis was carried out in a nitrogen atmosphere in order to remove a trace of an impurity; the electrolysis was carried out at 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 sodium fluoride was added, and the metered sample was introduced from the bottom of the cell, through the bubbler, into hydrogen fluoride maintained at 6—7°C,

---

* " Electrochemical Fluorination of Gases " Part II.

1) After this work had been completed, the authors read a review article (M. Schemisser and P. Sartori, *Chemie-Ing.-Techn.*, **36**, 9 (1964)) stating that the electrochemical fluorination of ethylene was not accomplished due to the polymerization of ethylene.

2) S. Nagase, K. Tanaka and H. Baba, This Bulletin, **38**, 834 (1965).

3) P. Sartori, *Angew. Chem.*, **75**, 417 (1963).

using a calibrated flow meter connected to a sample cylinder. In a few experiments, helium was admitted simultaneously with the sample into the bubbler. The sample was fluorinated at the anodic current density of 2.2 amp./dm^2. When the cell voltage became almost steady at 6—6.5 V. (after about 1 hr.), traps were immersed in ice and liquid nitrogen respectively, and electrolysis was carried out for the designated amp.-hr. period. Since the bubbler was found to be very effective in the fluorination of methane, all the present reactions were carried out using the bubbler.

The fluorinated gas evolved from the cell was passed through a condenser kept at -15°C and over sodium fluoride pellets in order to remove the hydrogen fluoride; then it was bubbled through a sodim sulfite solution containing a small amount of potassium iodide in order to eliminate a trace amount of explosive oxygen difluoride. The gas was subsequently passed through a trap in ice, and finally condensed in two traps placed in series in liquid nitrogen. Fluorination took place smoothly in all the experiments.

The product thus obtained was rectified in a low-temperature rectification unit and weighed in a glass ampule. The molecular weight of each fraction was measured by means of gas density balance. The mixture was then further separated by gas chromatography, using an activated charcoal column (2 m.) maintained at 120°C, using helium as the carrier.

The Fluorination of Ethylene.—The reaction conditions of six representative runs, and a typical example of the results of low-temperature rectification and chromatographic separation are given in Tables I and II respectively. As in the case of the fluorination of methane, the quantitative analysis by means of a gas chromatograph of the separated component was made on the assumption that the ratio of the peak areas of chromatogram is a direct measure of the percentage weight of the components.[4] However, in the case of fraction 1, which consisted of tetrafluoromethane, ethylene, and hexafluoroethane, the latter two components were not separated from each other chromatographically under the conditions applied; therefore this fraction was analyzed quantitatively by the use of the baseline method for the infrared spectrum.

Fraction 2 corresponded to hexafluoroethane but was contaminated by a negligible amount of trifluoromethane. Rather unexpectedly, ethane was also contained in this fraction, obtained from runs 2 and 5, in the amounts of 3 and 5 mol.% of the total fractions. (The amount of ethane was determined by means of the baseline method for the infrared spectrum).

Fraction 3 consisted of 1, 1, 1-trifluoroethane and pentafluoroethane. The azeotropic mixture of these two compounds is known to boil at -45°C.[5] Fraction 4 consisted of a mixture of isomers of 1, 1, 1, 2-tetrafluoroethane and 1, 1, 2, 2-tetrafluoroethane with the observed molecular weight of 102 to 103. The boiling point of the azeotropic mixture of these two compounds is known to be -29°C.[5]

Fraction 5 consisted mainly of a mixture of 1, 1-difluoroethane and 1, 1, 2, 2-tetrafluoroethane, plus a

TABLE I. CONDITIONS FOR FLUORINATION OF ETHYLENE[a]

Run No.	Total amount of C_2H_4 fed mol.	NaF used g.	He used ml./min	Temp. °C	Note
1	0.274	10	0	7—8	Effect of feed rate
2	0.446	10	0	6—7	
3	0.218	50	0	6—7	Effect of NaF
4	0.283	10	104[b]	6—7	Effect of diluent
5	0.563	10	150[c]	6—7	
6	0.309	10	0	16—17	Effect of temp.

a) Electrolysis was carried out for 76 amp.hr. in all the experiments.

b) Dilution ratio (C_2H_4: He) was 1 : 4 by volume.

c) Dilution ratio (C_2H_4: He) was 1 : 3 by volume.

TABLE II. RECTIFICATION OF FLUORINATED ETHYLENE[a]

Fract. No.	B. p., °C	Wt., g.	Component[b]
1	-105—-100	8.7	CF_4(trace),[c] CH_2=CH_2, CF_3CF_3[c]
2	-90—-77	5.9	CF_3CF_3, CHF_3 (trace),[c] CH_3CH_3
3	-49—-45	9.3	CF_3CH_3,[d] CF_3CHF_2[c]
4	-29—-23	5.0	CF_3CH_2F, CHF_2CHF_2
5	Hold up	3.9	CHF_2CH_3,[d] CHF_2CHF_2, X

a) This example was taken from the result of low-temperature rectification and chromatographic separation of the products obtained in run 2.

b) The components of each fraction in this table and in Table IV were arranged in the order of the peak appearance of gas chromatogram.

c,d) The infrared spectra of these compounds respectively agree with those listed in Weiblen's "Fluorine Cehmistry," Vol. II, Ed. by J. H. Simons, Academic Press Inc., New York (1954), p. 469, and "Infrared Spectral Data," American Petroleum Institute, Research Project 44, Carnegie Institute Technology, 1959, Serial number 977 and 979.

TABLE III. CONDITIONS FOR FLUORINATION OF ETHANE[a]

Run No.	Total amount of C_2H_6 fed mol.	NaF used g.	He used ml./min.	Temp. °C	Note
1	0.517	10	0	6—7	Effect of feed rate
2	0.607	10	0	6—7	
3	0.481	50	0	6—7	Effect of NaF
4	0.506	10	107[b]	6—7	Effect of diluent
5	0.573	10	0	16—17	Effect of temp.

a) Electrolysis was carried out for 108 amp.hr. in all the experiments.

b) Dilution ratio (C_2H_6: He) was 1 : 3 by volume.

---

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

[5] J. A. Cuculo and L. A. Bigelow, *J. Am. Chem. Soc.*, **74**, 710 (1952).

TABLE IV. RECTIFICATION OF FLUORINATED ETHANE[a]

Fract. No.	B. p., °C	Wt. g.	Component
1	−95—−92	25.8	CF_4(trace), CF_3CF_3, CH_3CH_3
2	−91—−89	2.4	CH_3CH_3
3	−50—−46	6.5	CF_3CH_3, CF_3CHF_2
4	−29—−22	3.2	CF_3CH_2F, CHF_2CHF_2
5	Hold up	2.8	CF_3CH_2F, CHF_2CHF_2

a) This example was taken from run 2.

small amount of a compound, X, which could not be identified chemically or spectroscopically.

A small amount (0.2—0.4 g.) of a tarry polymeric material whose infrared spectrum showed the presence of a C–F bond and a C–H bond was found in the residue in the electrolytic cell after the distillation of hydrogen fluoride from the cell.

The Fluorination of Ethane.—The fluorination of ethane was carried out under the reaction conditions shown in Table III. Table IV shows a typical example of the results of low-temperature rectification and chromatographic separation. The products were analyzed quantitatively by a method similar to that used for ethylene. Fraction 1 consisted of an azeotropic mixture of hexafluoroethane and ethane, along with an insignificant amount of tetrafluoromethane. The elements of this azeotropic mixture, reported to boil at −92°C,[6] could not be separated from each other by gas chromatography under the conditions used. In a few runs, a negligible amount of trifluoromethane was detected in this fraction.

Fraction 2 corresponded to ehtane, but it was often contaminated with hexafluoroethane. Fractions 3 and 4 were essentially the same as those of fractions 3 and 4 in Table II. The components of fraction 5 were the same as those of fraction 4. In the other runs, however, an unidentified compound whose infrared spectrum was identical with that of the compound X obtained from ethylene was present.

It was interesting that monofluoroethane* was obtained in a considerable amount under the mild reaction conditions of run 4.

Results and Discussion

The results obtained from the fluorination of ethylene and ethane are summarized in Tables V and VI respectively; these results show that the milder and controllable fluorination reaction can be carried out by the use of an electrolytic cell equipped with a bubbler.

TABLE V. COLLECTED RESULTS IN THE FLUORINATION OF ETHYLENE

Run No.	Total yield mol.%	Total current eff., %[a]	Product comp., mol.%							
			CF_3CF_3	CF_3CHF_2	CF_3CH_2F	CHF_2CHF_2	CF_3CH_3	CHF_2CH_3	CF_4	X[b]
1	78.0	60.8	46.2	17.1	9.3	14.4	6.2	4.3	2.5	0
2	50.3	56.1	23.6	9.6	18.0	7.9	32.3	8.6	trace	1.2
3	73.5	42.9	36.5	14.6	13.7	20.7	7.3	5.9	1.3	2.2
4	79.9	59.3	36.8	12.6	10.5	19.7	6.7	11.4	2.3	0
5	44.5	59.6	18.2	16.8	22.1	16.0	19.2	4.8	2.9	2.0
6	73.2	57.7	28.2	16.6	16.1	20.3	12.0	6.0	0.8	0

a) The calculation of current efficiency was based on the amount of current assumed to be necessary for forming fluorine with a discharging fluoride ion which would react with the sample according to the following equations. Total current efficiency shown is the sum total of the current efficiency for each component.

$$C_2H_4 + 10F = CF_3CF_3 + 4HF \quad (1)$$
$$C_2H_4 + 8F = CF_3CHF_2 + 3HF \quad (2)$$
$$C_2H_4 + 6F = CF_3CH_2F + 2HF \quad (3)$$
$$C_2H_4 + 6F = CHF_2CHF_2 + 2HF \quad (4)$$
$$C_2H_4 + 5F + H = CF_3CH_3 + 2HF \quad (5)$$
$$C_2H_4 + 3F + H = CH_3CHF_2 + HF \quad (6)$$
$$C_2H_4 + 12F = 2CF_4 + 4HF \quad (7)$$

b) The amounts of X were given in unit of grams in this table and in Table VI.

TABLE VI. COLLECTED RESULTS IN THE FLUORINATION OF ETHANE

Run No.	Total yield mol.%	Total current eff., %[a]	Product comp., mol.%						
			CF_3CF_3	CF_3CHF_2	CF_3CH_2F	CHF_2CHF_2	CF_3CH_3	CH_2FCH_3	X
1	48.5	65.0	56.2	14.2	12.1	10.3	7.2	0	0.9
2	40.7	62.2	51.2	14.8	13.4	10.4	10.2	0	0
3	40.4	49.6	49.5	20.6	10.3	13.9	5.7	0	1.6
4	48.1	52.7	44.8	8.6	10.7	9.4	7.5	19.0	1.8
5	54.1	79.6	53.0	13.0	12.1	17.9	4.0	0	1.9

a) The calculation of the current efficiency shown was made on the similar assumption to that in the case of ethylene, for instance, $C_2H_6 + 12F = C_2F_6 + 6HF$

---

6) J. D. Calfee, N. Fukuhara and L. A. Bigelow, ibid., **61**, 3552 (1939).

* The reference infrared spectrum obtained from the American Petroleum Institute, serial number 1302, was identical with this product.

With regard to the partial fluorination of these samples, the results obtained were not as striking as for methane.[1] The sample feed rate had a large effect, especially on the partial fluorination of ethylene. A higher feed rate made the reaction milder and gave less hexafluoroethane in the products. The amount of sodium fluoride and the electrolysis temperature also affected the results in the present experiments. Above all, the dilution of the feed with helium appeared to make the reaction milder and to give a large amount of less-fluorinated ethane from ethylene and a considerable amount of monofluoroethane from ethane.

Except for a kinetic study of fluorine addition to ethylene,[7] no information has been available on the fluorination of ethylene with elementary fluorine, but the kind and the ratio of the reaction products reported here appeared to be very close to what might be expected from the very mild fluorination of ethylene with elementary fluorine. Furthermore, the characteristics associated with the results obtained from the fluorination of ethane were comparable in many respects to those obtained from the vapor-phase fluorination of ethane with elementary fluorine,[6,8,9] which is known to proceed via a free-radical mechanism.

The fluorinating agent and the reaction mechanism in electrochemical fluorination are much in dispute.[10] However, the basic reaction which takes place during the present fluorination appears very likely to be a free-radical reaction on the anode surface. The effective dispersion of the reaction heat, the good agitation, the sparing solubility of the sample and fluorinated products, and the reaction in the very inert solvent, hydrogen fluoride, to fluorinating agent may account for the mildness of this fluorination reaction.

The important products from ethylene were 1, 1-difluoroethane and 1, 1, 1-trifluoroethane, which was isolated in a considerable amount. The formation of these may perhaps be represented simply as follows:

$$\mathrm{CH_2{=}CH_2} \xrightarrow{[\mathrm{F}]} \underset{\mathrm{(I)}}{\mathrm{CH_2F{-}CH_2F}} \xrightarrow{-\mathrm{HF}} \underset{\mathrm{(II)}}{\mathrm{CHF{=}CH_2}}$$

$$\xrightarrow{\mathrm{HF}} \underset{\mathrm{(III)}}{\mathrm{CHF_2{-}CH_3}} \xrightarrow{[\mathrm{F}]} \underset{\mathrm{(IV)}}{\mathrm{CF_3CH_3}}$$

The initial product I, which is well known to be unstable, may undergo dehydrofluorination to give II under these reaction conditions. The addition of hydrogen fluoride to II, which is known to proceed readily in accordance with Markownikoff's rule,[11] could yield III, which could be further fluorinated to give IV. The increasing stability of compounds with fluorine atoms attached to the same carbon atom[12] may suggest a possible pathway, although the reaction could and probably did follow different routes simultaneously.

In the case of ethane, which did not afford 1, 1-difluoroethane in a detectable amount, such isomerization could have occurred to a certain extent, but the lower concentration of the initial product I compared with that from ethylene can account for the observed fact. Ethylene may always give I in the initial step of the reaction.

A quite unexpected and interesting by-product from ethylene was ethane. It is believed that this was formed by the cathodic reduction of ethylene. Only one report has described the cathodic reduction, and that not in a typical electrochemical fluorination.[13]

The formation of a detectable amount of any other compound with a double bond or more carbon atoms than the parent compounds could not be confirmed through the experiments.

Summary

The electrochemical fluorination of ethylene and ethane has been carried out using a cell equipped with a bubbling arrangement. It appeared that the fluorination reaction could be controlled, especially for ethylene, in order to obtain either perfluoroethane or partially-fluorinated ethanes preferentially, in a reasonable yield and with reasonable current efficiency.

From ethylene, without any significant polymerisation or fragmentation, hexafluoroethane, pentafluoroethane, 1, 1, 1, 2-tetrafluoroethane, 1, 1, 2, 2-tetrafluoroethane, 1, 1, 1-trifluoroethane, 1, 1-difluoroethane, tetrafluoromethane, and a reduced product, ethane, and an unidentified minor product were formed. Ethane afforded similar fluorinated ethanes, together with monofluoroethane and a trace of tetrafluoromethane, but not 1,1-difluoroethane.

The influence of the operating conditions on these fluorination reactions and the mechanism involved have been discussed.

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

---

[7] G. A. Kapralova, L. Yu. Rusin, A. M. Chaikin and A. E. Shilov, *Dokl. Akad. Nauk, SSSR*, **150**, 1282 (1963).

[8] D. S. Young, N. Fukuhara and L. A. Bigelow, *J. Am. Chem. Soc.*, **62**, 1171 (1940).

[9] E. A. Tyczkowski and L. A. Bigelow, ibid., **77**, 3007 (1955).

[10] For example, see J. Burdon and J. C. Tatlow, "Advances in Fluorine Chemistry," Vol. I, Ed. by M. Stacey, J. C. Tatlow and A. G. Sharpe, Butterworths Scientific Publications, London (1959), p. 160.

[11] A. M. Lovelace, D. A. Rausch and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Co., New York (1958), p. 14.

[12] J. Hine, *J. Am. Chem. Soc.*, **85**, 3239 (1963).

[13] H. Schmidt and H. D. Schmidt, *J. pr. Chem.*, **2**, 105 (1955).