Reactions of Fluoroalkyl Radicals

Part 6.—Addition of Fluoromethyl Radicals to Ethylene

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The addition of fluoromethyl radicals to ethylene in the gas phase has been studied over the temperature range 17-182°C, using the abstraction of a hydrogen atom from hydrogen sulphide as the competing reaction:

 $CH_{2}F+CH_{2}=CH_{2}\xrightarrow{1}CH_{2}FCH_{2}CH_{2}$ $CH_{2}F+H_{2}S\xrightarrow{2}CH_{3}F+HS$

Values of 0.91 ± 0.18 and -1.32 ± 0.29 kcal mole⁻¹ have been determined for log (A_2/A_1) and E_2-E_1 respectively. Fluoromethyl radicals add readily to ethylene, their reactivity being intermediate between those of methyl and trifluoromethyl.

The addition of methyl and trifluoromethyl radicals to ethylene has been studied by several workers ¹⁻⁴; trifluoromethyl radicals react faster by about two orders of magnitude, the principal reason for the difference in reactivity being the much higher activation energy required by the methyl radicals.

In view of this great difference in reactivity it seemed of interest to examine the behaviour of a partly-fluorinated radical. Accordingly we have studied the gas phase addition of monofluoromethyl radicals to ethylene over the temperature range 17-182°C.

EXPERIMENTAL

The source of fluoromethyl radicals chosen was the photolysis of 1,3-difluoroacetone; a competitive technique was used, the addition reaction being measured relative to the hydrogen atom abstraction reaction from H_2S . Optimum conditions for experimental measurements involved the use of $C_2H_4+H_2S$ mixtures of ratio ~10; in this manner complicating side reactions were avoided.

APPARATUS AND PROCEDURE

The reaction cell was a quartz cylinder (volume 159 cm^3) which was housed in a heavy aluminium block furnace, the temperature of which was controlled to better than $\pm 0.1^{\circ}$ C by a Bikini-Fenwall relay unit. The light source was a Mazda 250 W ME/D lamp and a parallel beam arranged to fill the cell. The reaction cell was fitted with a small side-arm (volume 1 cm³); required amounts of the reactants were trapped into the side-arm at -196° C; the side-arm was then warmed to the furnace temperature in a small oil-bath.

The cell was connected to the usual type of high vacuum line comprising cold traps, McLeod gauge and gas burette. After reaction, the contents of the cell were expanded into the analytical line and trapped at liquid-nitrogen temperature. The non-condensable

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products were then normally removed by pumping. Analysis of the fraction mass-spectrometrically, however, showed it to contain mainly carbon monoxide together with small quantities of hydrogen (≤ 5 %). The condensable products which, when C₂H₄+H₂S mixtures were used, comprised almost entirely (>99 %) of methyl fluoride and n-propyl fluoride, were analyzed gas chromatographically, methyl fluoride being measured on a 1.3 m silica gel column at 50°C and n-propyl fluoride on a 3.7 m. 30 % diethyl adipate on 30/60 Chromosorb P column maintained at 0°C. Calibrations were performed at the end of each experiment.

MATERIALS

1,3-Difluoroacetone (Emanuel) contained two lower-boiling impurities, their concentrations being 1 and 0.1 %. Treatment with calcium chloride reduced the first impurity (1-fluoro-2-propanol?) to <0.1 %, the second impurity being unchanged. The ketone was used in this condition.

METHYL FLUORIDE was prepared from the tosylate using the method of Edgell and Parts.⁵ It was distilled at -110° C. n-Propyl fluoride was similarly prepared and vacuum distilled at -85° C. n-Pentyl fluoride (used for chromatographic identification only) was also prepared from the tosylate.

HYDROGEN SULPHIDE was prepared using a Kipp apparatus followed by pumping at -160° C and several vacuum distillations at -100° C.

ETHYLENE (Matheson cylinder) was used with no further purification beyond degassing.

RESULTS AND DISCUSSION

A competitive technique was employed, reaction (1) being measured relative to the abstraction of a hydrogen atom from hydrogen sulphide:

$$CH_{2}F + C_{2}H_{4} \rightarrow CH_{2}FCH_{2}CH_{2}$$

$$CH_{2}F + H_{2}S \rightarrow CH_{3}F + SH.$$

Photolysis of 1,3-difluoroacetone yields fluoromethyl radicals; these may react as follows:

$$CH_{2}F + CH_{2}FCOCH_{2}F \xrightarrow{3} CH_{3}F + CHFCOCH_{2}F$$
$$2CF_{2}H \xrightarrow{4} CH_{2} = CHF + HF$$
$$\xrightarrow{5} \rightarrow CH_{2}FCH_{2}F$$

CH₂FCH₂F, CH₂=CHF and CH₃F were observed, the latter being formed in only small quantities. Since CH₃F by reaction (2) was to be measured, it was necessary to know if reaction (3) contributed substantially to methyl fluoride formation. Accordingly, a known pressure of the ketone was photolyzed alone and also in the presence of a similar pressure of hydrogen sulphide, and the ratio $R_{CH_3F}/R_{(CH_2=CHF+CH_2FCH_2F)}^{\frac{1}{2}}$ measured in each case. When H₂S was present the ratio was 2200 times greater; we therefore conclude that $k_3 \ll k_2$ and that, in our work, methyl fluoride may be considered to arise entirely from reaction (2).

Using Pritchard's data ⁶ for the reaction of fluoromethyl radicals with 1,3diffuoroacetone we get $A_3 \sim 10^{10\cdot4}$ (mole⁻¹ cm³ sec⁻¹) and $E_3 = 8\cdot0$ (kcal mole⁻¹,) so that at 164°C log $k_3 \sim 6\cdot4$. Reasonable parameters for reaction (2) are $A_2 = 10^{11\cdot5}$

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and $E_2 = 3.0$ kcal mole⁻¹, so that log $k_2 = 10.0$ at 164°C and $k_2/k_3 \sim 4 \times 10^3$, which lends further support to the conclusion that only reaction (2) contributes appreciably to methyl fluoride formation.

ADDITION OF CH₂F RADICALS TO ETHYLENE

When fluoromethyl radicals are generated in the presence of ethylene+hydrogen sulphide mixtures a relatively simple reaction is observed. With mixtures of composition $[C_2H_4]/[H_2S] \sim 10$, complete inhibition of CHF==CH₂ and CH₂FCH₂F occurs, no products such as 3-fluoropropene, 1,4-difluorobutane or n-pentyl fluoride are observed, and the condensable reaction products comprise entirely methyl fluoride and n-propyl fluoride.

These observations indicate that (i) fluoromethyl radicals add readily to ethylene, (ii) under our experimental conditions, fluoropropyl radicals react by hydrogen-atom abstraction from hydrogen sulphide rather than by radical-radical auto- and crosscombination or disproportionation, and (iii) fluoropropyl radicals do not react further with ethylene to yield fluoropentyl radicals.

The addition will be discussed in terms of the following reactions together with (1) and (2):

$$CH_{2}FCH_{2}CH_{2} + H_{2}S \xrightarrow{6} CH_{2}FCH_{2}CH_{3} + SH$$

$$CH_{2}FCH_{2}CH_{2} + C_{2}H_{4} \xrightarrow{7} CH_{2}FC_{4}H_{8}$$

$$CH_{2}FC_{4}H_{8} + H_{2}S \xrightarrow{8} CH_{2}FC_{4}H_{9} + SH$$

$$CH_{2}F + CH_{2}FCH_{2}CH_{2} \xrightarrow{9} CH_{2}FCH = CH_{2} + CH_{3}F$$

$$\xrightarrow{10} \rightarrow CH_{2}FCH_{2}CH_{2}CH_{2}F.$$

If reactions (1) and (2) represent the fate of the fluoromethyl radicals and reaction (6) that of the fluoropropyl radicals, then the following relations hold (where R_x refers to the rate of formation of X).

$$R_{\text{CH}_{2}\text{FCH}_{2}\text{CH}_{2}} = k_{1}[\text{CH}_{2}\text{F}][\text{C}_{2}\text{H}_{4}] = R_{\text{CH}_{2}\text{FC}_{2}\text{H}_{5}},$$
$$R_{\text{CF}_{3}\text{H}} = k_{2}[\text{CH}_{2}\text{F}][\text{H}_{2}\text{S}].$$

Hence

$$R_{\rm CF_{3H}}[\rm C_{2}H_{4}]/R_{\rm CH_{2}FC_{2}H_{5}}[\rm H_{2}S] = k_{2}/k_{1}.$$

We have assumed in this treatment that the fluoropropyl radical formed by reaction (1) is stable; it is, however, possible that the energized radical so formed may be unstable and decompose reversibly, i.e.,

$$CH_2FCH_2CH_2 \rightarrow CH_2F + C_2H_4.$$

We examined the possible occurrence of this reaction at 145°C by photolyzing the ketone in the presence of H_2S/C_2H_4 mixtures of constant ratio but with the total pressure being varied over the range 20-160 mm Hg. Our data for k_2/k_1 under these conditions are shown in fig. 1; there is no variation in the rate constant ratio over this pressure range. We therefore conclude that reaction (-1) does not occur under our conditions and that the radical is stable with respect to decomposition.

The possibility exists that some of the fluoropropyl radicals formed may react with the mercaptyl radicals formed in the abstraction reactions. The occurrence of



FIG. 1.—Pressure-dependence of the $[CH_3F]/[C_3H_7F]$ ratio at 145°C; $[C_2H_4]/[H_2S]$ ratio = 10.

a disproportionation reaction such as (11) would not affect the validity of our mass balance relation but a combination reaction such as (12) would lead to an underestimate of the propyl radical yield and produce values for k_2/k_1 which are high:

$$CH_{2}FCH_{2}CH_{2} + SH \xrightarrow{11} CH_{2}FCH_{2}CH_{3} + S$$

$$\stackrel{12}{\rightarrow} CH_{2}FCH_{2}CH_{2}SH$$

In our non-condensable fraction we observed small amounts of H₂ ($R_{H_2} \le 5 \times 10^{-13}$ mole cm⁻³ sec⁻¹); this is attributed to the reaction :

$$2SH \xrightarrow{13} H_2 + S_2.$$

$$^{14} \xrightarrow{14} H_2S_2$$

Published data ⁷ indicate that $k_{13}/k_{14} \sim 0.2$ and $k_{13}+k_{14} \sim 8 \times 10^{12}$ mole⁻¹ cm³ sec⁻¹, so that $k_{13} \sim 1.6 \times 10^{12}$. These figures suggest a steady-state concentration of $\sim 5 \times 10^{-13}$ mole cm⁻³ for the mercaptyl radical in our experiments.

We did not observe n-pentyl fluoride to be formed (i.e., rate of formation $<1\times10^{-14}$ mole cm⁻³ sec⁻¹). If k_7 is assumed to be 10^8 mole⁻¹ cm³ sec⁻¹ then, under our experimental conditions, we find that the steady state concentration of fluoropropyl radicals to be $<1\times10^{-16}$ mole cm⁻³.

A reasonable rate constant for reaction (12) is 10^{13} mole⁻¹ cm³ sec⁻¹, so that $R_{CH_2FCH_2CH_2SH} < 5 \times 10^{-16}$ mole cm⁻³ sec⁻¹. This may be compared with typical values for $R_{CH_2FC_2H_5}$ of $\sim 2 \times 10^{-12}$ mole cm⁻³ sec⁻¹. It is therefore apparent that, at most, only a small proportion of fluoropropyl radicals are lost in this manner. Similar arguments may be used to show that the contribution to the total methyl fluoride yield of reaction (15) is negligible (<0.5 %). We therefore conclude that our mass-balance method is not invalidated by such reactions:

$$CH_2F + SH \rightarrow CH_3F + S.$$

This conclusion is supported by our observation that variation of the $[C_2H_4]/[H_2S]$ ratio from 10 : 1 to 2 : 1 at constant total pressure had no effect on the rate constant ratio.

Our experimental data are shown in table 1, and when treated by the method of least-mean-squares, are expressed by the equation :

$$\log (k_2/k_1) = 0.91 \pm 0.18 + (1320 \pm 290)/2.303 \ RT.$$

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To establish the parameters for reaction (1) we need to know the comparable data for reaction (2); this reaction has not been studied and the problems associated

TABLE	1.—Product	YIELDS	AND	RATIOS	FOR	THE	REACTIONS	OF	CH_2F	RADICALS	WITH
HaS+CaHA MIXTURES											

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<i>T</i> (°K)	t (sec)	[K]	[C ₂ H ₄]	$[C_2H_4]/[H_2S]$	[CH ₃ F]	[C ₃ H ₇ F]	$[CH_3F]/[C_3H_7F]$
290.0	1500	126	222	10.4	1.25	0.218	5.75
292.2	1500	126	220	10.3	1.29	0.178	7.25
313·0	1200	135	217	10.7	2.52	0.462	5.45
329.0	900	145	217	10.3	1.71	0.248	6.88
350-2	600	131	231	10.8	3.04	0.578	5.26
388·0	420	157	222	10.5	1.56	0.462	3.36
413·2	300	147	208	10.9	2.82	0.686	4.11
419 .6	900	143	760	10.1	2.28	0.654	3.49
419·6	120	33.8	209	10.3	0.940	0.208	4.52
419 .6	240	142	332	10.2	0.951	0.403	2.36
419·6	240	137	338	10.2	1.27	0.330	3.86
420.0	60	14.8	109	10.2	0.222	0.068	3.25
420·0	300	148	165	2.05	3.10	0.226	13.7
438·2	180	136	208	10.4	0.993	0.307	3.23
465.1	180	145	224	10.3	1.10	0.316	3.48
10.41	1	A V C II	and T	C componie	tions in	106 - 100 -	ICU El and

K = 1,3-difluoroacetone; K, C_2H_4 and H_2S concentrations in 10⁶ moles; [CH₃F] and [C₃H₇F] in 10⁶ moles.

with the pressure-dependence of the dimerization of fluoropropyl radicals ⁶ renders this difficult. We can therefore compare k_2/k_1 with corresponding rate constant ratios for other radicals, or estimate values for A_2 and E_2 :

$$CH_3 + H_2S \rightarrow CH_4 + SH; \log A_{16} = 11.4, E_{16} = 2.6, \log k (164^\circ) = 10.1$$

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 $CF_3 + H_2S \rightarrow CF_3H + SH$; $\log A_{17} = 11.6, E_{17} = 3.9, \log k (164^\circ) = 9.8.$

Reactions (16) and (17) have similar rate constants^{8,9} and we suggest the following Arrhenius parameters for reaction (2), $\log A_2$ (mole⁻¹ cm³ sec⁻¹) = 11.5, $E_2 \sim 3.0$ kcal mole⁻¹. Using these values, then we find

 $\log A_1$ (mole⁻¹ cm³ sec⁻¹) = 10.6, $E_1 = 4.3$ kcal mole⁻¹, $\log k$ (164°) = 8.45.

COMPARISON OF THE REACTIVITY OF RADICALS

In table 2 we show data for the Arrhenius parameters and velocity constants at 164°C for the addition of various atoms and radicals to ethylene. Fluoromethyl radicals react at a rate intermediate between those of the methyl¹ and trifluoromethyl⁴ radicals; this in accord with the conclusions of Pritchard⁶ regarding the ability of the radical to react by hydrogen-atom abstraction. The substitution of fluorine atoms for hydrogen markedly enhances the reactivity of the radical in reacting by addition, the effect being to reduce the activation energy requirement. If a smooth trend in the activation energy is assumed then it is tempting to predict kinetic data for the reaction of difluoromethyl radicals with ethylene and tentative values of $10^{11\cdot0}$ and $3\cdot3$ kcal mole⁻¹ are suggested for A_{18} and E_{18} respectively:

$$CHF_2 + C_2H_4 \rightarrow CF_2HCH_2CH_2.$$

At 164°C, the reactivities of CH_3 , CH_2F , (CHF_2) and CF_3 are in the ratio 1 : 6 : (50) : 320, so that each fluorine atom increases the radical reactivity by nearly an order of magnitude.

TABLE 2.—ARRHENIUS PARAMETERS AND VELOCITY CONSTANTS AT 164°C FOR ADDITION REACTIONS WITH ETHYLENE

 $R+CH_2 = CH_2 \rightarrow RCH_2CH_2$

R	$\log A$	E	log k (162°)	relative reactivity	ref.
CF ₃	11.4	2.4	10.2	320	4
CH ₂ F	10.6	4.3	8.45	6	this work
CH ₃	11.1	6.8	7.7	1	2
CCl ₃	9.5	3.2	7.9	1.6	10
Н	13.4	3.3	11.7	104	11
0		_	10.7-11.8	10 ³ -10 ⁴	12

A and k in mole⁻¹ cm³ sec⁻¹; E in kcal mole⁻¹.

Trichloromethyl radicals are much less reactive ¹⁰ than trifluoromethyl or fluoromethyl radicals although they require only a low activation energy. This is because of the low pre-exponential factor which reflects the steric limitations for such a bulky radical.

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