extent of 5% in 100 ml. of ether saturated with water. It is soluble in 100 ml. of benzene saturated with water to the extent of 0.3 g. Ester-free glycol may also be obtained by distillation of glycol (40 g.) containing ester from 1 g. of sodium hydroxide. However, the recovery of glycol is poor (78%) and the process has little to recommend it.

Summary

Experimental evidence has been presented in support of Lazier's conclusion that the hydrogenation of esters over copper chromite at 240 to 260° is a reversible reaction. The concentration of esters at equilibrium is a function of the pressure of hydrogen and is for pressures of 200 to 300 atm. of the order of 1%. Alcohols and glycols prepared at such pressures and separated from these reaction products by the ordinary methods of fractionation should contain at the most a few tenths of a per cent. of ester. Simple methods for obtaining ester-free hexamethylene glycol have been described.

MADISON, WISCONSIN RECEIVED AUGUST 19, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. IX. The Vapor Phase Fluorination of Methane[1]

BY ELBERT H. HADLEY AND LUCIUS A. BIGELOW

We have described before[2] the vapor phase fluorination of ethane, and the influence of nitrogen dilution upon this reaction. Methane was not investigated first, among other reasons, because preliminary experiments had shown that unexpected difficulties would probably be encountered. The present paper contains the results of a study of the fluorination of methane, in which these difficulties have largely been overcome.

The reactions were carried out in the usual way over a copper gauze catalyst[2] and the products rectified in the Booth–Podbielniak fractionating unit, to which we have added a differential manometer attached to the top and bottom of the distilling column, and provided with adequate mercury traps and a shunt. This device was to indicate immediately any obstruction of the distilling tube by subliming silicon tetrafluoride, or carbon dioxide, which could otherwise lead to disastrous consequences.

Table I shows the results obtained from a series of runs, expressed, as usual, in liquid volume per cent. of the total condensate, and calculated on a ten-hour basis. The figures, except for the total volumes, have been rounded off to the nearest 5%.

These results show definitely that when the volume ratio of fluorine to methane was 2:1, and the dilution ratio of fluorine to nitrogen was 1:5, the proportion of the product boiling higher than carbon tetrafluoride rose to a maximum of 45 liquid volume per cent. of the total condensate. This value could not practicably be increased, since at still higher dilution ratios the low boiling gases could not be condensed efficiently.

TABLE I

THE PRODUCTS OBTAINED BY RECTIFYING FLUORINATED METHANE

Liquid vol. % of material boiling	Gas volume ratio of fluorine to methane to nitrogen					
	1:1:0	1:1:1	2:1:0	2:1:2	2:1:4	2:1:10
All < −128° (mostly CH_4)	65	60	30	25	20	10
−128° (CF_4)	30	30	45	50	40	45
All > −128°	10	10	20	30	35	45
Total vol. of condensate for 10 hr. in ml.	26	25	14	14	11	11

A large amount of this higher boiling product was collected, passed four times through a 10% sodium hydroxide solution to remove most of the carbon dioxide and silicon tetrafluoride, dried, and finally rectified.

Runs were made under different operating conditions but the fractionation of the product obtained when the volume ratio of fluorine to methane to nitrogen was 2:1:10 will be described as typical. It is of interest that under these conditions no pure compounds distilled at first. Instead there was obtained a series of definite, heterogeneous constant boiling mixtures, with constant molecular weights.

In the distillation, some carbon tetrafluoride came over first and was discarded, leaving a 30-ml. sample. Then a minor fraction distilled, doubtless containing silicon tetrafluoride, followed by 8.5 ml. of mixture E (b. p. −89°, mol. wt. 85). After this came 6.5 ml. of mixture Z (b. p.

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[1] This paper has been constructed from portions of Mr. Hadley's Doctorate Thesis, presented to the Graduate School of Duke University in May, 1940.

[2] Calfee, Fukuhara and Bigelow, THIS JOURNAL, **61**, 3552 (1939); Young, Fukuhara and Bigelow, *ibid.*, **62**, 1171 (1940).

−86°, mol. wt. 101), and then several minor fractions, all mixtures. Following these, came 5 ml. of mixture D (b. p. −58°, mol. wt. 95), after which the temperature rose slowly to −13° at which point the mol. wt. was 156. It may be significant that an apparently identical fraction (b. p. −13°, mol. wt. 156) has been obtained by rectifying fluorinated propane.

All of these mixtures were heterogeneous, so the material boiling below −66° was recombined and condensed in a narrow tube, where it separated into clear distinct layers after alternate freezing and melting. Then the lower layer was frozen, and the upper layer allowed to boil off, thus making an effective separation.

The lower layer (11.5 ml.) was next distilled by itself. There came over first some of E, and then some of Z, followed by 5 ml. of pure hexafluoroethane (b. p. −78°, mol. wt. 138), leaving a small residue. The upper layer, (7 ml.) was then rectified. After a small fore fraction, some E came over, followed by 0.5 ml. of pure methyl fluoride (b. p. −78°, mol. wt. 35). Then the temperature rose slowly, and there came over finally 4.5 ml. of a homogeneous fraction Y (b. p. −75°, mol. wt. 49). These observations made it seem very likely that E (b. p. −89°, mol. wt. 85) was a mixture of methyl fluoride and hexafluoroethane. This assumption was proved by distilling a mixture of known samples of these compounds, which boiled at −89° with a mol. wt. of 85. The calculated average mol. wt. of an equimolar mixture is 86. Fraction Y could not be separated into components by distillation at reduced pressures (b. p. −97 to −96° at 220 mm.), and did not react with liquid bromine, but has not as yet been identified. When it was mixed with hexafluoroethane and distilled, Z was regenerated.

The mixture D (b. p. −58°, mol. wt. 95) which had been kept apart, and which also formed layers, was separated mechanically as described above. When the lower layer was distilled, there came over first some of the original mixture D, followed by 1.5 ml. of pure octafluoropropane (b. p. −36° (−38°[3]), mol. wt. 187 (calcd. 188)) The upper layer, on rectification, yielded at first again some of D, followed by 1.5 ml. of pure methylene fluoride (b. p. −52°, mol. wt. 52).

These products, as well as the others which were obtained by rectifying material prepared under different operating conditions, are listed in Table II, together with their boiling points and molecular weights.

TABLE II

PURE COMPOUNDS OBTAINED BY RECTIFYING FLUORINATED METHANE

Fract. of const. b. p. and mol. wt.	B. p. °C.	Mol. wt.	Compounds	B. p., °C. Known	B. p., °C. Found	Mol. wt. Calcd.	Mol. wt. Found
Mixture C	−89	94	CHF_3	−82	−82	70	72
			C_2F_6	−78	−79	138	137
Mixture D	−58	95	CH_2F_2	−52	−52	52	52
			C_3F_8	−38	−36	188	187
Mixture E	−89	85	CH_3F	−78	−78	34	35
			C_2F_6	−78	−79	138	138
Fluoroform[a]	..	..	CHF_3	−82	−82	70	71

[a] Small fraction, from an original distillation.

As will be seen, the constants obtained for the pure compounds agree well with the known values, leaving no doubt as to the identity of the products. Altogether there were isolated all the fluoromethanes, CH_3F, CH_2F_2, CHF_3 and CF_4, together with hexafluoroethane C_2F_6 and octafluoropropane C_3F_8. Some other as yet unidentified products were formed also.

All of these results are in accord with the current free radical chain mechanism now used[4] to explain vapor phase chlorination, and which may be illustrated as follows

$$F_2 \longrightarrow 2F\cdot \tag{1}$$
$$CH_4 + F\cdot \longrightarrow CH_3\cdot + HF \tag{2}$$
$$CH_3\cdot + F_2 \longrightarrow CH_3F + F\cdot \tag{3}$$

and so on until CF_4 is formed finally. Here (1) presumably must be either thermal or catalytic. The formation of C_2F_6 is easily explained by

$$CHF_3 + F\cdot \longrightarrow CF_3\cdot + HF \tag{4}$$
$$2CF_3\cdot \longrightarrow C_2F_6 \tag{5}$$

and that of C_3F_8 according to the equations

$$CH_2F_2 + F\cdot \longrightarrow CHF_2\cdot + HF \tag{6}$$
$$CHF_2\cdot + CF_3\cdot \longrightarrow CF_3CHF_2 \tag{7}$$
$$CF_3CHF_2 + F\cdot \longrightarrow CF_3CF_2\cdot + HF \tag{8}$$
$$CF_3CF_2\cdot + CF_3\cdot \longrightarrow C_3F_8 \tag{9}$$

Equation (7) is supported by the fact that we obtained definite evidence, although not conclusive proof, of the presence of some CF_3CHF_2 in our product. Still further support for the free radical interpretation can be found in a recent paper by Miller,[5] who has presented considerable evidence to show that direct fluorinations proceed by a non-ionic mechanism.

Summary

A study of the vapor phase fluorination of methane has been made. It has been found that under suitable conditions, the proportion formed of products other than carbon tetrafluoride could be increased to a maximum of 45 liquid volume per cent. of the total condensate.

There have been isolated from the products all of the possible fluoromethanes, together with hexafluoroethane C_2F_6, and octafluoropropane, C_3F_8.

Certain theoretical considerations have been outlined.

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[3] Simons and Block, THIS JOURNAL, **61**, 2962 (1939).

[4] See, for example, Hass, McBee and Weber, *Ind. Eng. Chem.*, **28**, 333 (1936).

[5] Miller, THIS JOURNAL, **62**, 341 (1940).