# The Orientation of Free-radical Addition to Olefins

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*Summary* The rate and orientation of addition of heptafluoropropyl radicals to a series of fluoro-olefins in the gas phase has been determined by a competitive method.

THE photochemical addition of heptafluoropropyl iodide to fluoroethylenes has been investigated in the gas phase using the experimental method described previously.[1] Accurate measurements of $C_6F_{14}$ could not be made so the results in Table 1 are competitive and have been put on an absolute scale by projecting a rate constant for the addition of $C_3F_7\cdot$ radicals to ethylene from data for other radicals.[2]

TABLE 1

*The addition of heptafluoropropyl radicals to olefins in the gas phase*

log *A* in l mol$^{-1}$ s$^{-1}$ *E* in kcal mol$^{-1}$

| Addition to $CH_2=$ | log *A* | *E* | Addition to $CFH=$ | log *A* | *E* | Addition to $CF_2=$ | log *A* | *E* |
|---|---|---|---|---|---|---|---|---|
| $CH_2=CH_2$ | 7·5[a] | 2·0[a] | $CFH=CH_2$ | 6·9 | 5·4 | $CF_2=CH_2$ | 6·0 | 9·2 |
| $CH_2=CHF$ | 7·1 | 3·1 | | | | $CF_2=CFH$ | 7·8 | 5·8 |
| $CH_2=CF_2$ | 7·2 | 3·9 | $CFH=CF_2$ | 7·8 | 4·1 | | | |

[a] Projected figures (others relative to this).

The very striking feature of these results is their similarity to our previous data for trichloromethyl radicals.[3,4] There is a marked decrease in rate for addition to $CFH=$ compared with addition to $CH_2=$, and a still greater decrease in rate for addition to $CF_2=$. It can be seen again that substituents on the carbon atom to which the radical becomes attached have a very big effect on the activation energy, whereas substituents on the carbon atom, where the odd electron is located in the initial adduct, only have a second-order influence.

Some measure of this second-order influence can be obtained from the now greatly extended data for the addition of trichloromethyl radicals to the $CH_2=$ end of some substituted ethylenes (Table 2). For the first six olefins the substituent has virtually no effect on the rate of addition. Only with 1,1-difluoroethylene and 3,3,3-trifluoropropene does there appear to be appreciable retardation. It seems probable that this is largely a polar effect influencing attack by the electrophilic trichloromethyl radical. The best interpretation of these results so far comes from the use of localisation energies calculated from extended Hückel theory with an additional parameter to allow for the electrophilic nature of the radical.[5]

TABLE 2

*Rate data for the addition of trichloromethyl radicals to the* $CH_2=$ *end of same unsymmetric olefins*

log *A* in l mol$^{-1}$ s$^{-1}$ *E* in kcal mol$^{-1}$

| Olefin | log *A* | *E* | Reference |
|---|---|---|---|
| $CH_2=CH_2$ | 6·5 | 3·2 | 3,4 |
| $CH_2=CHCl$ | 7·0 | 3·4 | |
| $CH_2=CHF$ | 6·4 | 3·3 | 3,4 |
| $CH_2=CHCN$ | 7·2 | 3·3 | this work |
| $CH_2=CHCH_3$ | 7·2 | 3·4 | 5 |
| $CH_2=CFCH_3$ | 6·8 | 3·2 | 5 |
| $CH_2=CF_2$ | 6·7 | 4·6 | 3,4 |
| $CH_2=CHCF_3$ | 7·4 | 4·8 | this work |

*(Received, June 8th,* 1970; *Com.* 886.)

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[3] J. M. Tedder and J. C. Walton, *Proc. Chem. Soc.*, 1964, 420.
[4] J. M. Tedder and J. C. Walton, *Trans. Faraday Soc.*, 1967, **63**, 2678.
[5] J. M. Tedder and J. C. Walton, *Progr. Reaction Kinetics.*, 1967, **4**, 55.