Free Radical Addition to Olefins. Part XVI.† Photolysis of Difluoroiodomethane in the Presence of Olefins

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Difluoroiodomethane has been photolysed in the presence of ethylene and fluoroethylenes. The products include di-iodopropanes formed by the addition of difluoroiodomethyl radicals, as well as mono-iodofluoropropanes formed by the addition of difluoromethyl radicals. The proportions of the various products and the effect of changing concentration and temperature can be rationalised in a reaction scheme in which the primary process leads to thermally excited difluoromethyl radicals [reaction (i)]. The excited difluoromethyl radicals can either add to the

$$\mathrm{CHF_2I\cdot} \xrightarrow[254\ \mathrm{nm}]{h\nu} \mathrm{CHF_2\cdot^*} + \mathrm{I(^2\mathit{P}_{\frac{1}{2}})} \qquad \text{(i)}$$

olefins or abstract hydrogen from the starting difluoroiodomethane [reaction (ii)]. The difluoroiodomethyl radicals

$$\mathrm{CHF_2\cdot^*} + \mathrm{CHF_2I} \longrightarrow \mathrm{CF_2I\cdot} + \mathrm{CH_2F_2} \qquad \text{(ii)}$$

so formed are necessarily thermal and it has been possible to obtain approximate Arrhenius parameters for the relative rates of addition of these radicals to the olefins, although the very small amounts of the adducts limit the precision of the data. The excited difluoromethyl radicals, on the other hand, add rapidly and very unselectively to the olefins. At low temperatures there is no chain reaction with the less reactive olefins and only at the highest temperatures are the chains sufficiently long for addition by thermal as distinct from excited radicals to predominate.

THE photolysis of trifluoromethyl iodide has been much used as a source of trifluoromethyl radicals in both qualitative and quantitative studies.[1-5] No thorough investigation has been made of the primary process, but reactions involving olefins invariably lead to long chain reactions so that interference by excited trifluoromethyl radicals formed in the primary step has never been a problem. On the other hand the primary process of the photolysis of methyl iodide has been the object of a number of studies. These studies show that photolysis by the 253.7 nm mercury line yields electronically excited iodine and thermally excited methyl radicals [reaction (1)].[6] If methyl iodide is photolysed in the

$$\mathrm{CH_3I} \xrightarrow{h\nu\ 254\ \mathrm{nm}} \mathrm{CH_3\cdot^*} + \mathrm{I(^2\mathit{P}_{\frac{1}{2}})} \qquad (1)$$

presence of an alkane (or an olefin) no chain reaction occurs, the abstraction of iodine from methyl iodide by an alkyl radical being a slow process with an appreciable activation energy.[7a] This means that the observed reactions of methyl radicals in such a system are attributable to thermally excited species. In this paper we report a study of the mechanism of the photochemical reaction of difluoroiodomethane with alkenes in the gas phase. It was anticipated that difluoromethyl radicals would behave more like trifluoromethyl radicals than methyl radicals. In the event this expectation was only partially realised, and the aim of obtaining rate parameters for difluoromethyl radicals for direct comparison with those of methyl and trifluoromethyl radicals was to some extent frustrated by the complexity of the system.

EXPERIMENTAL

Materials.—Difluoroiodomethane was prepared by treating iodoform with mercury(I) fluoride under nitrogen; fluorodi-iodomethane was also formed, and was reacted with mercury(I) fluoride in a similar manner to increase the yield.[8] Final purification was achieved by preparative g.l.c. which gave product 99.1% pure. The alkenes were obtained commercially and purified by trap-to-trap distillation.

Apparatus and Procedure.—Materials were handled on a conventional mercury-free vacuum line. Reactions were carried out in a cylindrical Pyrex vessel (202 ml) initiated by light from a Hanovia UVS 220 medium pressure mercury arc. Shorter wavelengths were excluded to avoid other primary process, and longer wavelengths could not be used because of the long reaction times required. Products were analysed using a Griffin and George D6 gas density balance chromatograph utilizing columns consisting of 6 ft of 15% Embaphase silicone oil on silanized Chromosorb G plus 6 ft of 20% silicone oil on Embacel or 3 ft of 15% tritolyl phosphate plus 15 ft of 20% silicone oil on Embacel. Peak areas were measured with a DuPont 310 curve resolver. Each reaction mixture was analysed about six times and the figures quoted in the Tables are the average results which are estimated to be accurate to ±5%.

Identification of Reaction Products.—Special preparative runs were performed in which the extent of reaction was greatly increased by using more alkene and a longer reaction

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† Part XV, D. S. Ashton, D. J. Shand, J. M. Tedder, and J. C. Walton, *J.C.S. Perkin II*, 1975, 320

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[4] S. E. Brasalavsky, F. Casas, and O. Cifuentes, *J. Chem. Soc. (B)*, 1970, 1059.

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

[6] D. Goodeve and C. F. Porret, *Proc. Roy. Soc.*, 1938, **A165**, 31.

[7] (*a*) F. W. Evans and M. Szwarc, *Trans. Faraday Soc.*, 1961, **57**, 1905; (*b*) J. M. Tedder and R. A. Watson, *J. Chem. Soc. (B)*, 1966, 1069.

[8] O. Bretschneider, W. Lachsinger, G. Miltschitsky, and O. Ruff, *Ber.*, 1936, **69B**, 299.

time. This allowed sufficient product to build up for identification by coupled g.l.c.–m.s. using the system described previously.[1,†] Secondary products were also formed in these runs which were not observed in the kinetic experiments and these are indicated by an asterisk. Difluoromethane was a minor product in all runs but it could not be separated from the unchanged olefins.

Ethylene. Four products were observed: CF_2I_2, CH_2ICH_2I*, $CHF_2CH_2CH_2I$, and $CF_2ICH_2CH_2I$.

Vinyl fluoride. CF_2I_2, CHF_2CH_2CHFI, CHF_2CHFCH_2I, CF_2ICH_2CHFI, and $CF_2ICHFCH_2I$ were formed.

1,1-*Difluoroethylene*. CF_2I_2, $CHF_2CH{=}CF_2$*, $CHF_2CH_2CF_2I$, $CHF_2CF_2CH_2I$, $CF_2ICH_2CF_2I$, and $CF_2ICF_2CH_2I$ were formed. This last product was too small for mass spectral analysis but the structure given was strongly indicated by retention time comparisons with other 1,1-difluoroethylene adducts.

Trifluoroethylene. CF_2I_2, CHF_2CHFCF_2I, CHF_2CF_2CHFI, $CF_2ICHFCF_2I$, CF_2ICF_2CHFI (identity assumed on basis of retention time comparisons), $CHF_2CHFCF_2CF_2CHFI$*, and $CHF_2CHFCF_2CHFCF_2I$* were formed.

Tetrafluoroethylene. CF_2I_2, $CHF_2CF_2CF_2I$, $CHF_2(CF_2CF_2)_2I$*, CF_2ICF_2I*, $CHF_2(CF_2CF_2)_3I$*, $CF_2ICF_2CF_2I$, $CF_2ICF_2CF_2CF_2I$*, and $CF_2I(CF_2CF_2)_2I$* were formed. In photolyses with tetrafluoroethylene and ethylene none of the telomers were observed, but cross-telomers $CHF_2CF_2CF_2CH_2CH_2I$, $ICF_2CF_2CH_2CH_2I$*, and $CF_2ICF_2CF_2CH_2CH_2I$ were identified from their mass spectra.

RESULTS

Vinyl Fluoride.—CHF_2I (0.75×10^{-3}m) was photolysed in the presence of vinyl fluoride (0.38×10^{-3}M). Four measurable product peaks were observed: CHF_2CH_2CHFI, CHF_2CHFCH_2I, CF_2ICH_2CHFI, and $CF_2ICHFCH_2I$. Difluorodi-iodomethane was also a product in all the kinetic runs but the yields were not measured because of poor resolution.

Vinyl Fluoride and Ethylene.—CHF_2I (0.75×10^{-3}M) was photolysed in the presence of vinyl fluoride (0.25×10^{-3}M) and ethylene (0.062×10^{-3}M). The products now included $CHF_2CH_2CH_2I$ and $CF_2ICH_2CH_2I$. The peaks corresponding to CHF_2CHFCH_2I and $CF_2ICHFCH_2I$ were small and were not measured.

1,1-*Difluoroethylene and Ethylene*.—CHF_2I (0.75×10^{-3}M) was photolysed in the presence of difluoroethylene (0.25×10^{-3}M) and ethylene (0.062×10^{-3}M).

Trifluoroethylene and Ethylene.—CHF_2I (0.75×10^{-3}M) was photolysed in the presence of $CHF{=}CF_2$ (0.25×10^{-3}M) and ethylene (0.13×10^{-3}M) over a range of temperatures.

Tetrafluoroethylene and Ethylene.—CHF_2I (0.75×10^{-3}M) was photolysed in the presence of tetrafluoroethylene (0.19×10^{-3}M) and ethylene (0.19×10^{-3}). In addition to the expected adducts cross-telomers $CHF_2CF_2CF_2CH_2CH_2I$ and $CF_2ICF_2CF_2CH_2CH_2I$ were detected in appreciable yields.

DISCUSSION

The expected products formed by the addition of difluoromethyl radicals to the fluoroethylenes, followed by iodine abstraction from difluoroiodomethane were present [reactions (2)—(4)]. However, an unexpected

$$\mathrm{CHF_2I} \xrightarrow{h\nu} \mathrm{CHF_2}\cdot + \mathrm{I}\cdot \tag{2}$$

$$\mathrm{CHF_2}\cdot + E \longrightarrow \mathrm{CHF_2}E\cdot \tag{3}$$

$$\mathrm{CHF_2}E\cdot + \mathrm{CHF_2I} \longrightarrow \mathrm{CHF_2}E\mathrm{I} + \mathrm{CHF_2}\cdot \tag{4}$$

(E = fluoroethylene)

feature of the results was the presence of difluorodi-iodomethane and of di-iodofluoropropanes which must be attributed to the addition of difluoroiodomethyl radicals [reactions (5)—(7)].

$$\mathrm{CF_2I}\cdot + \mathrm{CHF_2I} \longrightarrow \mathrm{CF_2I_2} + \mathrm{CHF_2}\cdot \tag{5}$$

$$\mathrm{CF_2I}\cdot + E \longrightarrow \mathrm{CF_2I}E\cdot \tag{6}$$

$$\mathrm{CF_2I}E\cdot + \mathrm{CHF_2I} \longrightarrow \mathrm{CF_2I}E\mathrm{I} + \mathrm{CHF_2}\cdot \tag{7}$$

We have recently reported that the photolysis of bromodichloromethane in the presence of ethylene and vinyl fluoride results in the formation of more adducts from attack by bromodichloromethyl radicals than by dichloromethyl radicals.[9] In other words, in that system hydrogen abstraction from bromodichloromethane proved a more important chain transfer process than bromine abstraction from the same molecule. The adducts formed by addition of difluoroiodomethyl radicals clearly indicate that some similar process is occurring here. However, in that work, propanes ($\mathrm{CHCl_2}E\mathrm{H}$ and $\mathrm{CBrCl_2}E\mathrm{H}$) formed when the initial adduct radicals ($\mathrm{CHCl_2}E\cdot$ and $\mathrm{CBrCl_2}E\cdot$) abstracted hydrogen, represented an appreciable proportion of the products. In the present study the corresponding fluoropropanes ($\mathrm{CHF_2}E\mathrm{H}$ and $\mathrm{CF_2I}E\mathrm{H}$) were not present in appreciable proportions. Furthermore the long reaction times and very small conversion show that the chains were very short so that hydrogen abstraction from difluoroiodomethane by thermal radicals seems unlikely to be a very important process.

The absorption maximum in the near u.v. of difluoroiodomethane occurs at 257 nm (ε 23.8 l mol^{-1} cm^{-1}); the bond strength $D(\mathrm{CHF_2{-}I})$ is unknown, but the corresponding values from trifluoromethyl iodide [$D(\mathrm{CF_3{-}I})$ 54 kcal mol^{-1}] and methyl iodide [$D(\mathrm{CH_3{-}I})$ 56.3 kcal mol^{-1}] suggest that it is unlikely to be <50 kcal mol^{-1} or >60 kcal mol^{-1}. This means that even if the primary process yields an electronically excited iodine atom the difluoromethyl radical will be thermally excited to *ca.* 30 kcal mol^{-1}. We have previously observed that 'hot' methyl radicals formed by the photolysis of methyl iodide abstract hydrogen from methyl iodide at ambient temperatures.[7b] There seems little doubt therefore that the major source of the difluoroiodomethyl radicals is hydrogen abstraction from difluoroiodomethane. We

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† Mass spectral data are given in Supplementary Publication No. SUP 21515 (3 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.

[9] J. C. Gibb, J. M. Tedder, and J. C. Walton, *J.C.S. Perkin II*, 1974, 807.

TABLE 1

Product ratios in photolysis of CHF_2I in the presence of vinyl fluoride

T/°C	t/h	$[CHF_2CH_2CHFI] : [CHF_2CHFCH_2I]$	$[CF_2ICH_2CHFI] : [CF_2ICHFCH_2I]$
47	39.9	2.92	5.88
75	30.6	3.53	5.59
94	21.3	3.92	5.38
120	16.8	4.79	5.66
147	16.3	4.88	4.27
170	5.5	5.01	4.65

TABLE 2

Product ratios in photolysis of CHF_2I in the presence of vinyl fluoride and ethylene

T/°C	t/h	$4[CHF_2CH_2CH_2I] : [CHF_2CH_2CHFI]$	$4[CF_2ICH_2CH_2I] : [CF_2ICH_2CHFI]$
38	24.2	3.09	3.28
39.5	16.4	3.57	3.38
63.5	16.9	3.50	3.17
84	23.9	3.13	2.91
107	16.8	3.06	2.79
133	17.4	2.99	2.76
150	5.2	3.10	2.64
180	3.2	2.96	2.53

TABLE 3

Product ratios in photolysis of CHF_2I in the presence of 1,1-difluoroethylene and ethylene

A

T/°C	t/h	$\frac{[CHF_2CH_2CF_2I]}{[CHF_2CF_2CH_2I]}$	$\frac{4[CHF_2CH_2CH_2I]}{[CHF_2CH_2CF_2I]}$	$\frac{[CF_2ICH_2CF_2I]}{[CF_2ICF_2CH_2I]}$	$\frac{[CF_2ICH_2CH_2I]}{[CF_2ICH_2CF_2I]}$*
35.5	14.5	2.81			35.3
45.5	46.6	2.91	4.38		
64	14.8	3.23			30.0
66	40	3.30	6.16		27.61
93	18.2	4.53	7.59		19.5
100				4.31	21.3
116	6.0	5.62			17.0
130	22.3	4.71	8.62		17.4
132	16.6	4.42	8.08		18.8
144 *	4.4	6.61			15.2
150				3.43	18.3
160	6.0	6.70	9.08		15.5
160	6.1		10.1		15.1
179.5 *	2.6	6.37			14.0
189	4.4	6.36	9.29	3.08	16.2

B Variation of CHF_2I concentration: $[CHF_2I]_i : [CF_2{=}CH_2]_i : [CH_2{=}CH_2]_i$ 12 : 4 : 1 throughout.

T/°C	$10^3[CHF_2I]_i$/M	$\frac{[CHF_2CF_2CH_2I]}{[CHF_2CH_2CF_2I]}$	$\frac{4[CHF_2CH_2CH_2I]}{[CHF_2CH_2CF_2I]}$
98	0.22	0.57	7.99
100	0.38	0.47	7.61
100	1.50	0.34	7.21
150	0.22	0.35	11.6
150	0.38	0.32	10.6
150	1.50	0.23	9.3

* [Ethylene] 0.12×10^{-3}M.

TABLE 4

Product ratios in the photolysis of CHF_2I in the presence of trifluoroethylene and ethylene

T/°C	t/h	$\frac{[CHF_2CHFCF_2I]}{[CHF_2CF_2CHFI]}$	$\frac{2[CHF_2CH_2CH_2I]}{[CHF_2CHFCF_2I]}$	$\frac{[CF_2ICHFCF_2I]}{[CF_2ICF_2CHFI]}$	$\frac{2[CF_2ICH_2CH_2I]}{[CF_2ICHFCF_2I]}$
50	47.20	1.17	2.96		
54.5	9.80	1.24			
66	21.50	1.25	4.10	2.27	12.8
81	5.70	1.21			
92	20.23	1.13	4.70	2.03	8.17
106	12.80	1.15	5.35	2.02	10.36
127	2.00	1.09			
135	5.10	1.10	6.42	1.85	12.03
136	15.52	1.20	4.23	1.58	7.96
162	6.00	1.07	6.51	1.49	9.69
170	2.08	1.04			
217	2.33	0.98	7.42		

must therefore modify reaction (1). The electronic state

$$\mathrm{CHF_2I} \xrightarrow{h\nu} \mathrm{CHF_2}^* + \mathrm{I}(^2P_{\frac{1}{2}}) \qquad (1^*)$$

(* Represents a thermally excited radical)

of the iodine atom is unknown, but we have assumed it to be $^2P_{\frac{1}{2}}$ by analogy with methyl iodide.

TABLE 5

Product ratios in photolysis of CHF_2I in the presence of tetrafluoroethylene and ethylene

T/°C	t/h	$\frac{[CHF_2CF_2CF_2I]}{[CHF_2CH_2CH_2I]}$	$\frac{[CHF_2(CF_2)_2(CH_2)_2I]}{[CHF_2CH_2CH_2I]}$	$\frac{[CF_2ICF_2CF_2I]}{[CF_2ICH_2CH_2I]}$	$\frac{[CF_2I(CF_2)_2(CH_2)_2I]}{[CF_2ICH_2CH_2I]}$
40	21.7	1.11	0.13	0.24	0.36
63	18.6	0.92	0.24	0.19	0.36
93	18.6	0.90	0.24	0.18	0.38
108	16.4			0.33	0.33
132	19.8	0.78	0.33	0.21	0.54
160	5.8	0.79	0.33		
181	3.0	0.75	0.29		
230	1.5	0.70	0.36		

We can now discuss the rate data for the difluoroiodomethyl radicals. These radicals are necessarily thermal and if reaction (7) represents the only fate of the propyl radicals ($CF_2IE\cdot$) then a study of the ratio of the various di-iodopropanes will enable the relative rate constants k_6/k_{6e} (where k_{6e} represents the rate constant when E = ethylene and k_6 represents the rate constant when E = fluoroethylene) to be calculated. The relevant data are shown in Table 6 together with the corresponding data for bromodifluoromethyl radicals.

In practice Table 6 probably suggests that the data for the difluoroiodomethyl radicals is better than it really is. The orientation ratios for attack at each end of the same unsymmetric olefin do not compare so well with previous data. Nonetheless the results clearly show that the difluoroiodomethyl radicals behave analogously to the other halogenomethyl radicals already studied.

TABLE 6

Relative Arrhenius parameters for the addition of difluoroiodomethyl and difluorobromomethyl radicals to ethylene and fluoroethylenes

	$CF_2I\cdot$ Radicals			$CF_2Br\cdot$ Radicals [a]		
Olefin	k (rel.) at 164°	$\log A_6 - \log A_{CH_2=CH_2}$	$E_6 - E_{CH_2=CH_2}$/kcal mol^{-1}	k (rel.) at 164°	$\log A - \log A_{CH_2=CH_2}$	$E - E_{CH_2=CH_2}$/kcal mol^{-1}
*CH_2=CH_2	1.0	0.00	0.00	1.0	0.00	0.00
*CH_2=CHF	0.38	-0.14 ± 0.01	0.55 ± 0.09	0.39	-0.21 ± 0.04	0.40 ± 0.15
*CH_2=CF_2	0.13	-0.05 ± 0.04	1.65 ± 0.41	0.14	0.03 ± 0.03	1.80 ± 0.40
*CHF=CH_2	0.08	-0.49 ± 0.06	1.19 ± 0.68	0.04	-0.61 ± 0.12	1.64 ± 0.45
*CHF=CF_2	0.10	-0.69 ± 0.17	0.55 ± 2.01	0.08	-0.99 ± 0.20	0.22 ± 0.50
*CF_2=CH_2	0.02	-0.19 ± 0.06	3.02 ± 0.69	0.004	-0.14 ± 0.04	4.43 ± 0.57
*CF_2=CFH	0.06	-0.25 ± 0.22	1.83 ± 2.65	0.05	-0.34 ± 0.08	2.00 ± 0.70
*CF_2=CF_2	0.76	0.40 ± 0.06	1.01 ± 0.73	0.13	1.05 ± 0.10	3.90 ± 0.80

* Represents site of attack. 1 cal = 4.184 J.

[a] J. M. Tedder and J. C. Walton, *J.C.S. Faraday I*, 1974, 308.

When we come to consider the results for the addition of difluoromethyl radicals to the fluoro-olefins, Tables 1—5 show a very different situation. The rate of addition to the CHF-end of vinyl fluoride, and to either end of difluoroethylene or trifluoroethylene appears to *decrease* compared with the rate of addition to ethylene as the temperature increases. In other words attack by difluoromethyl radicals appears to become more selective as the temperature rises. Possible explanations of this abnormal behaviour include (1) reversibility of the addition step; (2) the participation of termination processes particularly those involving disproportionation; (3) removal of products by hydrogen abstraction; and (4) the participation of excited radicals. Explanations (1) and (2) can be discounted since similar phenomena would have occurred with the difluoroiodomethyl radicals which were present in the same system. Although some propenes were formed, they were in small yield. Furthermore if hydrogen abstraction was important some evidence for it would again have been observed in the difluoroiodomethyl radical results. We are left with the conclusion that excited difluoromethyl radicals formed in the primary step are involved. Confirmation of the participation of excited radicals comes from the experiments with 1,1-difluoroethylene in which the total concentrations were varied, the relative concentrations of the reactants remaining constant (Table 3B). The orientation ratio for the addition of difluoromethyl radicals to 1,1-difluoroethylene, $[CHF_2CF_2CH_2I]$: $[CHF_2CH_2CF_2I]$, decreased with increasing concentration, *i.e.* the reaction became more selective. This can be attributed to deactivation of the excited difluoromethyl radicals by collision at the higher concentration. The ratio $[CHF_2CH_2CH_2I]$: $[CHF_2CH_2CF_2I]$ also decreased (*i.e.* became *more* selective) slightly with increasing total concentration of reactants. This apparently contradictory result (it only represents a 10% change) is almost certainly due to hydrogen abstraction from the ethylene adduct ($CHF_2CH_2CH_2I$). The difference between attack on ethylene, tetrafluoroethylene, and the CH_2-end of vinyl fluoride and attack at the other positions is due to the greater reactivity of the former sites. They are sufficiently reactive to sustain a chain process which necessarily involves thermal difluoromethyl radicals. Table 6 clearly shows the greater reactivity of ethylene, tetrafluoroethylene, and the CH_2-end of vinyl fluoride for attack by bromodifluoromethyl and by difluoroiodomethyl radicals. The increase in selectivity at the unreactive sites as the temperature rises is due to increasing involvement of thermal as distinct from excited radicals. At the highest temperatures studied a chain mechanism is near to being established in most cases, and there is some evidence that selectivity decreases at higher temperatures still. It is not possible to make studies at higher temperatures however, because the products start to decompose. In other words the orientation ratios and relative rates at temperature >160° probably represent the correct reactivity of thermal difluoromethyl radicals. Table 7 shows the relative rates of addition at 164° compared with those for difluoroiodomethyl radicals and for the addition of trichloromethyl radicals. The similarity of the $CHF_2\cdot$ rates at 164° with those for $CCl_3\cdot$ and $CF_2Br\cdot$ (see Table 6) strongly suggests that at this temperature the chains are sufficiently long for the contribution by excited radicals to be neglected. If it is assumed the chains are sufficiently long at all temperatures for the reactive sites (*i.e.* ethylene, tetrafluoroethylene, and $=CH_2$ in vinyl fluoride), we obtain relative Arrhenius parameters for the addition of $CHF_2\cdot$ to tetrafluoroethylene [$\log A_{2CF_2=CF_2} - \log A_{2CH2=CH_2} = -0.08 \pm 0.01$ l mol^{-1} s^{-1}; $E_{2CF_2=CF_2} - E_{2CH_2=CH_2} = 0.24 \pm 0.12$ kcal mol^{-1}] and to the CH_2-end of vinyl fluoride [$\log A_{2CH_2=CHF} - \log A_{2CH_2=CH_2} = -004 \pm 0.02$ l mol^{-1} s^{-1}; $E_{2CH_2=CHF} - E_{2OH_2=OH_2} = 0.26 \pm 0.30$ kcal mol^{-1}].

TABLE 7

Relative rates of addition of $CHF_2\cdot$ radicals to fluoro-olefins at 164° compared with $CCl_3\cdot$ and $CF_2I\cdot$ and radicals, taking ethylene as standard

Olefin	$CHF_2\cdot$	$CCl_3\cdot$ [a]	$CF_2I\cdot$
$CH_2=CH_2$	1.00	1.00	1.00
$CH_2=CHF$	0.32	0.56	0.38
$CH_2=CF_2$	0.10	0.25	0.13
$CHF=CH_2$	0.06	0.06	0.08
$CHF=CF_2$	0.15	0.22	0.10
$CF_2=CH_2$	0.015	0.004	0.02
$CF_2=CHF$	0.14	0.07	0.06
$CF_2=CF_2$	1.10	0.89	0.79

[a] H. W. Sidebottom, J. M. Tedder, and J. C. Walton, *Internat. J. Chem. Kinetics*, 1972, **4**, 249.

Compared with data for other radicals these are very reasonable values. The corresponding activation energy differences for $CF_3\cdot$[5] and $CH_3\cdot$[10] radicals with tetrafluoroethylene and ethylene are 1.74 and 2.5 kcal mol^{-1} and the logarithms of the *A*-factor ratios are —0.04 and —0.47 respectively. The significant feature of the addition of difluoromethyl radicals is that they are appreciably less selective than trifluoromethyl radicals, the orientation ratios ($\alpha : \beta$) at 164° being: for $\overset{\alpha}{C}H_2=\overset{\beta}{C}HF$-($CHF_2\cdot$, 1 : 0.20; $CF_3\cdot$, 1 : 0.09); $\overset{\alpha}{C}H_2=\overset{\beta}{C}F_2$ ($CHF_2\cdot$, 1 : 0·15; $CF_3\cdot$, 1 : 0.03) and for $\overset{\alpha}{C}HF=\overset{\beta}{C}F_2$($CHF_2\cdot$, 1 : 1.07; $CF_3\cdot$, 1 : 0.50). This is in accord with the observation that the ratio of attack at the more fluorinated end of unsymmetrical fluoro-olefins increases as the electronegativity of the attacking radical decreases. The present results confirm the significance of polar forces in determining the orientation of radical addition.

[5/769 *Received*, 23*rd April*, 1975]

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