Fluorination of propane and propene over cobalt(III) trifluoride and potassium tetrafluorocobaltate(III)

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Fluorination of propane and propene over cobalt(III) fluoride and potassium tetrafluorocobaltate(III) gave complex mixtures of products which have been identified to the 0.5% level. The reactions are valueless for preparative purposes. The mechanism of the fluorinations is not a simple F-for-H replacement, but requires an initial conversion of propane into propene followed by carbocation- and radical-mediated reactions: the carbocations can be quenched by fluoride ions, rearrange and eliminate, and the radicals can be oxidised to carbocations or quenched by fluorine atoms. Radical quenching tends to predominate late in the fluorination and carbocation reactions at the beginning.

Recent work by us[1,2] has shown that skeletal rearrangements, *e.g.* hexane to the 2- and 3-methylpentane, the 2,2- and 2,3-dimethylbutane and the methylcyclopentane skeletons, occur during fluorination over cobalt(III) trifluoride. These appeared to be carbocation rearrangements, but they did not proceed to completion, since thermodynamic equilibria were not achieved between either the hydrocarbons or the carbocations: it was suggested that this was because carbocation formation occurred only early in the fluorinations. We have also reported the fluorinations of ethane,[3] ethene,[3] butane[4] and 2-methylpropane[5] over $\mathrm{Co^{III}}$ species, where multi-component mixtures of polyfluoroalkanes were obtained, and attempted to model mathematically[4] the pathways taken by the multi-step reactions: the model was only partially successful.

We now report on the fluorination reactions named in the title, with the hope of understanding the role of carbocations better, reviewing the model, and hence getting closer to the details of the mechanisms of fluorination of aliphatic substrates over high valency transition metal fluorides. The mechanisms of the fluorination reactions of aromatic substrates are already relatively well established.[6]

Table 1 ^{19}F Chemical shift and coupling constant ranges in polyfluoro-propanes and -butanes[a]

Group	Shift range[b]	Group	Shift range[b]
$\mathrm{C}\mathit{F}_3$–CF_2	80.8–83.9	$\mathrm{C}\mathit{F}_2\mathrm{H}$–$\mathrm{CF}_2$	134.2–144.2
$\mathrm{C}\mathit{F}_3$–CFH	74.9–81.0	$\mathrm{C}\mathit{F}_2\mathrm{H}$–$\mathrm{CFH}$	130.6–134.1
$\mathrm{C}\mathit{F}_3$–CH_2	61.6–66.8	$\mathrm{C}\mathit{F}_2\mathrm{H}$–$\mathrm{CH}_2$	114.5–118.9
$\mathrm{C}\mathit{F}\mathrm{H}_2$–$\mathrm{CF}_2$	234.1–244.2	–CF_2–	103.1–135.3[c,d]
$\mathrm{C}\mathit{F}\mathrm{H}_2$–$\mathrm{CFH}$	230.9–239.6	–CFH–	184.0–220.5[e,d]
$\mathrm{C}\mathit{F}\mathrm{H}_2$–$\mathrm{CH}_2$	218.6–223.9		
System	**Coupling range/Hz[f]**	**System**	**Coupling range/Hz[f]**
$\mathrm{CF_2H}$ (*gem*)	51.0–56.5	$\mathrm{C}\mathit{F}_2\mathrm{H}$–$\mathrm{C}\mathit{F}_2$	< 4–5.7
$\mathrm{CFH_2}$ (*gem*)	45.0–48.5	$\mathrm{C}\mathit{F}_2\mathrm{H}$–$\mathrm{C}\mathit{F}\mathrm{H}$	8.0–13.3
CFH (*gem*)	44.3–50.6	$\mathrm{C}\mathit{F}_2\mathrm{H}$–$\mathrm{CF}\mathit{H}$	8.5–12.6
$\mathrm{CF_3}$–$\mathrm{CF_2}$	~ 0	$\mathrm{C}\mathit{F}_2\mathrm{H}$–$\mathrm{C}\mathit{H}_2$	14.4–16.3
$\mathrm{C}\mathit{F}_3$–$\mathrm{C}\mathit{F}\mathrm{H}$	9.9–11.1	$\mathrm{C}\mathit{F}_2\mathrm{H}$–C–$\mathrm{C}\mathit{F}$	1.2–10.2
$\mathrm{C}\mathit{F}_3$–$\mathrm{CF}\mathit{H}$	5.5–6.5	$\mathrm{C}\mathit{F}\mathrm{H}_2$–$\mathrm{C}\mathit{F}_2$	13.2–15.3
$\mathrm{CF_3}$–$\mathrm{CH_2}$	9.1–10.7	$\mathrm{C}\mathit{F}\mathrm{H}_2$–$\mathrm{C}\mathit{F}\mathrm{H}$	20.4–24.9[g]
$\mathrm{CF_3}$–C–CF	6.2–11.1	$\mathrm{C}\mathit{F}\mathrm{H}_2$–$\mathrm{CF}\mathit{H}$	11.3–15.8[g]
$\mathrm{CH_3}$–$\mathrm{CF_2}$	17.8–19.5	$\mathrm{C}\mathit{F}\mathrm{H}_2$–$\mathrm{C}\mathit{H}_2$	23.5–26.1
$\mathrm{C}\mathit{H}_3$–$\mathrm{C}\mathit{F}\mathrm{H}$	23.3–24.4	$\mathrm{C}\mathit{H}_2\mathrm{F}$–$\mathrm{C}\mathit{F}$	2.0–13.0[g]
$\mathrm{C}\mathit{H}_3$–$\mathrm{CF}\mathit{H}$	6.2–6.3	$\mathrm{C}\mathit{H}_2\mathrm{F}$–$\mathrm{C}\mathit{H}_2$	6.0
$\mathrm{CH_3}$–C–CF	0–2.9	$\mathrm{C}\mathit{H}\mathrm{F}_2$–$\mathrm{C}\mathit{F}$	2.8–12.1
		$\mathrm{C}\mathit{H}\mathrm{F}_2$–$\mathrm{C}\mathit{H}$	3.6–6.0 ·

[a] See ref. 4 for more figures on polyfluorobutanes; the only figures included in this table are those where the ranges have changed from those given there. [b] In ppm upfield of internal $\mathrm{CFCl_3}$. [c] 84.5 ppm in $\mathrm{CH_3CF_2CH_3}$. [d] Low end of range when there is a large number of vicinal H atoms. [e] 165.2 ppm in $\mathrm{CH_3CHFCH_3}$. [f] Some of these are probably composite values due to the spectra being analysed as first-order and not second. [g] Excluding 1,2-difluoropropane which appears to have anomalous coupling constants (present work and ref. 8).

Results

The fluorination reactions were carried out in the usual way[7] and are summarised later in Table 4. Fractional distillation was not very effective in achieving separations of the components (see Table 5) and nor was preparative gas chromatography; only three compounds have been obtained in a pure state. However, our knowledge[4,5] of the ^{19}F NMR spectra of the type of products likely to be formed is sufficiently well developed that there was no difficulty in identifying all the components of the fluorination mixtures down to the 0.5% level (see Table 3) by examining the ^{19}F NMR spectra of the crude fluorination mixtures and of the distillation fractions (Table 5). The chemical shift ranges established previously are closely followed here, *e.g.* $\mathrm{CF_2H}$ groups adjacent to $\mathrm{CH_2}$ resonate in the range (ppm upfield from $\mathrm{CFCl_3}$) 116.6–118.9 (lit.,[4] 114.5–117.9), those adjacent to CFH at 131.2–132.8 (130.6–134.1) and those adjacent to $\mathrm{CF_2}$ at 135.6–139.3 (134.2–144.2). The same point applies to $\mathrm{CF_3}$, $\mathrm{CF_2}$, CFH and $\mathrm{CFH_2}$ groups; again in some cases the ranges are broadened a little (Table 1). Coupling constants also followed the previous patterns, again with some of the ranges being broadened but not alarmingly so (Table 1). ^{1}H NMR spectra were of little value because of overlapping peaks. NMR parameters of new compounds and of compounds whose ^{19}F NMR parameters have not been recorded before are given in Table 2. Parameters for compounds listed in Table 3 but not in Table 2 agreed closely with those given in the literature.

There were two alkene products, 3-fluoroprop-1-ene and 3,3-difluoroprop-1-ene, and this is uncommon in fluorinations over $\mathrm{CoF_3}$; usually only saturated compounds are obtained from saturated starting materials. Their identity can be in little doubt: the former showed a triplet (J = 46.4 Hz) of doublets (J = 14.2 Hz) at 216.3 ppm (lit.,[9,10] 46.75 and 14.53 Hz, 218.6 ppm) in its ^{19}F NMR spectrum and the latter a doublet of doublets (55.7 and 8.4 Hz) at 113.4 ppm (lit.,[10] 55.9 and 8.63 Hz, no shift given). The fact that the smaller couplings are doublets clearly shows that there is only one NMR active nucleus on the

Table 2 ^{19}F NMR spectral data on polyfluoropropanes[a]

Compound	Compound number[b]	Chemical shifts[c]			Coupling constants/Hz[d]
		1	2	3	
1 2 3					
CFH_2–CFH–CFH_2	111	235.1	200.1	235.1	F1H1, 46.0; F1F2, 24.6 F1H2, 11.6; F1F3, 3.6 F2H2, 50.6; H1F2, 5.8
CFH_2–CF_2–CH_3	120	234.1	103.1		F1H1, 45.6; F1F2, 15.0 F1H3, 2.6; H1F2, 11.2 F2H3, 18.3
CFH_2–CF_2–CFH_2	121	238.6	121.3	238.6	F1H1, 45.8; F1F2, 15.0 F1F3, <0.5; F1H3, 2.7 H1F2, 11.4
CF_2H–CH_2–CF_2H	202	117.3		117.3	F1H1, 55.2; F1H2, 15.6
1,2 3 4					
CF_2H–CFH–CH_3	210	131.7[e]	132.8[e]	194.8	F1H1, 54.7; F2H1, 54.7 F1F3, 11.7; F1H3, 9.0 F1H4, 1; F2F3, 13.3 F2H3, 1.5; H1F3, 12.1 F3H3, 46.6; F3H4, 24.2
1 2 3					
CF_2H–CFH–CFH_2	211	132.2	208.7	239.6	F1H1, 53.3; F1F2, 11.5 F1H2, 8.5; H1F2, 4.5 F2H2, 47.0; F2F3, 24.9 F2H3, 12.0; F3H3, 45.0 H2F3, 11.7
CF_2H–CFH–CF_2H	212	132.7	221.9	132.7	F1H1, 53.7; F1F2, 12.5 F1H2, 9.4; F1F3, 4.5 H1F2, 7.7; F2H2, 45.8
CF_2H–CF_2–CH_3	220	135.6	109.0		F1H1, 53.2; F1F2, 4.5 F2H3, 18.2
CF_2H–CF_2–CFH_2	221	139.3	128.4	244.2	F1H1, 52.4; F1H3, 1.4 H1F2, 4.2; F2H3, 12.0 F2F3, 13.2; F3H3, 45.9
CF_2H–CF_2–CF_2H	222	138.8	135.3	138.8	F1H1, 53.2; F1F2, 4.5 H1F2, 0.5
CF_3–CFH–CH_3	310	81.0	195.1		F1F2, 11.2; F1H2, 5.5 F1H2, 46.7; F2H3, 24.4
CF_3–CFH–CFH_2	311	77.8	208.4	237.5	F1F2, 11.1; F1H2, 5.5 F2H2, 45.4; F2F3, 24.3 F2H3, 13.0; F3H3, 46.3
CF_3–CF_2–CFH_2	321	81.8	127.4	243.1	F1F3, 7.7; F2F3, 15.3 F2H3, 11.7; F3H3, 45.9
CF_2H–CH=CH_2	20=0	113.4			F1H1, 55.7; F1H2, 8.4

[a] The data listed are of either new compounds, or compounds whose ^{19}F NMR spectra have not been fully recorded before. The spectra were run on neat samples or mixtures. [b] See Appendix for an explanation of this numbering–naming system. [c] In ppm upfield from internal $CFCl_3$. [d] The spectra have been analysed as first-order (except for 210) and this may give rise to small errors in some coupling constants. [e] AB sub-spectrum with J_{AB} = 296 Hz.

carbon vicinal to the F, and hence that both compounds must be alkenes.

We have also detected very small amounts of three partially fluorinated 2-methylpropanes: they were identified by comparison of their ^{19}F NMR spectra with those obtained previously.[5] They presumably arose because of the 2-methylpropane impurity in the propane starting material (purchased as 99.3% pure and containing 0.52% 2-methylpropane).

The compounds identified together with their molar percentages are listed in Table 3: these percentages were estimated from the ^{19}F NMR spectra and should not be regarded as highly accurate, although the accuracy suffices for our present purposes. Later in this paper, we will refer to the compounds by the three-digit nomenclature used in the Tables (see Appendix for details).

A point we shall return to later concerns the apparently surprising absence of certain compounds and the presence of others. An explanation that can be rejected at this stage is that some of the missing compounds have very low boiling points and so were lost in the isolation process. However, 2-fluoropropane, which boils at −10.1 °C, has been detected and it has a lower boiling point than any of the other 'missing' compounds; indeed the missing 1,3-difluoropropane boils at 32 °C, making it one of the highest boiling polyfluoropropanes. Volatility might, of course, affect the amount of a particular compound isolated and hence distort the yield figures, but it cannot be an explanation for the absences mentioned. Indeed, 2-fluoropropane was almost undetectable in the reaction product when a water wash was introduced into the work-up process, presumably because it had evaporated.

The fluorination reactions are not of any great value for preparative purposes: the reaction mixture is too complex and single products too difficult to isolate. It might have value for the preparation of 1,1,2,3-tetra-, 1,2,3-tri- and 1,2-di-fluoropropanes, although the last is almost certainly easier to obtain by another method.[8]

Discussion

The mathematical model referred to above[4] was constructed on the basis that fluorinations of aliphatics proceeded by a simple F-for-H replacement and that the likelihood of a particular H being replaced depended on whether it was primary, secondary or tertiary and on how many fluorines were geminal and vicinal to it. The rate of replacement of an H by an F was primary < secondary < tertiary, and it was reduced by the presence of geminal or vicinal fluorines: these factors were given numerical values, which were obtained by trial and error, and

Table 3 Composition of crude fluorination products[a]

Compound no.[b]	Propane					Propene		
	CoF_3			$KCoF_4$		CoF_3	$KCoF_4$	
	150 °C[c]	200[d]	300	250	300	150	250	300
010	8	10	5	6	8	6	8	16
10=0	0	0	0	12	1	0	8	14
110	0	0	0	59	14	0	40	20
111	14	17	0	4	28	20	15	17
120	4	3	2	1	4	2	1	2
121	5	6	7	< 1	3	9	0	1
200	5	3	2	5	9	5	8	6
20=0	2	3	2	1	3	0	3	4
201	4	4	2	0	0	5	0	0
202	1	1	4	1	0	< 1	0	0
210	8	8	5	11	21	1	17	19
211	32	32	4	0	6	40	< 1	1
212	7	5	7	0	2	8	< 1	< 1
220	1	1	6	< 1	1	0	< 1	< 1
221	4	4	10	0	0	2	0	0
222	1	2	8	0	0	0	0	0
301	< 1	< 1	1	0	0	1	0	0
302	< 1	< 1	8	0	0	< 1	0	0
310	< 1	0	1	0	0	0	0	0
311	1	1	7	0	0	1	0	0
312	1	< 1	10	0	0	< 1	0	0
313	< 1	< 1	1	0	0	0	0	0
320	0	0	< 1	0	0	0	0	0
321	< 1	< 1	3	0	0	0	0	0
322	0	0	1	0	0	0	0	0

[a] Mole% calc. from ^{19}F NMR spectra: compounds can be detected down to < 0.5% and often to 0.1%; all figures < 0.5% are recorded as '< 1'. [b] See Appendix for nomenclature. [c] Mean of five fluorinations. [d] Mean of two fluorinations.

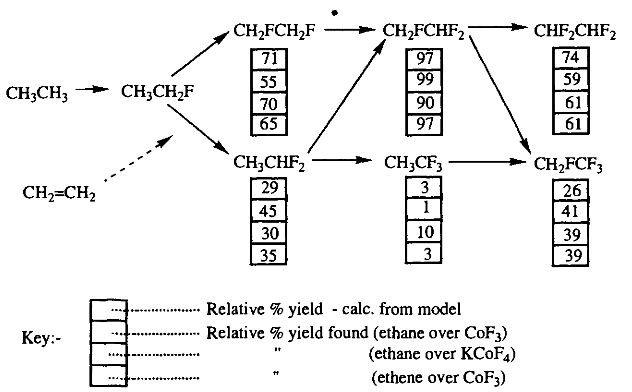


Fig. 1 Calculated[4] and found[3] percentages of products in the fluorination of ethene and ethane. 'Relative % yield' means that the % yields (calc. and found) for each degree of fluorination have been normalised to add up to 100 (*e.g.* at the tetrafluoro level 74 + 26 = 100): this is a feature of the model.

another two parameters, concerned with the probability of release of a fluorinated species from the fluorinating agent, were also introduced. The model was not wholly successful with the fluorination of butane, (some 10–25% of the product could not be rationalised *via* the model) but was better with 2-methylpropane, but again there were anomalies. The lack of success with butane could have come about because it was dehydrogenated to some extent to but-2-ene before the fluorination got underway. The model (minus the two parameters for release of a fluorinated species from the fluorinating reagent, which had very little effect[4]) has now been applied to ethane (Fig. 1) and propane (Fig. 2). As is obvious, it does not work at all well for propane, although it seems just about satisfactory for ethane. It is interesting that the product distributions in the fluorination of ethene and propene fit the model predictions for their saturated counterparts about as well as those compounds themselves. A possibility that has to be considered therefore is whether these fluorinations are proceeding *via* an initial desaturation to propene and ethene, just as butane was suspected to go, at least in part, to but-2-ene.[4]

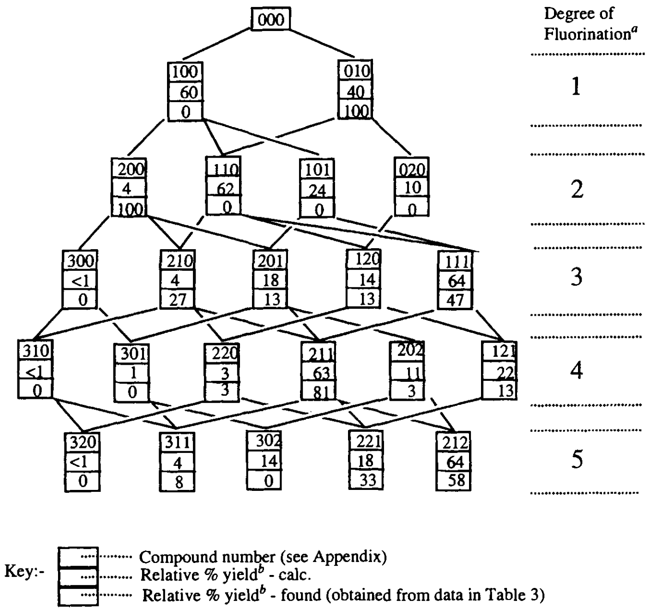


Fig. 2 Possible fluorination pathways and calculated and actual yields from propane over CoF_3 at 150 °C. [a] This has not been carried beyond five fluorines because the amount of product with more than five fluorines is very small and so errors in determining relative % yields are very large. [b] See caption to Fig. 1 for 'relative % yield'.

One feature of the propane fluorination that may have a bearing on the poor fit of the model is the relatively low degree of fluorination of propane (41% of the maximum possible, *i.e.* all the product being C_3F_8) compared with butane (69%).[4] The worst propane agreements (Fig. 2) are at low degrees of fluorination, 1–2 fluorine atoms, whereas there was only one fluorinated butane (2,2,3-trifluorobutane), and that in small amount (< 1%), with a comparable degree of fluorination and that too did not fit the model.[4] It may be that the model would have been just as bad with the butane fluorination had there been significant amounts of products with 1–3 fluorine atoms. Whatever the explanation, it is clear that any model that predicts a 60:40 ratio of 1-fluoropropane to its 2-isomer against an outcome of 0:100 has to be wrong. Furthermore, matters are almost as bad at the two-fluorine level; the only product detected in the cobalt trifluoride fluorination reactions was 1,1-difluoropropane and this was predicted to occur to only 4%. However, the prediction was not as bad with the $KCoF_4$ fluorination reactions; here 1,2-difluoropropane was present as 92% of the difluoro-compounds (predicted 62%) and the 1,1-isomer as 8% (4%), but even so, no 1,3-difluoro-compound was detected although 24% had been predicted.

We have tried to improve the model by a steady-state approach. In this we used the same parameters as before and began with pure propane, allowed it to 'react' to give mono-fluoro-isomers, then repeated the calculation with more propane and with the mono-fluoro-isomers formed in the first iteration being allowed to 'react' to give the difluoro-isomers. We continued this iterative procedure until further iterations made very little difference to the product ratios. This version of the model has the apparent advantage that it provides predictions of the relative amounts of all products and not just amongst those with the same degree of fluorination. However, this approach was no better than the simple model in its predictions of the amounts of mono- and di-fluoro-compounds. We have therefore abandoned the simple F-for-H replacement model for the fluorination of aliphatics: no model which is quite so bad at predicting the mono- and di-fluoro-products can be retained even if it is better, almost certainly fortuitously, at higher levels of fluorination. A tentative, but positive, conclusion that we do draw from our model attempts is that the fluorination of aliphatics does not proceed *via* simple F-for-H replacement and we will now address alternative mechanisms.

It would be unreasonable to attempt to rationalise all the results at this stage of the investigation. We will therefore just discuss some of the more striking features. First, though, some more general comments may be apposite.

In any fluorination of a saturated aliphatic, the first step could be either electron-transfer from the substrate to a high oxidation metal ion, followed by H^+ loss, or H-atom abstraction [reactions (1)–(3)]. The outcome, the formation of

$$RH + Co^{3+} \longrightarrow RH^{+} + Co^{2+} \qquad (1)$$

$$RH^{+} \longrightarrow R^{\cdot} + H^{+} \qquad (2)$$

$$RH + CoF_3 \longrightarrow R^{\cdot} + HF + CoF_2 \qquad (3)$$

$R^{\cdot}$, is the same in each case and so it is not essential to select reactions (1) or (3). It is perhaps pertinent that even if reaction (1) does occur early in fluorination, it would become slower and slower as the degree of fluorination increased because ionisation potentials rise as the degree of fluorination increases (*e.g.*[11] IP C_2H_6 = 11.6 eV; IP C_2F_6 > 14 eV). Reaction (3) might become easier or more difficult as fluorination progresses; α-fluorine atoms seem to strengthen C–H bonds and β-fluorine atoms weaken them, but this trend is not wholly clear.[12] It is therefore conceivable, but not of course certain, that reaction (1) prevails at the beginning of fluorination and reaction (3) at the end and that with weak fluorinating agents, reaction (3) always predominates.

There are two obvious fates for the $R^{\cdot}$ radicals. They could be oxidised or fluorine-atom transfer could occur [reactions (4) and (5)]. If reaction (4) occurs, then typical carbocation

$$R^{\cdot} + Co^{3+} \longrightarrow R^{+} + Co^{2+} \qquad (4)$$

$$R^{\cdot} + CoF_3 \longrightarrow RF + CoF_2 \qquad (5)$$

reactions should be observed: (*i*) quenching with F^- to give RF, (*ii*) rearrangements, both skeletal and H-migrations and (*iii*) loss of H^+. Reaction (*ii*) is known, *e.g.* skeletal rearrangement of any C_6 non-cyclic hydrocarbon occurs on fluorination and mixtures of all or most perfluoro-C_6 compounds are produced.[1] Hydrogen migration has been inferred.[3] Skeletal rearrangements seem only to occur early in fluorination, since bicyclo[2,2,2]octane is fluorinated to give a mixture of skeletally rearranged products, whereas the same bicyclo-structure remained intact when a partially fluorinated compound was further fluorinated.[13] This is quite reasonable: reaction (4) would be expected to become more difficult as the degree of β-fluorination of $R^{\cdot}$ increased (α-fluorination can make the oxidation easier). For example,[11,14] IP $C_2H_5^{\cdot}$ = 8.4 eV; IP $CH_3CF_2^{\cdot}$ = 7.9 eV, but IP $CF_2HCH_2^{\cdot}$ = 9.1 eV. It is not obvious that reaction (5) will be much affected by the degree of fluorination. It is therefore conceivable that reaction (4) will prevail at low degrees of fluorination and reaction (5) at high or with weak fluorinating agents.

The elimination reaction (*iii*) has been observed, albeit under special conditions, during fluorination: cyclohexane was converted into benzene and tetrahydrothiophene into thiophene by cobalt fluoride.[15] Elimination of HF, presumably by the E2 mechanism, is known[16] to occur with $KCoF_4$, but not with CoF_3, when highly fluorinated compounds are further fluorinated.

There is a further reaction to consider: a fluorinating agent might act as a Lewis acid and cause an RF compound to ionise [reaction (6)]. This ought to occur less readily as the degree of

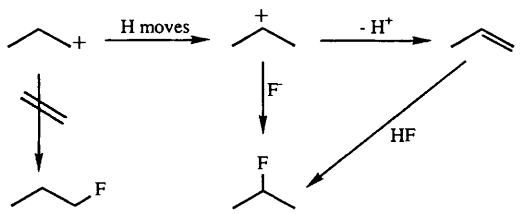
$$RF + CoF_3 \longrightarrow R^{+}CoF_4^{-} \qquad (6)$$

fluorination of $R^{\cdot}$ increases, R^+ becoming less stable, and to a lesser extent with $KCoF_4$ than with CoF_3 because the latter would be expected to be a stronger Lewis acid. Such ionisations have been clearly identified[17] when there was an oxygen α to the fluorine being ionised.

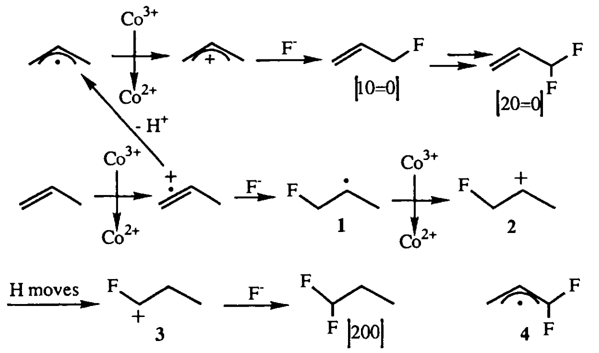
The salient features of the propane–propene fluorinations can now be discussed with reactions (1)–(6) in mind. The points that will be considered will be related to the missing compounds alluded to in the introduction: (*i*) why is 1-fluoropropane missing (<0.5%) from the fluorination products but 2-fluoropropane is present? (*ii*) 1,1-Difluoropropane is present, but its 2,2-isomer is not, and how can the 1,1-compound be present when its apparent precursor, 1-fluoropropane, is missing? (*iii*) 1,3-Difluoropropane is missing, but its 1,2-isomer is present, but only in the $KCoF_4$ fluorinations.

(*i*) There is an obvious rational for the absence of 1-fluoropropane. If carbocations do form early in fluorination, then rearrangement of the 1-cation to the 2-cation could occur before the 1-ion had been quenched by fluoride ion. Propene could form as well (Scheme 1) and addition of HF to it could also give 2-fluoropropane.

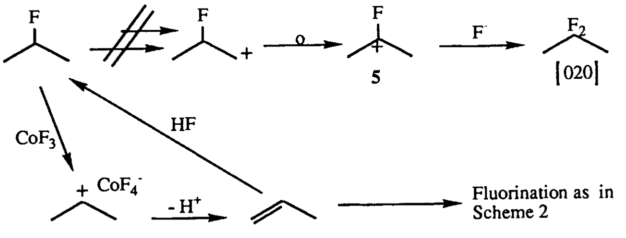
(*ii*) The presence of 1,1-difluoropropane even though its apparent precursor, 1-fluoropropane, is absent can be explained by a similar H-migration. Suppose propene is the starting point (Scheme 2), and that it is oxidised to its radical cation (a sequence beginning with an F-atom transfer can also be formulated, but since the preferred mechanism[6] of aromatic fluorination begins with the oxidation of the aromatic to its radical cation, we prefer to begin here in the same way). This species can then undergo the steps shown to the cation **2**. This would then rearrange to cation **3**, because the difference



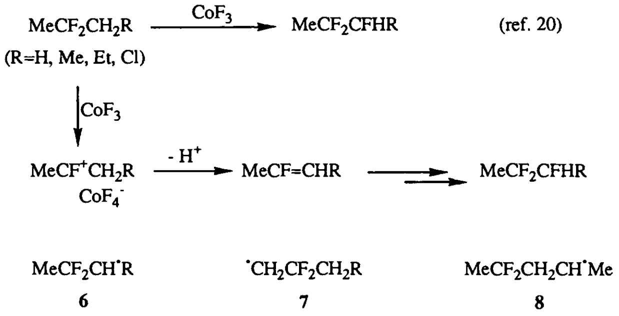
Scheme 1



Scheme 2



Scheme 3



Scheme 4

between the stabilising effect of an α-F on **3** and the destabilising effect of a β-F on **2** could easily be[14] as much as 60 kJ mol^{-1}. This leads naturally to 1,1-difluoropropane without the need for 1-fluoropropane as an intermediate.

The analogue of 1,1-difluoropropane in the butane fluorination[4] would be 2,2-difluorobutane: this was not observed, but its further fluorination product, 2,2,3-trifluorobutane, was, and it was attributed[4] to initial formation of but-2-ene.

The two alkenes identified (10=0 and 20=0) might have formed from allylic species by steps beginning with the loss of H^+ from the radical cation (Scheme 2). 3,3,3-Trifluoroprop-1-ene (30=0) could conceivably form by an extension of the same sequence. The fact that it was not observed could be attributed to the relative difficulty of oxidising 20=0 to its radical cation (expected IP of 20=0 $\approx$ 10.5 eV; IP propene[11] = 9.7 eV).

The absence of 2,2-difluoropropane is rather more difficult to explain. Any cation that forms by H-removal from 2-fluoropropane ought to rearrange to the 2-fluoropropyl ion **5**, as this would be easily the most stable mono-fluoro species, indeed it could well be the most stable cation possible of all the fluorinated and non-fluorinated propyl cations, as fluorine in the α-position probably has a net stabilising effect on a positive charge.[18] If this is so, then 2,2-fluoropropane ought to be present. All we can suggest is that fluorinating agents react with 2-fluoropropane *only* as Lewis acids [reaction (5)], and thus form propene (Scheme 3). If this is the explanation, then it follows that the fluorination of propane proceeds entirely *via* propene. If propene is an intermediate, then the fluorination of propene and propane over transition metal fluorides should give the same product distributions. This is nearly, but not quite, so (Table 3). However, fluorinations with transition metal fluorides are exothermic once initiated. Pure propene would be expected to be initially more reactive than propane, so the exotherm would be greater with it and hence some discrepancies beyond the errors of measurement are inevitable.

Electrochemical results[19] are of interest here, as the *only* difluoropropane isolated from the electrochemical fluorination of propene was the 2,2-isomer. This could have formed as shown in Scheme 2 because the frustrating Lewis acid reaction did not occur as there is no Lewis acid of the type required present in electrochemical fluorination. Japanese workers[20] have shown that the reactions in Scheme 4 occur. Their explanation is based on calculations that show that radicals of type **6** are more stable than those of type **7** or **8**, and since these are likely intermediates in the fluorinations, then the results are understandable. Another explanation arises from our work. The 2,2-difluoro-compounds could undergo Lewis acid reaction, followed by elimination and further fluorination as shown in Scheme 4.

(*iii*) 1,3-Difluoropropane can only arise from 1-fluoropropane, which is not present [point (*i*)]. That 1,2-difluoropropane is present in the $KCoF_4$ fluorinations but not in the CoF_3 can perhaps be rationalised by considering the possible fates of radical **1** (Scheme 2). This radical can either oxidise, as in Scheme 2, or it could be quenched by an F-atom to give 1,2-difluoropropane. The outcome is understandable if CoF_3 only oxidises, but the weaker $KCoF_4$ mainly quenches, but oxidises to some extent (some 200 is formed in $KCoF_4$ fluorinations). It should also be noted, in comparing CoF_3 fluorination reactions with $KCoF_4$, that the latter is a weaker fluorinating agent and hence that products with more than three fluorines are far less evident than with CoF_3 and hence that it is impossible to compare the two reagents except at low degrees of fluorination.

Conclusions

In summary, we suggest that fluorination of saturated aliphatic substrates over transition metal fluorides begins by first forming alkenes, and that this is followed by competing steps involving carbocations (mainly at the beginning of the fluorination) and radical quenching by fluorine atom transfer (mainly later on). Early in the fluorination, typical carbocation reactions, rearrangement, elimination and quenching with F^-, can occur in competition with each other. Carbocation formation can also occur by reaction of alkyl fluorides containing few fluorines with the fluorinating agents then acting as Lewis acids. All these factors also vary relative to one another depending on the fluorinating agent, *e.g.* a powerful agent like CoF_3 is more likely than a weak one, such as $KCoF_4$, to produce carbocations.

Experimental

Fluorinations

These were carried out in an electrically heated tubular nickel reactor (96 × 16 cm) of the type described before.[4,5,7] This was packed with cobalt(III) fluoride (6 kg) or potassium tetrafluorocobaltate(III) (6 kg), which were stirred during the fluorinations. The substrate (propane or propene) was added in a stream of nitrogen (5 dm^3 h^{-1}) over a period of 4–6 h; the nitrogen flow was increased (20 dm^3 h^{-1}) after the addition was complete and the products were collected in a cooled (−40 °C) copper trap followed by a liquid-air cooled trap in cases where unreacted propane was to be recovered. All crude fluorination products were analysed by ^{19}F NMR spectroscopy at this point. The results are summarised in Table 4. Water at 0 °C was then added to the copper trap and the aqueous and organic layers were separated by filtration through a silicone-treated filter paper (Whatman 1PS); this material was used for fractional distillation.

Fractional distillation

Crude fluorination product (262 g from several runs with propane over CoF_3 at 150 °C) was fractionally distilled through a 1.2 m vacuum-jacketed, silvered, Oldershaw column, using a condenser cooled with propanone–solid CO_2. Fractions with bp <20 °C were collected in receivers cooled in liquid air and the remainder in receivers cooled in ice. The results are summarised in Table 5. Hitherto unreported boiling points of polyfluoropropanes are given in Table 6.

Purification of components

(*a*) 1,1,2,3,3-Pentafluoropropane (212). Distillation fraction 5 (Table 5) was re-distilled and a fraction bp 38–41 °C was then separated by GLC (dinonyl phthalate on Chromosorb P, 1 : 5; column 3.5 m × 35 mm diameter; N_2 carrier gas) to give 1,1,2,3,3-pentafluoropropane, bp 40–41 °C (Found: C, 26.1; H, 2.8. $C_3H_3F_5$ requires C, 26.9; H, 2.3%). ^{19}F NMR spectra showed this material to be *ca.* 95% pure with the major impurity being 1,1,3-trifluoropropane (201).

(*b*) 1,1,2,3-Tetrafluoropropane (211). Further distillation of fraction 8 gave 98% pure 1,1,2,3-tetrafluoropropane, bp 55 °C (Found: C, 31.1; H, 3.4. $C_3H_4F_4$ requires C, 31.0; H, 3.5%).

(*c*) 1,2,3-Trifluoropropane (111). The residue remaining after the fractional distillation consisted largely of the title compound, compound 211, and two polyfluoro-2-methylpropanes: it was separated as in (*a*) to give 1,2,3-trifluoropropane, bp 66 °C (Found: C, 36.4; H, 4.8. $C_3H_5F_3$ requires C, 36.7; H, 5.1%). ^{19}F NMR spectra showed this material to be *ca.* 90% pure, with the major impurity being 2-(difluoromethyl)-1,2,3-trifluoropropane (compound **16** of ref. 5).

(*d*) Attempts were made to purify compounds 121, 210, 221 and 311 by GLC of the appropriate distillation fractions: none were successful, all the fractions containing substantial amounts of at least two components.

Table 4 Fluorination of propane and propene over cobalt(III) fluoride and potassium tetrafluorocobaltate(III)

Starting material	Reagent	T/°C	Mass of starting material/g	Mass of product/g	Recovered starting material/g
Propane	CoF_3	150	60	55	20
Propane	CoF_3	200	100	42	20
Propane	CoF_3	300	40	60	0
Propane	$KCoF_4$	250	50	30	*a*
Propane	$KCoF_4$	300	120	90	*a*
Propene	CoF_3	150	60	20	*a*
Propene	$KCoF_4$	250	60	35	*a*
Propene	$KCoF_4$	300	60	45	*a*

[a] Not measured.

Appendix

In this paper we have introduced a new system for naming polyfluoro-organic compounds. The current 'Freon' system becomes rather complex for the types of compounds that are being introduced to replace the chlorofluorocarbons that have been or will be phased out as a result of the Montreal convention which controls the emission of chemicals which damage the ozone layer.

Our proposal merely requires that a fluorohydrocarbon be named by a set of digits, each of which correspond to the number of fluorines on an atom. For example, $CF_2HCF_2CH_3$ is 220 and $CFH_2CFHCH_2CFH_2$ is 1101: in the first case '022' is equally unambiguous, but we prefer to apply the convention that larger numbers come earlier, so 220 is preferred (and 1101 is preferred over 1011 in the second example). We have extended the system to include alkenes by using the '=' symbol to indicate the position of the double bond and hence $CF_3CH{=}CHF$ is 30=1.

The system can also be extended to ethers quite easily by employing the letter 'E' to indicate the position of the oxygen. For example, $CF_3CFHOCF_2H$ becomes 31E2.

We have also devised ways of applying the procedure to fluoro-compounds containing other types of functional group and to chlorofluoro-compounds.

A very similar, but not identical, system has also been devised by Woolf.[21]

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Table 6 Boiling points of new polyfluoropropanes[a]

Compound no.[b]	Bp/°C	Compound no.[b]	Bp/°C	Compound no.[b]	Bp/°C
111	+66	202	+39	211	+55
201	+45	210	+22	220	−4

[a] Estimated from fractional distillation, the temperature at which the compound in question was in a maximum amount (accurate to ± 2 °C). [b] See Appendix for nomenclature system.

Table 5 Fractional distillation of polyfluoropropanes obtained from propane and CoF_3 at 150 °C

Fraction	Mass/g	Boiling range/°C	Compounds in fraction[a]
1	10.5	−3–+4	(010), 200, 20=0, $\underline{220}$, 310, 312, (313), 321
2	9.9	4–17.5	(120), $\underline{200}$, (20=0), 220, 222, 302, (311), $\underline{312}$
3	29.5	17.5–24.5	120, 121, $\underline{210}$, $\underline{221}$, 222, (301), 302, 311, (312)
4	18.2	24.5–32	$\underline{121}$, (202), 210, $\underline{221}$, 301, 311
5	39.6	32–41.5	121, 201, 202, 211, $\underline{212}$, 221
6	30.8	41.5–49	(121), 201, 202, $\underline{211}$, $\underline{212}$
7	65.6	49–54	(201), $\underline{211}$, 212
8	39.9	54–65	111, $\underline{211}$[b]

[a] Underlined compounds are present as >20% of a fraction, and compounds in parentheses in <3%. See Appendix for an explanation of the compound nomenclature system. [b] 2-Difluoromethyl-1,2-difluoropropane, 2-difluoromethyl-1,2,3-trifluoropropane and 1,2,3-trifluoro-2-(fluoromethyl)propane were also present in trace amounts (numbered 14, 16 and 19 in ref. 5).

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