Effect of Lone-pair Repulsion on the Reactivity and Selectivity of Fluoroalkyl Radicals

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Summary The relative rates of addition of trifluoromethyl, pentafluoroethyl, heptafluoroisopropyl, and nonafluoro-t-butyl radicals to ethylene and vinyl fluoride show that these radicals become increasingly selective as they become branched and there is a direct correlation between the logarithm of orientation of addition to vinyl fluoride of each radical and the pK_a's of the corresponding perfluoroalkyl hydrides [CF_3H, CF_3CF_2H, $(CF_3)_2CFH$, and $(CF_3)_3CH$]; these observations suggest that repulsion between the lone pair electrons on an α-fluorine atom and the unpaired electron on the trivalent carbon atom plays an important part in determining the reactivity of these radicals.

WE have recently reported Arrhenius parameters for the addition of perfluoroisopropyl radicals to ethylene and fluoroethylenes.[1] The results suggested that steric compression is important in determining the rate and orientation of radical addition to olefins. We have now extended our studies to perfluoroethyl and perfluoro-t-butyl radicals. In both cases the appropriate perfluoroalkyl iodide was photolysed to yield the corresponding radicals, and the relative rates were determined by product analysis.

In the Table we compare the new data with the recent data for perfluoroisopropyl radicals[1] together with earlier data for trifluoromethyl radicals.[2] The Table shows that the orientation ratio for addition to vinyl fluoride changes by a factor of twenty going from trifluoromethyl to perfluoro-t-butyl radicals, with the other two radicals showing intermediate selectivity. At the same time the rate of addition to the CH_2 end of the vinyl fluoride relative to ethylene remains almost constant throughout the series. This observation confirms our general conclusion that a substituent attached to a double bond has a large effect on the rate of radical addition to the carbon atom to which it is attached but only a secondary effect on the rate of addition at the other olefinic carbon atom.[3] Since we would expect the three α-fluorine atoms in the trifluoromethyl radical to exert a similar inductive withdrawal to the three trifluoromethyl groups in the perfluoro-t-butyl radicals, we at first assumed the enhanced selectivity must be due to steric compression in the transition state. This supposition appeared to be confirmed by Hammet σ-values for the CF_3–, CF_3CF_2–, and $(CF_3)_2CF$–groups, which are similar [unfortunately no data are available for the $(CF_3)_3C$–groups].[4] However, in 1964 Andreades determined the acid dissociation constants of the corresponding perfluoroalkyl hydrides [including $(CF_3)_3CH$] and found they increased by ten orders of magnitude from fluoroform to perfluoro-t-butyl hydride.[5] These data have been re-evaluated by Holtz who has shown that the pK_a's determined by Andreades correlate with the sum of the Taft σ* constants (p$K_a \alpha \Sigma\sigma^*$).[6] The Figure shows the logarithm of the orientation ratio for the addition of each perfluoroalkyl radical to vinyl fluoride, plotted against the pK_a values determined by Andreades. Since Holtz has shown there is a linear relation between the pK_a's and the Taft inductive parameters, the orientation ratio also has a direct correlation with the inductive parameters. Holtz suggests that the fluoro-alkyl carbanions with α-fluorine atoms are destablished by *p–p* lone pair repulsion.[7] Since these fluoroalkyl radicals contain one

TABLE. Orientation ratios, relative rate constants at 164 °C and relative Arrhenius parameters for the addition of $CF_3\cdot$, $CF_3CF_2\cdot$, $(CF_3)_2CF\cdot$, and $(CF_3)_3C\cdot$ to vinyl fluoride (ethylene as standard)

$$R_f\cdot + CH_2{=}CH_2 \xrightarrow{k_e} R_fCH_2CH_2\cdot$$
$$R_f\cdot + CH_2{=}CHF \xrightarrow{k} R_fCH_2CHF\cdot$$
$$R_f\cdot + CHF{=}CH_2 \xrightarrow{k'} R_fCHFCH_2\cdot$$

	Radicals			
	$CF_3\cdot$[a]	$CF_3CF_2\cdot$[b]	$(CF_3)_2CF\cdot$[c]	$(CF_3)_3C\cdot$[b]
Orientation ratio k'/k	0·12	0·061	0·016	0·0054
$CH_2{=}CFH$ k/k_e[d]	0·48	0·55	0·53	0·48
log A/A_e[d]	−0·07	+0·05	+0·14	+0·17
$E - E_e$[d,e]	0·49	0·62	0·83	0·98
$CFH{=}CH_2$ k'/k_e[d]	0·056	0·034	0·0088	0·0026
log A'/A_e[d]	−0·29	−0·22	−0·28	−0·43
$E' - E_e$[d,e]	1·92	2·51	3·55	4·31

[a] Ref. 2. [b] Present work. [c] Ref. 1. [d] Subscript e = ethylene. [e] E in kcal mol^{-1}.

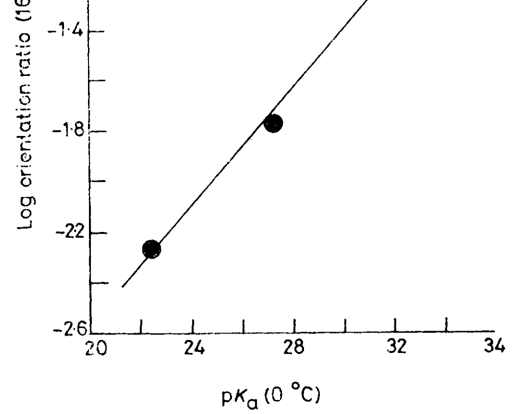

FIGURE. Correlation of log orientation ratio of perfluoroalkyl radicals with the pK_a of the corresponding perfluoroalkyl hydrides.

non-bonded electron in the carbon orbital which contains two electrons in the carbanion, similar repulsion will be present. An M.O. interpretation of the properties of halogenomethyl radicals by Epiotis and his co-workers leads to the same conclusion.[8] In other words some of the reactivity of trifluoromethyl radicals can be attributed to the destabilizing effect of this lone pair repulsion by the α-fluorine atoms. It is important to notice that this repulsion is less significant with the other halogen atoms so that trichloromethyl radicals although exerting a similar inductive withdrawal of electrons suffer very little destabilisation from lone pair repulsion.[7] The increased selectivity of the perfluoro-t-butyl radical is caused by inhibition of attack at the CHF-end of vinyl fluoride which could be due to a polar effect, unmasked by the lone pair repulsion. As the data show this polar effect mainifests itself by increasing the activation energy, the pre-exponential terms remaining almost constant.

However, although the excellent correlation between the acidity of the perfluoroalkyl hydrides and the orientation ratios for addition by the perfluoroalkyl iodides points to a polar effect, it must be remembered that the lone pair repulsion as well as reducing the electronegativity of the radical also bends the three bonds joined to the trivalent carbon atom out of the plane. Thus the perfluoro-t-butyl radical as well as being the most electronegative in the series will also be the most planar.[9,10] It is clear therefore that while lone pair repulsion is a major factor, it is less certain whether it operates more through polarity than through steric hindrance.

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