Free Radical Addition to Olefins. Part XVII.[1] Addition of Fluoroiodomethane to Fluoroethylenes

By **John P. Sloan**, **John M. Tedder**,* and **John C. Walton**, Department of Chemistry, University of St. Andrews, St. Andrews KY16 9ST

Fluoroiodomethane has been photolysed in the gas phase in the presence of ethylene and fluoroethylenes. The main products of these reactions are adducts from the addition of fluoroiodomethyl radicals to the alkene. Experiments using carbon dioxide as an inert diluent or di-t-butyl peroxide as a thermal initiator indicate that excited fluoroiodomethyl radicals are important in the photolytic runs. Only with the two most reactive olefins, ethylene and tetrafluoroethylene, was a chain process sustained at any but the highest temperature. Orientation data and relative rates have been estimated for the addition of fluoromethyl radicals to vinyl fluoride, 1,1-difluoroethylene, and trifluoroethylene at 164°. The relative rate of fluoromethyl radical addition to ethylene and tetrafluoroethylene has been compared over a wide temperature range and the relative Arrhenius parameters [$A_{CF_2=CF_2}/A_{CH_2=CH_2} = 0.76 \pm 0.2$; $E_{CF_2=CF_2} - E_{CH_2=CH_2} = -1.3 \pm 0.3$ kcal mol^{-1}] are compared with similar data for methyl, difluoromethyl, and trifluoromethyl radicals. The activation energy difference shows a continuous decrease from trifluoromethyl to methyl radicals.

THE addition of fluoromethyl radicals, generated from 1,3-difluoroacetone, to ethylene has been studied by Sangster and Thynne.[2] They found fluoromethyl radicals to be intermediate in reactivity between methyl and trifluoromethyl radicals. This is the only investigation of the addition reactions of this radical, although several reports of its combination [3,4] and abstraction [5-7] reactions have appeared.

The preceding paper[1] describes the photolysis of difluoroiodomethane in the presence of fluoro-olefins and evidence was presented to show that the initial photolytic step yielded an electronically excited iodine atom and a thermally excited difluoromethyl radical which added unselectively to an olefin present. With reactive olefins, ethylene, tetrafluoroethylene, and vinyl fluoride, unexcited difluoromethyl radicals formed by iodine transfer were sufficiently reactive to maintain a chain process [reactions (1)—(3) where E = olefin]. With the

$$\mathrm{RI} \longrightarrow \mathrm{R}\cdot^{*} + \mathrm{I}(^{2}P_{\frac{1}{2}}) \qquad (1)$$

$$\mathrm{R}\cdot^{*} + E \longrightarrow \mathrm{R}E\cdot \qquad (2^{*})$$

$$\mathrm{R}E\cdot + \mathrm{RI} \longrightarrow \mathrm{R}E\mathrm{I} + \mathrm{R}\cdot \qquad (3)$$

$$\mathrm{R}\cdot + E \longrightarrow \mathrm{R}E\cdot \qquad (2)$$

other olefins reaction (2), as distinct from reaction (2*), is too slow for a chain reaction to be established at temperatures below 150°. Difluoroiodomethane and difluoromethyl radicals differ substantially from trifluoromethyl iodide and trifluoromethyl radicals; photolysis of trifluoromethyl iodide in the presence of olefins leads to chain reactions even at ambient temperatures.[8] The photolysis of fluoroiodomethane in the presence of olefins would therefore be unlikely to lead to a chain process at low temperatures (<150°) except possibly for the two most reactive olefins. However, by studying the photolysis over a range of temperatures it should be possible to detect when a chain process had been established and so obtain relative rates and orientation ratios for fluoromethyl radicals at those temperatures.

RESULTS AND DISCUSSION

Photolysis of fluoroiodomethane, as expected, gave fluoromethyl radicals, and in the presence of a fluoroethylene the major products were the adducts which were identified as described in the Experimental section. Ethylene was chosen as the standard alkene and for each fluoroethylene in turn a series of runs was carried out in which the rates of formation of the adducts were measured relative to that of the ethylene adduct and are shown in Tables 1—6.

TABLE 1

Fluoroiodomethane with vinyl fluoride and ethylene. Relative rates of formation of products

$[CH_2FI]_i = 2.0 \times 10^{-3}$, $[CHF{=}CH_2]_i = 0.67 \times 10^{-3}$, $[CH_2{=}CH_2]_i = 0.33 \times 10^{-3}$M

T/°C	t/h	CH_2FCH_2CHFI	$CH_2FCHFCH_2I$	$CH_2FCH_2CH_2I$
44	113.5	0.59	0.20	1.00
60	94.0	0.60	0.20	1.00
60	64.9	0.57	0.20	1.00
98	64.8	0.55	0.18	1.00
118	65.5	0.52	0.16	1.00
132	45.3	0.55	0.18	1.00
139	47.0	0.54	0.14	1.00
147	75.4	0.53	0.17	1.00
164	22.7	0.58	0.16	1.00
166	20.7	0.54	0.15	1.00
193	20.3	0.56	0.17	1.00
154	29.0	1.00	0.29	*a*
183	46.0	1.00	0.33	*a*
198	24.0	1.00	0.31	*a*

[a] No ethylene present.

The extent of reaction was small in these runs, amounting to <10% consumption of the minor reactant in each case. A substantial excess of fluoroiodomethane was taken to minimize cross-combination reactions between

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[1] Part XVI, J. P. Sloan, J. M. Tedder, and J. C. Walton, preceding paper.

[2] J. M. Sangster and J. C. J. Thynne, *Trans. Faraday Soc.*, 1969, **65**, 2110.

[3] T. F. Graham, G. O. Pritchard, and M. Venugopalan, *J. Phys. Chem.*, 1964, **68**, 1786.

[4] G. O. Pritchard and R. L. Thomarson, *J. Phys. Chem.*, 1967, **71**, 1674.

[5] M. J. Perona and G. O. Pritchard, *Internat. J. Chem. Kinetics*, 1969, **1**, 509.

[6] J. A. Kerr and D. M. Timlin, *Internat. J. Chem. Kinetics*, 1971, **3**, 69.

[7] J. A. Kerr and D. M. Timlin, *Internat. J. Chem. Kinetics*, 1971, **3**, 1.

[8] J. N. Cape, A. C. Greig, J. M. Tedder, and J. C. Walton, *J.C.S. Faraday I*, 1975, 592.

TABLE 2

Fluoroiodomethane with 1,1-difluoroethylene and ethylene.

(A) Relative rates of formation of products. Photolytic initiation $[CH_2FI]_i = 2.0 \times 10^{-3}$, $[CH_2{=}CF_2]_i = 0.67 \times 10^{-3}$, $[CH_2{=}CH_2]_i = 0.33 \times 10^{-3}$ M

T/°C	t/h	$CH_2FCH_2CF_2I$	$CH_2FCF_2CH_2I$	$CH_2FCH_2CH_2I$
42	116.1	0.50	0.26	1.00
60	80.0	0.46	0.26	1.00
77	77.7	0.38	0.22	1.00
83	70.0	0.29	0.15	1.00
98	41.4	0.27	0.14	1.00
100	39.4	0.26	0.13	1.00
117	29.0	0.23	0.11	1.00
130	23.3	0.20	0.090	1.00
144	22.9	0.18	0.074	1.00
152	21.6	0.20	0.085	1.00
160	24.5	0.16	0.066	1.00
169	21.0	0.17	0.081	1.00
182	21.1	1.00	0.41	*a*

(B) Thermal initiation with di-t-butyl peroxide (0.5×10^{-5}M) * $[CH_2FI]_i = 1.0 \times 10^{-3}$, $[CH_2{=}CF_2] = 0.38 \times 10^{-3}$, $[CH_2{=}CH_2]_i = 0.13 \times 10^{-3}$M

T/°C	t/h	$CH_2FCH_2CF_2I$	$CH_2FCF_2CH_2I$	$CH_2FCH_2CH_2I$
103	90.8	0.057	0.056	1.00
123	39.5	0.049	0.065	1.00
139	20.0	0.052	0.073	1.00
163	6.3	0.078	0.085	1.00
182	3.5	0.116	0.081	1.00

* Considerable amounts of telomers were also observed.

TABLE 3

Fluoroiodomethane with trifluoroethylene and ethylene. Relative rates of formation of products

$[CH_2FI]_i = 2.0 \times 10^{-3}$, $[CHF{=}CF_2]_i = 0.67 \times 10^{-3}$, $[CH_2{=}CH_2]_i = 0.33 \times 10^{-3}$M

T/°C	t/h	$CH_2FCHFCF_2I$	CH_2FCF_2CHFI	$CH_2FCH_2CH_2I$
60	59.0	0.43	0.85	1.00
81	65.6	0.39	0.78	1.00
100	27.3	0.36	0.71	1.00
116	24.0	0.34	0.68	1.00
131	23.1	0.32	0.62	1.00
143	23.1	0.32	0.62	1.00
160	21.6	0.29	0.59	1.00
168	21.7	0.27	0.57	1.00

TABLE 4

Variation of trifluoroethylene concentration.

$[CH_2FI]_i = 2.0 \times 10^{-3}$M; T 100 °C; Ratio $[CHF{=}CF_2]_i : [CH_2{=}CH_2]_i$ maintained at 2.0

$10^3[CHF{=}CF_2]_i$/M	t/h	CH_2FCHF-CF_2I	CH_2FCF_2-$CHFI$	CH_2FCH_2-CH_2I
0.17	64.4	0.30	0.60	1.00
0.33	20.0	0.33	0.63	1.00
0.33 *	27.3	0.36	0.71	1.00
0.67	27.3	0.36	0.71	1.00

* Interpolated from temperature variation series.

TABLE 5

Addition of carbon dioxide.
Relative rates of product formation at 150 °C

$[CH_2FI]_i = 2.0 \times 10^{-3}$, $[CHF{=}CF_2]_i = 0.67 \times 10^{-3}$, $[CH_2{=}CH_2]_i = 0.33 \times 10^{-3}$M

$10^3[CO_2]$/M	t/h	CH_2FCHF-CF_2I	CH_2FCF_2-$CHFI$	CH_2FCH_2-CH_2I
0.0 *		0.30	0.60	1.00
3.0	18.5	0.27	0.53	1.00
6.0	27.0	0.26	0.53	1.00
18.0	60.0	0.22	0.51	1.00

* Interpolated from temperature variation series.

fluoromethyl radicals and adduct radicals and telomerization reactions. Telomerization was significant only in the reactions utilizing tetrafluoroethylene and ethylene from which the major product was the cross-telomer-$CH_2FCF_2CF_2CH_2CH_2I$. The adducts are formed by addition of fluoromethyl radicals to the fluoroethylenes (E) followed by iodine abstraction from the fluoroiodomethane [reactions (4) and (5)]. In competitive

$$CH_2F\cdot + E \longrightarrow CH_2FE\cdot \qquad (4)$$

$$CH_2FE\cdot + CH_2FI \longrightarrow CH_2FEI + CH_2F \qquad (5)$$

experiments this mechanism predicts that the rate of formation of each adduct from an unsymmetrical fluoroethylene should be independent of the absolute concentrations of the olefins, provided the proportion of fluoroethylene to ethylene remains constant. Table 4 confirms this prediction for the trifluoroethylene experiments. Alkenes such as $CH_2FCH{=}CH_2$ (from ethylene) although identified in the high conversion preparative runs were not detectable in the kinetic runs, and no other products attributable to termination reactions were observed. Small amounts of $CHFI_2$ were observed in some of the experiments together with traces of other long retention time products, none of which were present in sufficient quantity for identification. By analogy with the mechanism of CHF_2I addition to alkenes[1] it seems very probable that they are adducts $CHFIEI$ from addition of the $CHFI\cdot$ radical to the alkene E.

TABLE 6

Fluoroiodomethane with tetrafluoroethylene and ethylene. Relative rates of product formation

$[CH_2FI]_i = 2.0 \times 10^{-3}$, $[CF_2{=}CF_2]_i = 0.17 \times 10^{-3}$, $[CH_2{=}CH_2]_i = 0.33 \times 10^{-3}$M

T/°C	t/h	CH_2FCF_2-CF_2I	$CH_2F(CF_2)_2$-$(CH_2)_2I$	CH_2FCH_2-CH_2I
44	49.5	0.59	2.59	1.00
68	43.1	0.47	2.10	1.00
88	28.3	0.48	1.78	1.00
102	19.0	0.58	1.75	1.00
110	22.0	0.52	1.57	1.00
133	24.5	0.51	1.45	1.00
151	22.2	0.62	1.26	1.00
168	18.1	0.44	1.21	1.00
168	5.5	0.76	0.96	1.00

The Tables show that very much longer reaction times were necessary in order to obtain sufficient product for analysis, than was necessary with difluoroiodomethane. Since the extinction coefficients for both compounds are similar (CHF_2I $\varepsilon_{257.5}$ 23.8 ± 0.6; CH_2FI ε_{256} 23.3 ± 0.8 $dm^3\ cm^{-1}\ mol^{-1}$) it is unlikely that the quantum yield is substantially different. The longer reaction times may therefore be attributed to a large extent to the lower reactivity of the fluoromethyl radicals towards the ethylenes present. Table 1 shows almost no difference in the relative rates of attack by fluoromethyl radicals on ethylene and the CH_2-end of vinyl fluoride. However the ratio of the rates of the formation of CH_2FCH_2CHFI and $CH_2FCHFCH_2I$ shows some variation with temperature. Like the results with difluoromethyl radicals with the less reactive olefins, the addition of fluoromethyl radicals appears to become *more* selective as the temperature rises, up to temperatures >140°. Undoubtedly the reason is the same, at the lower temperatures there is no chain reaction and the addition is almost entirely due to excited fluoromethyl radicals formed in the primary process, as the temperature increases so a chain reaction starts and the addition due to thermal radicals becomes more selective.

Examination of Table 2A shows that both the ratios $[CH_2FCH_2CF_2I] : [CH_2FCH_2CH_2I]$ and $[CH_2FCF_2CH_2I] : [CH_2FCH_2CH_2I]$ decrease with temperature at least to temperatures >150°. This again represents an increase in selectivity and is undoubtedly due to the importance of excited radicals at the lower temperatures where a chain reaction is not sustained. There appears to be a maximum in the ratio for attack at each end of difluoroethylene at 144°, *i.e.* $[CH_2FCF_2CH_2I] : [CH_2FCH_2CF_2I]$ so that probably 0.44 represents a reasonable estimate of the orientation ratio at temperatures >150°. Similarly the relative rate of attack on ethylene is *ca.* 11.5—12 times faster than the rate of attack on the CH_2-end of difluoroethylene.

Table 2B provides confirming evidence for the importance of excited fluoromethyl radicals. In these experiments the reaction was initiated by the thermal decomposition of di-t-butyl peroxide [reactions (6)—(9)].

$$[(CH_3)_3CO]_2 \longrightarrow 2CH_3\cdot + 2(CH_3)_2CO \quad (6)$$

$$CH_3\cdot + CH_2FI \longrightarrow CH_3I + CH_2F\cdot \quad (7)$$

$$CH_2F\cdot + E \longrightarrow CH_2FE\cdot \quad (8)$$

$$CH_2FE\cdot + CH_2FI \longrightarrow CH_2FEI + CH_2F\cdot \quad (9)$$

Under these conditions all the fluoromethyl radicals are formed by iodine abstraction and are therefore thermally equilibrated. The method means that there are much higher radical concentrations than in the photolysis experiments, which leads to the formation of telomers and to an increase in the importance of radical–radical reactions. The same adducts were observed as in the photolytic reactions, but additional products, tentatively identified as 2 : 1 and cross-telomers, were also formed. Table 2B nonetheless shows that the ratio $[CH_2FCF_2CH_2I] : [CH_2FCH_2CH_2I]$ increases rapidly with temperature, *i.e.* the reaction becomes less selective, as would be expected in the absence of excited radicals. The fact that this ratio at the highest temperature is more than a factor of two larger than the same ratio in Table 2A is due to the formation of telomers in the peroxide-initiated experiments. This also accounts for the erratic and low values of the ratio of the two adducts to difluoroethylene ($[CH_2FCH_2CF_2I] : [CH_2FCF_2CH_2I]$). The ' normal ' adduct radical ($CH_2FCH_2CF_2\cdot$) takes part in telomerisation with ethylene much more readily than the ' reverse ' adduct radical ($CH_2FCF_2CH_2\cdot$). The variation of the product ratio $[CH_2FCF_2CH_2I] : [CH_2FCH_2CH_2I]$ with temperature in the peroxide initiated experiments corresponds to an activation energy of *ca.* 1.8 ± 0.8 kcal mol^{-1} which is somewhat less than we would expect from the data previously obtained with other radicals. However the scatter of the results is sufficient to make any quantitative deduction impossible.

Table 3 shows the results for trifluoroethylene and again the reaction appears to become more selective as the temperature rises (*cf.* $[CH_2FCHFCF_2I] : [CH_2FCH_2CH_2I]$). This is a result we have previously attributed to excited radicals and the absence of a chain reaction. Table 5 provides very convincing evidence for the participation of excited radicals. In a series of four runs at *ca.* 150° increasing concentrations of carbon dioxide were added and as Table 5 shows this resulted in a small, yet nonetheless unequivocal increase in selectivity due to quenching of the thermally excited fluoromethyl radicals by carbon dioxide. A further test, namely the change of wavelength of the incident light was not possible because the reaction times were already so great that longer wavelengths were impractical, shorter wavelengths led to other primary processes.

The mechanism of the photolytic reactions with fluoroiodomethane is clearly very similar to that of difluoroiodomethane.[1] One significant difference was the extent of adduct formation from CHFI· radicals. These are probably formed when the excited fluoromethyl radicals abstract hydrogen from fluoroiodomethane [reactions (10 and (11)]. The fluorodi-iodomethane

$$CH_2F\cdot^* + CH_2FI \longrightarrow CH_3F + CHFI\cdot \quad (10)$$

$$CHFI\cdot + CH_2FI \longrightarrow CHFI_2 + CH_2F\cdot \quad (11)$$

formed when CHFI· radicals abstract iodine was observed in most of the reactions, but adducts derived from this radical were minor, as described above. The analogous radical $CF_2I\cdot$ derived in the same way from CHF_2I gave rise to considerable quantities of adducts with all the alkenes.[1] The reason for this difference probably lies in the differing reactivities of the CHFI· and $CF_2I\cdot$ radicals in addition reactions with alkenes. The $CF_2I\cdot$ radicals being fully halogenated and hence more electrophilic, almost certainly add much more rapidly than do CHFI· radicals; just as $CF_3\cdot$ radicals [9] add nearly three orders of magnitude more rapidly to ethylene than do $CH_3\cdot$ radicals.[10] The CHFI· radicals therefore add rather more slowly to the alkenes, and since the adducts are non-chain products this is sufficient to push the amount of them formed below the limits of detection.

The adduct ratios obtained from the unsymmetrical fluoroethylenes are compared with the corresponding data for methyl and other fluorine-substituted methyl radicals in Table 7.

The proportion of reaction attributable to excited radicals is quite small at 164° so that the adduct ratios given for $CH_2F\cdot$ radicals are probably close to the rate constant ratio $k_2 : k'_2$ from addition by thermal $CH_2F\cdot$ radicals (where k_2 is the rate constant for addition to the

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[9] J. M. Sangster and J. C. J. Thynne, *J. Phys. Chem.*, 1969, **73**, 2746.

[10] L. Endrenyi and D. J. LeRoy, *J. Phys. Chem.*, 1967, **71**, 1334.

least substituted end of the unsymmetrical olefin and k'_2 is for addition to the reverse end). The fluorine-substituted methyl radicals become appreciably less selective with all three fluoroethylenes as the number of fluorine atoms in the radicals decreases (and hence their electronegativity decreases). This trend supports the contention that polar forces are important in the transition state of radical addition reactions. The significance of these results is more fully discussed elsewhere.[11]

TABLE 7

Adduct ratios (α : β) from the addition of fluorine-substituted methyl radicals to unsymmetrical fluoroethylenes at 164 °C

Radical	α β $CH_2=CHF$	α β $CH_2=CF_2$	α β $CHF=CF_2$	Ref.
$CH_2F\cdot$	1 : 0.30	1 : 0.44	1 : 2.04	This work
$CHF_2\cdot$	1 : 0.20	1 : 0.15	1 : 1.07	1
$CF_3\cdot$	1 : 0.09	1 : 0.03	1 : 0.50	8

The reaction of CH_2FI with tetrafluoroethylene was basically normal in behaviour so that an Arrhenius plot of the relative rate of addition should give $k_2 : k_{2e}$ where k_{2e} is the rate constant for addition of thermally equilibrated fluoromethyl radicals to ethylene. Allowance for the cross-telomer in the tetrafluoroethylene runs was made as described previously.[8] Arrhenius plots are shown for the present results and those of related radicals in the Figure. The line for methyl radicals was obtained by combining the absolute rate data of Sangster and Thynne for methyl plus tetrafluoroethylene [12] with the Arrhenius parameters recommended by Kerr and Parsonage for methyl plus ethylene.[13] The lines for trifluoromethyl and difluoromethyl radicals are previous work from this laboratory.[1,8] The excellent consistency and the coherent progression in the results is a strong argument in favour of their validity. The relative rate constants and Arrhenius parameters calculated by the least squares procedure are given in Table 8.

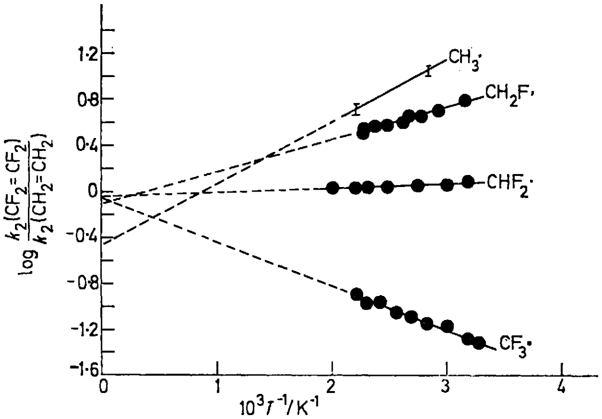
TABLE 8

Arrhenius parameters for the addition of fluorine-substituted methyl radicals to vinyl fluoride and tetrafluoroethylene

	$CF_2=CF_2$			CH_2-end of $CH_2=CHF$			
Radical	k_2/k_{2e} 164 °C	$E_2 - E_{2e}$ */ kcal mol^{-1}	A_2/A_{2e}	k_2/k_{2e} 164 °C	$E_2 - E_{2e}$ */ kcal mol^{-1}	A_2/A_{2e}	Ref.
$CH_3\cdot$	6.0	−2.5	0.34				12, 13
$CH_2F\cdot$	3.4	-1.3 ± 0.3	0.76 ± 0.2	0.28	-0.16 ± 0.3	0.23 ± 0.2	This work
$CHF_2\cdot$	1.1	-0.24 ± 0.12	0.83 ± 0.2	0.32	0.26 ± 0.3	0.45 ± 0.2	1
$CF_3\cdot$	0.12	1.7 ± 0.2	0.87 ± 0.2	0.15	1.2 ± 0.3	0.60 ± 0.1	8

* 1 cal = 4.184 J.

The relative rate of addition to tetrafluoroethylene increases progressively for the series methyl to trifluoromethyl radicals; fluoromethyl and difluoromethyl radicals being intermediate in reactivity. Enthalpy factors are of decisive importance since this trend is determined by the relative activation energies which decrease from methyl to trifluoromethyl radicals. Fully halogenated alkyl radicals, including trifluoromethyl, trichloromethyl, difluorobromomethyl, bromodifluoromethyl, perfluoro-n-propyl, *etc.* all add preferentially to ethylene, whereas methyl, fluoromethyl, and to a lesser extent difluoromethyl, add preferentially to tetrafluoroethylene. This trend in the relative rates and activation energies parallels the change in electronegativity of the radicals, indicating that polar forces in the transition state play the most important role. The trend in the relative rates and activation energies also parallels the change in size and hybridization of the attacking radicals so that steric effects may also make a significant contribution to the changing enthalpy. The A factor ratios for trifluoromethyl, difluoromethyl, and fluoromethyl are all virtually identical; lying slightly below 1.0. Transition state calculations [8] for trifluoromethyl radicals predict an A factor ratio slightly less than 1.0. The main differences in the $\Delta S^‡$ values of the transition states for addition of a radical to ethylene as opposed to tetrafluoroethylene come from the loosening of the double bond in the alkene which generates an internal rotation, and from the CH_2 or CF_2 twisting vibration generated when the radical adds to the alkene. Both these factors are practically independent of the attacking radical, so that transition



Arrhenius plots from the relative rates of addition of fluorine-substituted methyl radicals to tetrafluoroethylene. $CH_3\cdot$ line obtained by combining data of Sangster and Thynne [12] for $CH_3\cdot$ plus $CF_2=CF_2$ with the Arrhenius parameters recommended by Kerr and Parsonage [13] for $CH_3\cdot$ plus $CH_2=CH_2$. $CH_2F\cdot$ line this work. $CHF_2\cdot$ line from ref. 1. $CF_3\cdot$ line from ref. 8

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[11] D. S. Ashton, D. J. Shand, J. M. Tedder, and J. C. Walton, *J.C.S. Perkin II*, 1975, 320.

[12] J. M. Sangster and J. C. J. Thynne, *Internat. J. Chem. Kinetics*, 1969, **1**, 571.

[13] J. A. Kerr and M. J. Parsonage, 'Evaluated Kinetic Data on Gas Phase Addition Reactions,' Butterworths, London, 1972, p. 219.

state theory predicts a constant A factor ratio for all these radicals, provided the transition states occur at approximately the same position on the reaction co-ordinate. The experimental results suggest that this is the case for the fluorine-substituted methyl radicals, but that the transition state for methyl itself, which has a rather lower $A_2 : A_{2e}$ value, must occur somewhat earlier on the reaction co-ordinate. Alternatively the lower A factor ratio for methyl might indicate experimental error, and this reaction is presently being reinvestigated.

The relative rates and activation energies for addition of the three radicals to the CH_2-end of vinyl fluoride compared with CH_2 in ethylene, also shown in Table 8, are all very similar, as would be expected. The activation energies follow the same trend as the tetrafluoroethylene results, though the range is much smaller; and they can be interpreted in the same terms. The A factor ratios are all somewhat less than 1.0. in agreement with predictions of transition state theory.[8]

EXPERIMENTAL

Materials.—Fluoroiodomethane was prepared by the action of mercury(I) fluoride on di-iodomethane at 120° in an atmosphere of nitrogen. Final purification was by preparative g.l.c. giving material of *ca.* 99.4% purity. Commercial di-t-butylperoxide was washed with 10% iron(II) sulphate solution, repeatedly with water, and then distilled under reduced pressure. The fluoroethylenes were obtained commercially and purified by trap to trap distillation.

Procedure.—Materials were handled on a mercury-free vacuum line, the procedure being essentially the same as that described previously.[8] Photolyses were carried out in a cylindrical quartz vessel (140 ml) with light from Hanovia UVS 220 medium pressure mercury arc, using a Pyrex disc as a filter. In the thermally initiated experiments a Pyrex reaction vessel (202 ml) was used. Products were analysed using a Griffin and George D6 gas density balance chromatograph. An 18 ft column consisting of 12 ft of 15% tritolylphosphate plus 6 ft of 24% dinonyl phthalate packed on 60—100 mesh Embacel was utilized, except for the reactions with 1,1-difluoroethylene and trifluoroethylene for which a 12 ft column of 15% tritolylphosphate on 60—100 mesh Embacel was employed. Peak areas were measured with a DuPont 310 curve resolver. Each reaction mixture was analysed about five times and the average values given in the Tables are probably accurate to ±5% except where otherwise stated.

Identification of Products.—Preparative experiments taken to a high percentage consumption of the reactants were used for coupled g.l.c.–m.s. as described previously.[8,†] Products with an asterisk were not detectable in the kinetic experiments.

Ethylene. CH_2FI (2.0×10^{-3}M) and $CH_2{=}CH_2$ (1.0×10^{-3}M) were photolysed with unfiltered light at 172° for 6.7 h. Four products were observed: $CH_2FCH{=}CH_2$*, $CH_2FCH_2CH_2I$, CH_2ICH_2I*, and $CHFI_2$.

Vinyl fluoride. CH_2FI (2.0×10^{-3}) and $CH_2 = CHF$ (1.0×10^{-3}M) were photolysed at 183° for 46 h. Four products were observed: $CH_2FCH{=}CHF$*, CH_2FCH_2CHFI, $CH_2FCHFCH_2I$, and $CHFI_2$.

1,1-*Difluoroethylene.* CH_2FI (2.0×10^{-3}M) was photolysed with $CH_2{=}CF_2$ (0.7×10^{-3}M) at 204° for 16 h using unfiltered light. Four products were observed: $CH_2FCH{=}CF_2$*, $CH_2FCH_2CF_2I$, $CH_2FCF_2CH_2I$, and $CHFI_2$.

Trifluoroethylene with ethylene. CH_2FI (2.0×10^{-3}M) was photolysed with $CHF{=}CF_2$ (0.7×10^{-3}M) and $CH_2{=}CH_2$ (0.3×10^{-3}M) at 220° for 6 h using unfiltered light. Four products were observed: $CH_2FCH{=}CH_2$*, $CH_2FCHFCF_2I$, CH_2FCF_2CHFI, and $CH_2FCH_2CH_2I$.

Tetrafluoroethylene. CH_2FI (2.0×10^{-3}M) and $CF_2{=}CF_2$ (0.8×10^{-3}M) were photolysed at 152° for 25 h. Four products were observed: $CH_2FCF_2CF_2I$, $CH_2F(CF_2CF_2)_2$*I, $CH_2F(CF_2CF_2)_3I$*, and $CH_2F(CF_2CF_2)_4I$*. In reactions containing ethylene an additional product, identified as the cross-telomer $CH_2FCF_2CF_2CH_2CH_2I$, was observed.

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[†] Mass spectral data are given in Supplementary Publication No. SUP 21516 (4 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue. Items less than 10 pp. are supplied as full size copies.