REACTIONS OF HEXAFLUOROPROPENE WITH METHANOL AT ATMOSPHERIC PRESSURE

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The reactions of hexfluoropropene with methanol in an autoclave under pressure were studied in detail in 1953 and 1956, and it was found that a mixture of 2H-hexafluoropropyl methyl ether and methyl pentafluoropropenyl ether (I) was formed. In the present investigation we have shown that in the absorption of hexafluoropropene by a solution of sodium methoxide in methanol, as well as the above-stated products, a high-boiling fraction (b.p. 93-125°) is obtained in an amount which increases with increase in the sodium methoxide concentration (10-15% of the weight of the hexafluropropene taken). In absence of methanol (dry sodium methoxide in toluene) we obtained only methyl pentafluoropropenyl ether, whose structure was proved by its IR spectrum and by chromatographic comparison* with a known sample [3].

We investigated the high-boiling fraction by means of gas-liquid chromatography and found that its composition depends on the method of isolation. If in the isolation the possibility of hydrolysis is excluded, then the high-boiling fraction is found to consist completely of the two isomers 2H-pentafluoro-1,1- and -1,3-dimethoxypropanes (III) and (IV) – products of the addition of methanol to methyl pentafluoropropenyl ether (I) and methyl pentafluoroallyl ether (II).

$$CF_3-\underset{(I)}{CF}=CF-OCH_3+CH_3OH\rightarrow CF_3-\underset{(III)}{CFH}-CF(OCH_3)_2$$
$$CF_2=CF\underset{(II)}{-}CF_2-OCH_3+CH_3OH\rightarrow \underset{(IV)}{CFH}(CF_2OCH_3)_2$$

It is impossible to separate these by fractional distillation because of the closeness of their boiling points, and unfortunately the previously undescribed vicinal diether (III) cannot be isolated from the mixture in the pure state by chemical methods. For example, when the mixture is hydrolyzed with 50% H_2SO_4 the diether (IV) is left unchanged, but the diether (III) is converted into methyl 2H-tetrafluoropropionate (V):

$$CF_3-CFH-CF(OCH_3)_2\xrightarrow{H_2O}CF_3-\underset{(V)}{CFH}-COOCH_3$$

Under more severe conditions (dissolution of the mixture of diethers in concentrated H_2SO_4) 2H-pentafluoro-1,3-dimethoxypropane is also hydrolyzed – first to methyl 2,3,3-trifluoro-3-methoxypropionate (VI), and then to dimethyl fluoromalonate (VII):

$$\underset{(IV)}{CHF(CF_2OCH_3)_2}\xrightarrow{H_2O}\underset{(VI)}{CH_3OCF_2CFHCOOCH_3}\xrightarrow{H_2O}\underset{(VII)}{CFH(COOCH_3)_2}$$

If after the completion of the reaction of hexafluoropropene with methanol the reaction mixture is poured into water, then in the high-boiling fraction obtained (III) and (IV) are almost absent and this fraction consists mainly of products of their hydrolysis – methyl 2H-tetrafluoropropionate and the esters (VI) and (VII). In the treatment of the high-boiling fraction obtained in this way with concentrated H_2SO_4, apart from 2H-tetrafluoropropionic and fluoromalonic ester we also isolated methyl fluoroacetate, which probably resulted from the partial hydrolysis and decarboxylation of dimethyl fluoromalonate:

$$CHF(COOCH_3)_2\xrightarrow{H_2O}[CHF(COOH)-COOCH_3]\xrightarrow{-CO_2}CH_2FCOOCH_3$$

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*Liquid phase – Rheoplex 400 on Celite 545.

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TABLE 1

Compound	δ, p.p.m. rel. to HMDS		J, Hz	
	CH_3	>CH—	HF^1	$HF^2=HF^3$
$CF_3^2—CF^1H—COOCH_3$	3,95	5,30	45,0	6,4
$CF_3^2—CF^1H—CF(OCH_3)_2$	3,35	4,80	44,0	6,2
$CF^1H(CF_2^2OCH_3)_2$	3,61	4,55	45,0	5,9
$CF_3^2CF^1H—CF_2^3OCH_3$	3,64	4,67	44,0	5,8
$CF_3—CF=CF—OCH_3$	3,84			

TABLE 2

Expt.	Amt. taken		C_3F_6 absorbed, moles	Obtained, %	
	Na, g-atom	methanol, moles		$CH_3OCF_2CFHCF_3$	high-boiling fraction
1	1	5	1,56	64	17
2	1	10	2,75	74	12
3	1	25	—	77	7

Further proof of the structure of the unknown 2H-pentafluoro-1,1-dimethoxypropane (III) was obtained by a study of the spectra. Thus, the IR spectrum of the mixture of 2H-pentafluoro-1,1- and 1,3-dimethoxypropanes contains no absorption in the region 1650-2000 cm^{-1} characteristic for unsaturated or carbonyl compounds. The PMR spectrum of the mixture was determined with a TsLA 55-35 NMR spectrometer and is given below (Table 1).

We did not succeed in interpreting the PMR spectrum of the mixture of pentafluorodimethoxypropanes completely. It contains a doublet of quartets due to a hydrogen nucleus with a chemical shift and spin-spin interaction constants characteristic for the CF_3CFH group, which could be assigned, it would appear, to pentafluoro-1,1-dimethoxypropane, but we were unable to discern the spin-spin interaction of this proton with the fluorine atom of the $CF(OCH_3)_2$ group. Apart from the doublet of quartets of CF_3CFH, the spectrum contains a doublet of quintets of the CF_2CFHCF_2 group of pentafluro-1,3-dimethoxypropane and a number of split signals which we were unable to assign with an adequate degree of reliability. However, two strong signals of methyl protons can be clearly distinguished in the spectrum; one of these with a chemical shift of 3.61 p.p.m. can be assigned to 2H-pentafluoro-1,3-dimethoxypropane (compare with 2H-hexafluoropropyl methyl ether with $\delta(CH_3)$ 3.64 p.p.m.), and therefore the other with a chemical shift of 3.35 p.p.m. could belong to 2H-pentafluoro-1,1-dimethoxypropane.

EXPERIMENTAL

2.3 g of sodium was dissolved in 16 g of absolute methanol in a two-necked flask fitted with reflux condenser cooled with a mixture of solid carbon dioxide and acetone and a gas-inlet tube which passed to the bottom of the flask, and dry hexafluoropropene was passed through the solution at such a rate that liquid did not drop back very quickly from the reflux condenser. The reaction stopped after the absorption of 23.5 g of hexafluoropropene.

All that would distill from a boiling water bath was removed from the resulting solution. The distillate was poured into water, and the precipitated oil was washed several times with water, dried, and distilled. We obtained 15.9 g (56%) of 2H-hexafluoropropyl methyl ether, b.p. 54-55° and n_D^{20} 1.2842, identical to the previously described substance [1, 2].

The residue remaining after the removal of methanol and 2H-hexafluoropropyl methyl ether was vacuum-distilled to dryness with collection of the distillate in a trap (−78°). The distillate was washed with water and dried, and we obtained 4 g of a liquid, b.p. 93-125°.

The effect of the sodium methoxide concentration on the yields of products is shown in Table 2.

The high-boiling fractions from several experiments were combined and fractionated through a column. From 29 g we obtained 4 g of methyl 2H-tetrafluoropropionate, b.p. 95° (748 mm) and identical to the substance obtained earlier [1, 2], and 17 g of a fraction with b.p. 120-122° (748 mm); n_D^{20} 1.3273. Found %: C 31.07; H 3.64; F 49.07. $C_5F_5H_7O_2$. Calculated %: C 30.94; H 3.63; F 48.96.

Chromatographic analysis* showed that this fraction was a 1 : 2 mixture of 2H-pentafluoro-1,3- and -1,1-dimethoxypropanes. The 2H-pentafluoro-1,3-dimethoxypropane was identified with a known sample [4].

Hexafluoropropene was absorbed in a methanolic solution of sodium methoxide in a similar way, but after the completion of the reaction the whole mixture was poured into water, and the oil was separated,

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*Here and below we used a column containing oil of specification VTU No. 255-72-61 supported on diatomite. Carrier gas helium. Yields were calculated by measuring the areas of the corresponding peaks.

dried, and distilled. When 2H-hexafluoropropyl methyl ether had been distilled off, we obtained a residue in the same amount as in the preceding experiment. Such residues from several experiments were combined and fractionated through a column. From 24.9 g we obtained 14.6 g of methyl 2H-tetrafluoropropionate and 10.3 g of a fraction with b.p. 120-210°, which distilled without decomposition at a residual pressure of 26 mm over the range 72-100° and was found to be a mixture of 2H-pentafluoro-1,3-dimethoxypropane (8%), 2H-pentafluoro-1,1-dimethoxypropane (3%), methyl 2,3,3-trifluoro-3-methoxypropionate (36%), and dimethyl fluoromalonate (39%). For identification purposes methyl 2,3,3-trifluro-3-methoxypropionate was synthesized from methyl trifluoroacrylate and methanol by the method described in [5] and was converted into dimethyl fluoromalonate by treatment with concentrated H_2SO_4.

10.3 g of the fraction of b.p. 150-210° was dissolved with cooling in 20 ml of concentrated H_2SO_4 and left for 6 h at 0°; it was then poured into water, and the oil was separated, dried, and distilled. We obtained: a) 3 g of methyl fluoroacetate, b.p. 103-105° (745 mm); n_D^{20} 1.3680. Found %: C 38.95; H 5.43; F 20.67. $C_3H_5FO_2$. Calculated %: C 39.13; H 5.43; F 20.69. [6] gives b.p. 104.5°; n_D^{20} 1.3679. b) 2.5 g of dimethyl fluoromalonate, b.p. 80-83° (13 mm); n_D^{20} 1.4008. [7] gives b.p. 80-82° (12 mm), and [8] gives b.p. 70-72° (20 mm); n_D^{25} 1.3709.

1) The high-boiling fraction of b.p. 120-122° (748 mm) (1 g) was boiled for 5 min with 50% H_2SO_4. The oil was then separated from the aqueous layer, washed with water, dried, and vacuum-distilled into an ampule cooled with liquid nitrogen. We obtained 0.71 g of liquid, whose composition was determined chromatographically: 2H-pentafluoro-1,1-dimethoxypropane 0.5%, 2H-pentafluoro-1,3-dimethoxypropane 39%, methyl 2H-tetrafluoropropionate 55%, and methyl 2,3,3-trifluoro-3-methoxypropionate 4.5%.

2) 4 g of the fraction of b.p. 120-122° was dissolved with cooling in 5 ml of concentrated H_2SO_4, and the solution was left for 4 h at 0° and then treated as in the preceding experiment. We obtained 2.0 g of a liquid which consisted of a mixture of methyl 2H-tetrafluoropropionate (75%) and dimethyl fluoromalonate (25%).

A mixture of sodium methoxide (from 4.6 g of sodium), 30 g of hexafluoropropene, and 100 ml of toluene was heated at 70-80° for 5 h with shaking, after which all that would distill up to 110° was driven off, and the distillate was fractionated through a column. We obtained 19.2 g (59%) of methyl pentafluoropropenyl ether; b.p. 51.5° (743 mm); n_D^{20} 1.2970; d_4^{20} 1.3595. IR spectrum: ν_{max} 1765 s (C=C) (cm^{-1}). Found %: C 29.81; H 2.09; F 57.20. $C_4H_3F_5O$. Calculated %: C 29.64; H 1.87; F 58.62. [4] gives b.p. 52-52.5°; n_D^{20} 1.3045.

In a completely analogous way we obtained ethyl pentafluoropropenyl ether in 42% yield; b.p. 71-72° (743 mm); n_D^{20} 1.3103; d_4^{20} 1.2884. IR spectrum: ν_{max} 1765 s (C=C) (cm^{-1}). Found %: C 33.73; H 3.07; F 52.14. $C_5H_5F_5O$. Calculated %: C 34.10; H 2.86; F 53.95.

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CONCLUSIONS

1. In the reaction of hexafluoropropene with methanol in presence of sodium methoxide, apart from the already known products of the addition of methanol at the double bond and the replacement of one of the fluorine atoms, 2H-pentafluoro-1,1- and -1,3-dimethoxypropanes are formed.

2. By the reaction of anhydrous sodium alkoxides with hexafluoropropene alkyl pentafluoropropenyl ethers are formed.

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