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THE FLUORINATION OF ETHANE AND ETHENE OVER POTASSIUM TETRAFLUOROCOBALTATE(III) AND COBALT TRIFLUORIDE

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Abstract—Fluorination of ethane and ethene with $KCoF_4$ and CoF_3 over a range of temperatures gave, in all cases, mixtures of polyfluoroethanes, $C_2H_{6-n}F_n$ n = 1–6, with very little C–C bond cleavage. Apart from an initial easy saturation of ethene to CH_2FCH_2F, both substrates had a similar reactivity. Hydrogen appeared to be replaced by fluorine almost randomly in all fluorinations. CH_2FCH_2F is a stable compound, contrary to literature reports.

Although perfluorination of non-cyclic hydrocarbons over high-valency transition metal fluorides (HVMFs) is well known,[1] there are no reports of partial fluorination. Partial fluorinations of two ethanes and one ethene which already contained some fluorine have been described;[2] Holub and Bigelow[2a] treated 1,1,2-trifluoroethane and 1,1,2,2-tetrafluoroethane with cobalt trifluoride and obtained CHF_2CHF_2 and C_2F_5H from the former and C_2F_5H and C_2F_6 from the latter; and Rausch, Davis and Osborne[2b] used several HVMFs to convert 1,1-difluoroethene into CF_3CH_2F and CF_3CHF_2. We now report the first partial fluorinations of two non-cyclic hydrocarbons, ethane and ethene, over cobalt trifluoride and the milder[3] potassium tetrafluorocobaltate. Reactions were carried out at various temperatures and the results are summarised in Tables 1 and 2 (all the compounds are known). These show that cobalt trifluoride is, as usual,[3] more reactive than potassium tetrafluorocobaltate, and, of course, that the degree of fluorination rises with increasing temperature. Apart from the reactivity difference, there is no clear distinction between the product distributions with the two reagents, and for synthetic purposes there is obviously no great merit in the HVMF route to partially fluorinated ethanes, except perhaps for 1,2-difluoroethane from ethene and $KCoF_4$. Indeed, apart from this compound, there is no great difference between ethane and ethene either in degree of fluorination or in product distribution. It seems clear from Table 2 that ethene gives 1,2-difluoroethane very easily and that the fluorination then continues much as for ethane.

The product ratios for pairs of isomers are not quite those expected for a random fluorination but are not far from it if allowance is made for obvious experimental errors (preferential loss of high volatiles, e.g. CH_3CF_3, b.p. −46.7°C compared with CH_2FCHF_2, b.p. 5.0°; analysis difficulties with minor amounts of the higher volatiles). If all the hydrogens of ethane were equally reactive at all stages of the fluorination, then the ratio of CH_2FCH_2F to CH_3CHF_2 in the product would be 3:2, that of CH_3CF_3 to CH_2FCHF_2 1:9, and that of CH_2FCF_3 to CHF_2CHF_2, 2:3. Table 1 shows that the actual ratios are not far from these values with both reagents. Even for ethene (Table 2) similar ratios seem to occur although CH_3CF_3 is usually absent.

The presence of CH_3CHF_2 and CH_3CF_3 in ethene fluorinations may be due to either or both of two causes. First, addition of hydrogen fluoride (produced during the fluorination) to ethene would give fluoroethane; against this is the absence of fluoroethane in the ethene/$KCoF_4$ reaction, although it *is* formed in the ethane fluorination.

Table 1. Fluorination of ethane with CoF_3 and $KCoF_4$

Run no.[a]	temp (°C)	% C recovery	Product composition, mol %										
			C_2H_6	C_2H_5F	CH_2FCH_2F	CH_3CHF_2	CH_2FCHF_2	CH_3CF_3	CHF_2CHF_2	CH_2FCF_3	C_2F_5H	C_2F_6	CF_4
1	190	97.8	87.0	0.3	7.3	0.7	2.9	-	0.1	-	-	-	1.4
2	420	86.4	9.3	-	25.4	10.9	29.1	3.3	9.8	6.2	1.6	2.1	2.1
3	165	84.9	-	-	1.2	1.0	7.6	0.1	2.7	1.9	37.5	39.8	8.2

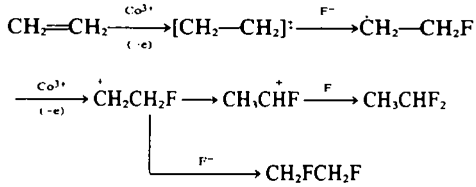
[a]1,2 $KCoF_4$; 3 CoF_3.

Table 2. Fluorination of ethene with CoF_3 and $KCoF_4$

Run no.[a]	temp (°C)	% C recovery	Product composition, mol %										
			C_2H_4	CH_2FCH_2F	CH_3CHF_2	CH_2FCHF_2	CH_3CF_3	CHF_2CHF_2	CH_2FCF_3	C_2F_5H	C_2F_6	CF_4
1	105	99.4	94.0	4.7	0.1	1.1	-	0.1	-	-	-	-
2	200	93.4	2.1	67.0	7.1	21.4	-	2.3	-	-	-	-
3	300	94.7	0.6	45.7	5.1	37.2	-	5.8	1.8	-	1.9	1.9
4[b]	115	91.7	-	9.1	5.0	32.1	0.9	14.7	9.3	11.1	14.8	2.5

[a]1–3 $KCoF_4$; 4 CoF_3. [b]CHF_3, 0.5%.

Secondly, a carbonium ion rearrangement of the following type may occur:



$$CH_2{=}CH_2 \xrightarrow[(-e)]{Co^{3+}} [CH_2{-}CH_2]^{+\cdot} \xrightarrow{F^-} \dot{C}H_2{-}CH_2F$$

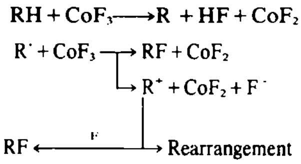
$$\xrightarrow[(-e)]{Co^{3+}} \overset{+}{C}H_2CH_2F \longrightarrow CH_3\overset{+}{C}HF \xrightarrow{F} CH_3CHF_2$$

$$\overset{+}{C}H_2CH_2F \xrightarrow{F^-} CH_2FCH_2F$$

The first three steps—oxidation to a radical cation, quenching by F^-, and further oxidation to a carbonium ion—are all in accord with our recently proposed[4] theory of fluorination with HVMFs. The rearrangement step should certainly be possible since carbonium ions with α-fluorines are more stable than their β-fluoro-isomers.[5]

We can say little about the mechanism of fluorination of saturated, noncyclic, hydrocarbons from our results. Reaction probably does not proceed to any great extent via olefinic intermediates because: (i) if olefins were formed at each of the early steps (by dehydrogenation or dehydrofluorination) then some *small* amounts of olefinic products would be expected and there are none; (ii) if ethane were dehydrogenated to ethene, then CH_2FCH_2F should be formed equally from both substrates and it is not (Tables 1 and 2); and (iii) fluoroethane is formed in the ethane/$KCoF_4$ reaction and this cannot arise from ethene (formed by dehydrogenation) and hydrogen fluoride because it is not found in the corresponding ethene reaction. These arguments do not exclude olefinic intermediates entirely and, indeed, some might be expected since it is known[6] that cyclohexane can give some benzene and tetrahydrothiophen some thiophen by treatment with HVMFs, albeit in low yields and under special conditions.

We prefer a reaction sequence along the following lines:



$$RH + CoF_3 \longrightarrow R^{\cdot} + HF + CoF_2 \quad (1)$$

$$R^{\cdot} + CoF_3 \longrightarrow RF + CoF_2$$

$$R^{\cdot} + CoF_3 \longrightarrow R^+ + CoF_2 + F^-$$

$$RF \xleftarrow{F^-} R^+ \longrightarrow \text{Rearrangement}$$

The near random nature of the fluorinations, mentioned earlier, is in accord with this as reaction (1) would not be expected to be highly selective between the various hydrogens in RH. Ethene can be fitted into the scheme after an initial saturation to CH_2FCH_2F, perhaps by the route outlined previously. We feel that it is not profitable to discuss the mechanism further at this stage.

Ethane and ethene have also been fluorinated by the electrochemical method,[7] which we have previously argued[4] follows an oxidative mechanism, similar to one proposed for HVMFs. It is difficult to compare the electrochemical results with ours, however, because the degree of fluorination was, in the main, much higher, One point of note is the ratio of CH_3CF_3 to CH_2FCHF_2†; this was significantly higher than in our fluorinations. This could be due to the much lower boiling point of the former which could enable it to escape from the reaction vessel.

Ethene has also[8] been fluorinated with XeF_2 and XeF_4 to give CH_3CHF_2, CH_2FCH_2F and CHF_2CH_2F. It was proposed that the first product arose by a radical rearrangement analogous to the carbonium ion one proposed here; this, or its carbonium ion version, certainly seems more likely than hydrogen fluoride addition since no fluoroethane was found, although with other substrates such addition did seem to occur; cyclohexene, for example, gave[8] appreciable quantities of fluorocyclohexane.

1,2-Difluoroethane is mentioned in the literature[9] as being unstable, even at 0°C, and even explosive as well as being very easily hydrolysed by water to 1,2-dihydroxyethane. It is also said[8] to rearrange slowly in carbon tetrachloride solution to 1,1-difluoroethane. Our isolation of the compound in major amounts from fluorinations at 420°, and the storage of it in glass for over a year at room temperature without any sign of change, discredit these reports. Further, attempts to hydrolyse it with water have proved unsuccessful.

EXPERIMENTAL

Fluorination of ethane with potassium tetrafluorocobaltate (III). Ethane, metered with a calibrated flow-meter, was introduced into the heated (190°–420°C) fluorination reactor at 7 dm^3/hr. The reactor was of the stirred type described previously[1] and it contained $KCoF_4$ (2 kg). After the addition, the reactor was flushed with N_2 (15 dm^3/hr) for 2 hr. The effluent gases were passed over heated (80°) NaF pellets (to remove HF) and the products collected in two liquid-air-cooled glass traps in series. The combined products were separated into four fractions by trap-to-trap distillation; the traps were maintained at −180°(4), −78°(3), −35.6°(2) and −15°(1). The results are summarised in Table 3.

The contents of traps 1 and 2 were analysed by ^{19}F NMR; GLC analyses were in agreement, but the NMR results are used in this paper. Traps 3 and 4 were analysed by IR (gas phase); Beer's law was applied to strong peaks known to occur in individual components. The major inaccuracy of this procedure lies in the measurement of gas pressure; there is also the likelihood of underestimating minor components unless they have a distinctive, strong, peak. By way of example, trap 1, run 2 (310°C) contained (mole %): C_2H_5F (5.1), CH_2FCH_2F (21.3), CH_3CHF_2 (17.4), CH_2FCHF_2 (39.5), CF_3CH_3 (1.7), CHF_2CHF_2 (9.4) and CF_3CH_2F (5.6). Traps 3 and 4 contained only C_2H_6, C_2H_4, C_2F_6, CF_4 and SiF_4 in all cases. Table 1 was constructed from this type of data and from Table 3.

The contents of each trap were separated by GLC (the order of retention time is the same as that of b.p.) and identified by IR[10] (except 1,1,2-trifluoro-ethane whose spectrum is not in the literature; this was identified by NMR; $CH^AF_2{}^BCH_2{}^CF^D$: ^{19}F signals (internal $CFCl_3$, upfield shifts); F^B, 130.9 (int. 2 ddt); F^D, 242.4 (int. 1 ttd); ^1H signals (δ values); H^A, 5.92 (int. 1 ttd); H^C 4.46 (int. 2 dtd): coupling constants (Hz): J_{AB}, 54.5; J_{CD}, 46.2; J_{AC}, 3.5; J_{AD}, 7.0; J_{BC}, 14.0; J_{BD}, 16.6. These values compare closely with those given in the literature[11]).

Fluorination of ethane with cobalt(III) fluoride. This was carried out in the same way as for $KCoF_4$; the results are summarised in Table 3.

Table 3. Fluorination of ethane with $KCoF_4$ and CoF_3

Run no.[a]	temp (°C)	Input (g)	Output (g)	Wt. (g) in Traps 1	2	3	4
1	190	10.7	12.7	2.8	[b]	0.5	9.3
2	420	17.0	38.8	17.0	17.4	0.6	3.8
3	165	13.2	47.0	1.2	3.9	21.8	20.1

[a] 1,2 $KCoF_4$; 3 CoF_3. [b] Trace.

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†This compound is called "X" in Ref. 7*a*. Dr. Nagase has informed us that it is now known to be CH_2FCHF_2.

Table 4. Fluorination of ethene over $KCoF_4$ and CoF_3

Run no.[a]	temp (°C)	Input (g)	Output (g)	Wt. (g) in Traps 1	2	3	4
1	105	10.7	11.6	1.6	-	[b]	10.0
2	200	10.7	23.2	23.0	-	-	0.2
3	300	13.4	35.4	30.5	2.8	1.8	0.3
4	115	10.7	34.7	11.2	12.1	7.0	4.4

[a] 1–3 $KCoF_4$; 4 CoF_3. [b] Trace.

Fluorination of ethene. Ethene was fluorinated over $KCoF_4$ and CoF_3 in the same way as ethane; the results are summarised in Table 4.

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