Tetrahedron Vol. 36, pp. 701 to 707
Pergamon Press Ltd., 1980. Printed in Great Britain

TETRAHEDRON REPORT NUMBER 79

THE IMPORTANCE OF POLARITY AND STERIC EFFECTS IN DETERMINING THE RATE AND ORIENTATION OF FREE RADICAL ADDITION TO OLEFINS

RULES FOR DETERMINING THE RATE AND PREFERRED ORIENTATION

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(*Received* 9 *October* 1979)

We have recently written review articles which have summarised 15 years of research work into the factors which control the rate and orientation of the addition of free radicals to olefins.[1] In these articles we emphasised that no simple property could be used to determine the orientation of free radical addition. Instead we showed that the rate and orientation of free radical addition to olefins depend on "the complex interplay of polar, steric and bond-strength terms".[1a] Unfortunately this has led some workers to fall back on more definite but incorrect hypotheses and it is the purpose of the present report to try and provide a qualitative theory which will suffice for the majority of organic chemists.

The kinetics of free radical addition to olefins provides the most complete quantitative study of directive effects of a gas phase reaction in organic chemistry, and we hope that the rationalisation of the data will prove a challenge to theoretical chemists. In the meantime the present report interprets the results in the familiar qualitative pictures of the organic chemist.

The first factor considered by the mechanistic organic chemist is polarity. The importance of polarity in determining the overall rate of addition of radicals to symmetrical olefins is well illustrated by the relative rates of addition of the radicals $CH_3\cdot$,[2] $CH_2F\cdot$,[3] $CHF_2\cdot$[4] and $CF_3\cdot$[5] to ethylene and tetrafluoroethylene.

Table 1. The ratio of radical addition rates $CF_2{=}CF_2/CH_2{=}CH_2$

Radical	$k_{C_2F_4}/k_{C_2H_4}$ (164°C)
$CH_3\cdot$	9.5
$CH_2F\cdot$	3.4
$CHF_2\cdot$	1.1
$CF_3\cdot$	0.1

Methyl radicals are thus "nucleophilic" and their rate of addition is accelerated by electronegative substituents in the olefin, while trifluoromethyl radicals are "electrophilic" their rate of addition retarded by electronegative substituents and as we shall see accelerated by electron repelling alkyl groups. Table 2 compares the relative rates of addition and orientation ratios for addition to monosubstituted ethenes ($CH_2{=}CHX$).

In every reaction in Table 2, the radicals add preferentially to the unsubstituted α-site. The attack occurs at the α-position in most cases not because this position is activated but because the β- or substituted site is very deactivated. It is also clear that the orientation of addition is not governed by polar factors, for example the electrophilic trifluoromethyl radical and the nucleophilic Me radical both add preferentially to the α-sites in propene and 1,1,1-trifluoropropene in sharp contrast to the orientation of ionic addition of hydrogen chloride which yields exclusively $CH_3CHClCH_3$[17] and $CF_3CH_3CH_2Cl$[18] from propene and 1,1,1-trifluoropropene respectively. There is some evidence of polar effects, for

Table 2. Relative rates ($2k_\alpha/k_e$) and orientation ratios ($\alpha:\beta$) for the addition of methyl, trifluoromethyl and trichloromethyl radicals to mono-substituted ethenes ($\overset{\alpha}{C}H_2{=}\overset{\beta}{C}H{-}X$)

X	$CH_3\cdot$		$CF_3\cdot$		$CCl_3\cdot$	
	$2k_\alpha/k_e$	$\alpha:\beta$	$2k_\alpha/k_e$	$\alpha:\beta$	$2k_\alpha/k_e$	$\alpha:\beta$
H	1	1;1	1	1:1	1	1:1
CH_3	0.7	1:0.15[6]	2.3	1:0.1[10]	4	1:0.07[13]
F	0.9	1:0.20[2]	0.48	1:0.09[5]	0.7	1:0.08[14]
Cl	4.2	1:>0.01[7]	1.3	1:>0.01[11]	2.5	1:>0.01[15]
Br	-	-	1.2	1:>0.01[11]	-	-
CF_3	0.9	1:0.33[8]	0.40	1:>0.02[10]	0.9	1:>0.01[16]
$CN^{(b)}$	34.	- [9]	0.72	1:>0.01[11]	4.5	1:>0.01[18]
CH_3O	-	-	2.1	1:>0.01[11]	-	-
$CH_2{=}CH-$	8.1	1:0.01[6]	20.	1:>0.01[12]	-	-

(k_e= the rate of addition to ethylene)

((b) Data for ethyl radicals)

example, the relative rate of addition of trifluoromethyl and trichloromethyl radicals to propene is enhanced (relative to ethylene) which the relative rate of addition to trifluoropropene is retarded. Similarly the proportion of Me radical attack at the β-position is greater with 1,1,1-trifluoropropene than with propene itself. However these effects are small and must be regarded as of secondary importance.

Since the predominant effect of all the vinylic substituents is to deactivate the site to which they are attached often by several powers of ten, resonance stabilisation of the adduct radical can play little part in determining the orientation of addition. Indeed, polarity, though only of minor importance in determining the orientation ratios for monosubstituted olefins, would seem to be more significant. The only molecule in Table 2 where electron delocalisation in the adduct radical is clearly important is butadiene. Delocalisation of the unpaired electron over adjacent filled nonbonding orbitals, important in ionic reactions, requires separation of charge ($R\cdot + CH_2{=}CH{-}\ddot{X} \rightarrow R{-}CH_2{-}\dot{C}H{-}\ddot{X} \leftrightarrow R{-}CH_2{-}\bar{C}H{=}\overset{+}{X}$) and is therefore unimportant in radical processes. The same is not true for π-orbitals ($R\cdot + CH_2{=}CH{-}CH{=}CH_2 \rightarrow R{-}CH_2{-}\dot{C}H{-}CH{=}CH_2 \leftrightarrow R{-}CH_2{-}CH{=}CH{-}\dot{C}H_2$) and the relatively high rate of attack on butadiene by both Me and trifluoromethyl radicals (and possibly the high rate of attack by Et radicals on acrylonitrile where polar and resonance effects go hand in hand) may be attributed to resonance. However, the orientation of addition is decided more by retardation of attack at the substituted β-site than by activation at the α-position.

Table 2 showed that the relative rate of addition of trifluoromethyl radicals to the α-positions of vinyl fluoride ($2k_\alpha/k_e = 0.48$) and 1,1,1-trifluoropropene ($2k_\alpha/k_e = 0.40$) were very similar. Table 3 compares the orientation ratios for the addition of trifluoromethyl radicals to some fluoro-ethenes and propenes. Some of the data for this table comes from qualitative studies and the figures are approximations. Nevertheless the table clearly shows that for the addition of a trifluoromethyl radical a substituent trifluoromethyl group and a substituent F atom have very similar directive effects in contrast to their

Table 3. Orientation ratios ($\alpha:\beta$) for the addition of $CF_3\cdot$ radicals to fluoroethenes and propenes

	X = F[5]	X = CF_3[10,19,20]
	$\alpha:\beta$	$\alpha:\beta$
$\overset{\alpha}{C}H_2{=}\overset{\beta}{C}H{-}X$	1:0.09	1:0.02
$CHF{=}CH{-}X$	1:1	1:0.3
$CF_2{=}CH{-}X$	1:2.0	1:1.5
$CF_2{=}CF{-}X$	1:1	1:0.25

directive effects in electrophilic addition and aromatic substitution (CF_3 *meta* directing, F *ortho, para* directing). The bulkier trifluoromethyl group always deactivates the position to which it is attached slightly more than a single F atom. However two F atoms (while not having twice the effect) are more deactivating than a single trifluoromethyl group, i.e. the relative rates of attack at different sites by the trifluoromethyl radical is in the order

$$CH_2{=} > CHF{=} > CF_3CH{=} > CF_2{=} > CF_3CF{=}.$$

Both the trifluoromethyl group and the F atom are electron withdrawing and would be expected to deactivate the addition of a trifluoromethyl radical for polar as well as steric reasons and all the reactions in Table 3 are slower than the reaction of trifluoromethyl radicals with ethylene. The Me group on the other hand is electron repelling, and as we have seen activates attack by the electrophilic trifluoromethyl radical. The orientation ratios ($\alpha:\beta$) for the addition of trifluoromethyl radicals to ethylene, propene and 2-methylpropene are as follows (the relative rates $2k_\alpha/k_e$ allows for two identical sites in ethylene):

	$\overset{\alpha}{C}H_2{=}\overset{\beta}{C}H_2$	$\overset{\alpha}{C}H_2{=}\overset{\beta}{C}HCH_3$	$\overset{\alpha}{C}H_2{=}\overset{\beta}{C}(CH_3)_2$
$\alpha:\beta$	1:1	1:0.1[10]	1:0.08[11]
$2k_\alpha/k_e$	1	2.3	6.0

The introduction of a second Me subsituent in 2-methylpropene, which would be expected to enhance the proportion of attack at the β-position compared to propene, in fact reduces it, but the relative rate ($2k_\alpha/k_e = 6.0$) for the α-position of 2-methylpropene shows that, as expected, the introduction of the second Me group enhances the overall rate of attack. This shows that although polarity controls the overall rate of addition, steric effects play the predominant part in determining the orientation. The data in Table 3 and for 2-methylpropene show that a second similar substituent, although increasing the steric effect, has a comparatively small influence on the orientation ratio.

The experimental data for the addition of trichloromethyl radicals to some poly-substituted olefins are shown in Table 4.

Table 4. The relative rates and orientation ratios $\alpha:\beta$ for the addition of trichloromethyl radicals to some olefins (164°)

	$\overset{\alpha}{C}H_2{=}\overset{\beta}{C}H{-}CH_3$ [11]	$\overset{\alpha}{C}H_2{=}\overset{\beta}{C}H{-}F$ [14]
$\alpha:\beta$	1:0.07	1:0.08
$2k_\alpha/k_e$	9	0.7
	$CHF{=}CF_2$ [14]	$CHCl{=}CF_2$ [21]
$\alpha:\beta$	1:0.29	1:25
$2k_\alpha/k_e$	0.18	0.13

Table 4 shows that the orientation of trichloromethyl radical addition to propene and vinyl fluoride is almost the same but the rate of addition varies by more than a power of ten, i.e. in this example the steric effect governs the orientation of addition while polarity governs the overall rate. The second two examples in Table 4 confirm this conclusion. The polar influences of a substituent F atom and a substituent Cl atom are similar but their "size" is very different, so that in this case the rates of addition are similar but the orientation is very different.

So far we have only considered the "size" of substituents in the olefin. However if steric effects are important the "size" of the radical should be important. Table 5, page 704, shows the orientation ratios for the addition of bromofluoromethyl radicals.

The effect of the increase in the size of the radical as Br replaces F is clearly manifest especially when it is remembered that F is considerably more electronegative than Br (i.e. on polar grounds the relative rate of attack at the β-position should increase with replacement of F by Br).

Table 5. The orientation ratios ($\alpha:\beta$) of the addition of fluorobromomethyl radicals to vinyl fluoride and trifluoroethylene (164°)

	$\overset{\alpha}{CH_2}=\overset{\beta}{CHF}$	$\overset{\alpha}{CHF}=\overset{\beta}{CF_2}$
$CF_3\cdot$[5]	1:0.094	1:0.5
$CF_2Br\cdot$[22]	1:0.089	1:0.47
$CFBr_2\cdot$[23]	1:0.085	1:0.36
$CBr_3\cdot$[24]	1:0.040	1:0.24

A more pronounced steric effect is observed with the branched radicals (Table 6). The similarity of the $2k_\alpha/k_e$ values confirms that the large variation in orientation ratios ($\alpha:\beta$) is due to specific hindrance to attack at the β-position.

The attack on a double bond by a radical probably takes place at one end of the bond along a pathway perpendicular to the plane of the olefin. The attack on a triple bond will likewise be at one end of the bond and at right angles to the molecular axis of the acetylene. Recently we have found that the orientation ratios for the addition of free radicals to acetylenes are only slightly smaller than those for the analogous olefins.

Table 6. The orientation ratios for the addition of branched chain radicals to vinyl fluoride (164°)

Radical	$\overset{\alpha}{CH_2}=\overset{\beta}{CHF}$	
	$\alpha:\beta$	$2k_\alpha/k_e$
$CF_3\cdot$[5]	1:0.1	0.5
$CF_3CF_2\cdot$[25]	1:0.06	0.6
$(CF_3)_2CF\cdot$[26]	1:0.02	0.5
$(CF_3)_3C\cdot$[27]	1:0.005	0.5

Table 7 shows that the orientation ratios for addition to substituted acetylenes are similar to those for like substituted olefins. This means that the steric effects we have been discussing are not simply physical obstruction (aptly called "steric screening" by Rüchardt), but are due to repulsion between the incoming radical and substituents attached directly to the olefin site. The mutual repulsion between the incoming radical and a vinyl or acetylenic substituent will be similar and therefore have similar directive effects in both additions.

Table 7. The orientation ratios for the addition of trifluoromethyl radicals to olefins $H_2C=CHX$ and acetylenes $HC\equiv CX$ (164°)

Olefin[13,8]	$\alpha:\beta$	Acetylene[12]	$\alpha':\beta'$
$CH_2=CHCH_3$	1:0.09	$CH\equiv CCH_3$	1:0.2
$CH_2=CHCF_3$	1:0.02	$CH\equiv CCF_3$	1:0.07

Table 8 compares the addition of Me and the three fluoromethyl radicals to ethylene and the fluoroethenes. It again shows that Me radicals add fastest to the most fluorine substituted olefin and trifluoromethyl radicals add fastest to the least fluorine substituted olefin (see Table 1). All four radicals preferentially attack the unsubstituted end of vinyl fluoride and their orientation ratios are similar, confirming that the electronegativity of the radical plays little part in determining the orientation of addition to this molecule. The similarities of the orientation ratios show that the cardinal factor determining the ratios is a property of vinyl fluoride which hinders attack at the substituted end.

In all the cases considered so far, orientation appears to be controlled by "steric effects" and the

Table 8. Orientation ratios ($\alpha:\beta$) and relative (k/k_e) rates of addition to fluoroolefins (164°) by $CH_3\cdot$, $CH_2F\cdot$, $CHF_2\cdot$ and $CF_3\cdot$

	α β $CH_2=CHF$		α β $CH_2=CF_2$		α β $CHF=CF_2$	
	k/k_e	$\alpha:\beta$	k/k_e	$\alpha:\beta$	k/k_e	$\alpha:\beta$
$CH_3\cdot$[2]	1.1	1:0.2	-	-	5.8	1:2.1
$CH_2F\cdot$[3]	0.4	1:0.3	-	1:0.4	-	1:2.0
$CHF_2\cdot$[4]	0.4	1:0.2	0.1	1:0.1	0.3	1:0.9
$CF_3\cdot$[5]	0.5	1:0.1	0.2	1:0.04	0.05	1:0.5

(k_e= rate constant for addition to ethylene)

relative rate by "polar effects". Table 8 shows that this simple division can no longer be sustained. The limited data for 1,1-difluoroethylene show that polarity can influence the orientation of addition; the extent of attack at the β-position decreasing as the radical becomes more electrophilic. This conclusion is confirmed by data for trifluoroethylene where Me and fluoromethyl radicals preferentially attack the β-position (i.e. *the preferred orientation of addition is reversed*). The total polarity difference between the α and β positions of trifluoroethylene is no greater than that of vinyl fluoride, but we have seen that the introduction of a second F atom onto a vinylic site does not double the "steric hindrance" so that the steric difference between the two positions in trifluoroethylene is less than that between the two positions in vinyl fluoride, and polarity becomes the predominant factor.

This reversal of addition is very significant because it demonstrates the complexity of the factors which control the orientation and rate of radical addition. The preferred orientation of electrophilic addition is the same for most electrophiles regardless of their nature but in radical addition this is not the case. However this does not mean that we cannot develop rules to predict the rate and orientation of these reactions.

Radical addition reactions being highly exothermic should have early transition states. However, we have found that the variation of the pre-exponential factors in the rate expression shows that appreciable bond deformation has taken place and in particular bonding has proceeded sufficiently in the transition state for there to be an appreciable decrease in the double bond character of the olefin.[4] In an important review article[28] Rüchardt has argued persuasively that "steric effects" are important in free radical reactions, although he cautiously excludes free radical addition reactions because of their exothermic character (he considers they will, therefore, have early transition states in which steric compression will be less important).

Rüchardt considers three destabilizing factors to be important in the ground state of a free radical:

(a) Mutual repulsion of nuclei.

(b) Mutual repulsion of bonding electrons.

(c) Repulsion of non-bonded atoms when their mutual distance approached Van der Waals distances. Rüchardt goes on to emphasize that any influence that reduces the angle between orbitals or bonds, consequently encounters strong resistance. Any radical addition to an olefin involves just such angle changes and even though the reaction is exothermic and the transition state therefore early, nonetheless, the experimental evidence is that appreciable bond deformation occurs very early in the addition process.

We can now re-examine the experimental results in the light of Rüchardt's ideas. The same preferred orientation for the addition of Me and trifluoromethyl radicals to propene and 1,1,1-trifluoropropene can be attributed to steric repulsion of the substituent CF_3– and CH_3– groups overcoming the effect of polarity.

The most interesting results are those involving a change in preferred orientation in the addition of radicals to trifluoroethylene and are therefore worth discussing again. Trifluoromethyl radicals (and difluoromethyl radicals) add preferentially to the least substituted end, but the ratio $\alpha:\beta$ is larger (1:0.5) than for addition to vinyl fluoride ($\alpha:\beta = 1:0.1$) (Table 1). This confirms that the repulsion attributable to a single F at (CHF=) is proportionally greater than that attributable to two F atoms (CF_2=). The orientation of addition of a Me radical to vinyl fluoride is governed by the steric repulsion of the single F atom which overrides the polar effect. In the addition of Me radicals to trifluoroethylene the smaller difference in steric repulsion between the two sites (CHF= and CF_2=) allows polarity to become the deciding factor.

We conclude that although polarity can play a large part in determining the relative rates of addition of free radicals to olefins, the orientation of addition to mono-substituted olefins is more often determined by the steric factors Rüchardt discusses in his important review. Although most radical addition reactions are exothermic the approach of the radical to the olefinic centre is close enough in the transition state for mutual repulsion of the nuclei, mutual repulsion of the bonding electrons and repulsion of adjacent non-bonded atoms to control the orientation of addition in mono-substituted olefins. This steric hindrance is predominantly though not entirely, an enthalpy effect increasing the activation energy and only having a small effect on the pre-exponential term. The rate and orientation of free radical addition to mono-substituted olefins is governed principally by polarity and steric effects respectively, and resonance stabilisation of the incipient adduct radical much invoked in student texts, only plays a minor role.

When there is more than one substituent on the vinylic sites, the orientation becomes harder to predict, although steric repulsion remains the dominant factor controlling the orientation of addition (see especially Table 8).

We can now attempt to draw up a set of "rules". According to our terms of reference, these should be couched in qualitative concepts, to provide a useful guide to a synthetic organic chemist.

(1) The preferred orientation of the addition of a free radical to a mono-substituted ethene will invariably be to the unsubstituted end of the double bond. This can be attributed to steric repulsion which overrides other influences.

(2) Polarity can have a major effect on the overall rate of addition of radicals to olefins. Me radicals behave as "nucleophiles" and their addition is facilitated by electron withdrawing substituents in the olefin while trifluoromethyl radicals behave as "electrophiles" where addition is retarded by electron withdrawing and assisted by electron repelling substituents.

(3) The orientation of free radical addition to polysubstituted ethenes is controlled principally by steric repulsion, but if the steric effects are in mutual opposition to each other, polarity can be the deciding factor.

(4) Even when the orientation of addition in a polysubstituted ethene is determined principally by steric repulsion, polarity can influence the magnitude of the orientation ratio, making it larger or smaller depending on the relative electronegativity of the radical and substituents in the olefin.

(5) Vinyl substituents with π-orbitals (e.g. CH_2=CH–; C_6H_5–, etc.) which can overlap the half-filled atomic orbital of the radical centre can enhance the rate of addition at the remote end of the double bond, but vinylic substituents with non-bonded pairs of electrons (e.g. F–, Cl–, CH_3O–, etc) have no appreciable "resonance" effect. Most radical additions are exothermic and have early transition states which means delocalisation of the unpaired electron in the adduct radical is of small importance. Donor groups (i.e. those with non-bonded pairs) which can only delocalise the unpaired electron through the creation of a dipole therefore have a negligible stabilising effect.

These rules are entirely qualitative and assume that other extraneous factors are not affecting the reaction. Important effects which can change the proportion of two adducts in the overall products of a free radical addition reaction include reversibility of addition (important with thiol radicals), instability of the adduct radical ($R\cdot + XCH{=}CHY \rightarrow RCHX\dot{C}HY \rightarrow RCH{=}CHY + X\cdot$ important when X=Cl, Br or CHO), and different fates for the two adducts radicals. In radical cyclisation reactions new steric effects are encountered and these are not discussed in the present report. It is also important to remember that the simple qualitative arguments cannot satisfactorily account for some of the smaller effects observed. For instance, 1,1-difluoroethylene is particularly unreactive towards free radicals. This lack of reactivity is associated with a high π-bond dissociation energy, a property which can only be explained in qualitative terms by using *ad hoc* hypotheses. The kind of repulsive destabilisation evoked by Rüchardt and found to be applicable to free radical addition will not be accounted for in Hückel type theories, and all-electron calculations will be necessary to get a true picture.

The introduction of "rules" will, we hope, help nonspecialists to predict the relative rates and regiospecificity of free radical addition reactions. However, it will we hope also provide a challenge to research workers to find "exceptions" and thereby encourage further research into free radical reactions.

Finally acknowledgement must be made to all those workers who, though not necessarily quoted in the present article, did so much to lay the foundations.

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