The Effect of Radical Size and Structure on the Orientation of Addition of Perfluoroalkyl Radicals to Fluoro-alkenes

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Summary The orientation of the addition of $CF_3\cdot$, $C_2F_5\cdot$, n-$C_3F_7\cdot$, n-$C_4F_9\cdot$, n-$C_7F_{15}\cdot$, n-$C_7F_{18}\cdot$, and $(CF_3)_2CF\cdot$ radicals to $CFH{=}CH_2$, $CF_2{=}CH_2$, and $CFH{=}CF_2$ has been determined in the gas phase.

The photochemical addition of trifluoromethyl iodide to olefins was first demonstrated by Banus, Emeléus, and Haszeldine.[1] This reaction was subsequently used to study directive effects in free radical addition.[2] These studies were largely carried out before coupled g.c./m.s. was available but nonetheless the orientation of the addition of trifluoromethyl radicals to a wide variety of olefins was established. We have used this technique to study the orientation and to determine the Arrhenius parameters for the addition of perfluoropropyl radicals to unsymmetric fluoroalkenes in the gas phase.[3] We report here the

TABLE. *Relative rates of addition of perfluoroalkyl radicals to unsymmetrical alkenes at* 150°

Radical	CH_2CHF	$CH_2{=}CF_2$	$CHF{=}CF_2$
$CF_3\cdot$	1:0·094 ± 0·006	1:0·032 ± 0·004	1:0·42 ± 0·01
$CF_3CF_2\cdot$	1:0·054 ± 0·001	1:0·011 ± 0·001	1:0·29 ± 0·02
$CF_3CF_2CF_2\cdot$[3]	1:0·050 ± 0·003	1:0·009 ± 0·0005	1:0·25 ± 0·01
$CF_3(CF_2)_2CF_2\cdot$	1:0·050 ± 0·001	1:0·0071 ± 0·0009	1:0·24 ± 0·01
$CF_3(CF_2)_5CF_2\cdot$	1:0·049 ± 0·004	1:0·0066 ± 0·0006	1:0·23 ± 0·02
$CF_3(CF_2)_6CF_2\cdot$	1:0·043 ± 0·003	1:0·0060 ± 0·0004	1:0·22 ± 0·01
$(CF_3)_2CF\cdot$	1:0·020 ± 0·001	1:0·0010 ± 0·0005	1:0·062 ± 0·01

orientation determined for the addition of a complete series of fluoroalkyl radicals to vinyl fluoride, vinylidene fluoride, and trifluoroethylene also in the gas phase. The electronic characteristics of perfluoroethyl, n-propyl, n-butyl, n-heptyl, and n-octyl radicals are almost identical. Any change in the orientation in going along the series must therefore be attributed largely to steric effects.

The perfluoroalkyl radicals were generated in the gas phase in the presence of the appropriate alkene by photolysis of the corresponding perfluoroalkyl iodide. The products of the reactions were identified by coupled g.c./m.s. and quantitatively analysed by gas chromatography.

Four products were identified from the reaction of each perfluoroalkyl iodide with each olefin: iodine, the radical dimer, and the two adducts formed by addition of the radical to each of the olefin. For example with 1,1-difluoroethylene the adducts are formed as shown in reactions (2), (2′), (3), and (3′).

$$R_F\cdot + CH_2 = CF_2 \longrightarrow R_FCH_2CF_2\cdot \qquad (2)$$

$$\searrow R_FCF_2CH_2\cdot \qquad (2')$$

$$R_FCH_2CF_2\cdot + R_FI \longrightarrow R_FCH_2CF_2I + R_F\cdot \qquad (3)$$

$$F_FCF_2CH_2\cdot + R_FI \longrightarrow R_FCF_2CH_2I + R_F\cdot \qquad (3')$$

With this particular alkene the amount of 'reverse' adduct $R_FCF_2CH_2I$ formed was extremely small, and in order to analyse it the extent of reaction had to be increased, leading to a build up of 'normal' adduct in the system. Under these conditions two minor additional products were observed, $R_FCH{=}CF_2$ and $R_FCH_2CF_2H$. Traces of the analogous products were also observed in the reactions with vinyl fluoride.

The adduct ratios are shown in the Table for the gas phase reactions at 150°. The adduct ratios from 1,1-difluoroethylene have been corrected by including $R_FCH{=}CF_2$ and $R_FCH_2CF_2H$ which are also derived from the radical $R_F\,CH_2CF_2\cdot$ so that the figures in the Table represent the relative rates of addition of the radical to the two ends of the alkene.

The present results for trifluoromethyl radicals with vinyl fluoride and trifluoroethylene are in excellent agreement with those obtained in the liquid phase by Haszeldine and his co-workers.[1,2] For the radicals $CF_3\cdot$, $CF_3CF_2\cdot$, and $(CF_3)_2CF\cdot$ a substantial increase in selectivity is observed. This could be attributed to a change in the polar character of the radicals, but the decrease in electrophilic character of the perfluoroisopropyl radical might be expected to reduce its selectivity whereas the Table shows it to be the most selective of the radicals studied. In the linear series $C_2F_5\cdot$, n-$C_3F_7\cdot$, n-$C_4F_9\cdot$, n-$C_7F_{15}\cdot$, and n-$C_8F_{17}\cdot$ the change in orientation is very small but nonetheless quite significant. Since these effects cannot be due to electronic factors, the size of the radical chain appears to be important in the transition state, *i.e.* the actual size and shape of an attacking radical as well as its relative electronic properties can have an effect on the course of the reaction. It is perhaps relevant that Watkins and O'Deen found the relative rates of addition of hydrocarbon n-alkyl radicals to ethylene to decrease with increasing chain length.[4]

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