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THE IMPORTANCE OF POLARITY, BOND STRENGTH AND STERIC EFFECTS IN DETERMINING THE SITE OF ATTACK AND THE RATE OF FREE RADICAL SUBSTITUTION IN ALIPHATIC COMPOUNDS

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CONTENTS

The present report is intended to companion Tetrahedron Report 79.[1] There are many excellent reviews of various aspects of free radical substitution.[2-5] This report is not a comprehensive review but an account of the conclusions which can be drawn from the work that has been done over the last 25 years. It is an attempt to provide qualitative theory which will enable most organic chemists to predict the effect substituents have on the course of free radical substitution reactions.

Free radical substitution reactions involve two atom (or group) transfer steps.

$$A-B+X^{\cdot} \rightarrow A^{\cdot}+B-X \quad (1)$$

$$A^{\cdot}+X-Y \rightarrow A-Y+X^{\cdot}. \quad (2)$$

Very often two transfer processes represent the propagating steps of a chain reaction which is only terminated by radical–radical reactions:

$$X^{\cdot}+X^{\cdot} \xrightarrow{M} X_2 \quad (3)$$

$$X^{\cdot}+A^{\cdot} \rightarrow AX \quad (4)$$

$$A^{\cdot}+A^{\cdot} \rightarrow A_2. \quad (5)$$

It is not the purpose of the present Report to discuss the initiation steps or the kinetics and mechanism of free radical chain reactions. All that concerns us at present is that the substitution of Y for B is determined by the transfer step (1) (sometimes called the abstraction of B, especially when B is hydrogen). The relative rates of attack will be discussed in terms of the Arrhenius equation. Rate constant $k = Ae^{-E/RT}$.

Kinetic considerations

Table 1 shows the logarithm of the "A"-factors and the activation energies for H abstraction from methane. The pre-exponential terms are between two or three orders of magnitude greater for atoms than for radicals. This is expected since there is loss of rotational entropy as the transition state involving a radical is formed, while no such loss occurs with the atoms. Notice however the very small variation in the "A"-factors for the six radicals. The table also shows that there is no simple relationship

between the Activation Energy and the heat of reaction. The reactions involving H atoms, Cl atoms, Me radicals and MeO radicals are all almost thermoneutral and yet the activation energies vary from 3.9 k cal mol^{-1} to 14.1 k cal mol^{-1}. The explanation of this apparent paradox will be discussed below.

Table 1 shows that the pre-exponential term (or "A"-factor) varies very little for different radicals abstracting H from methane. Table 2 shows that the pre-exponential term also varies very slightly as the Me radical abstracts H atoms from different sites in branched chain alkanes. The change in rate by a factor of 500 is entirely attributable to the decrease in activation energy. It is therefore the activation energies we will be considering in most of our discussion.

The strength of the bond broken and the Evans–Polanyi equation

The first factor we shall consider which affects reaction (1) is the strength of bonds being broken D(A – B). If there is no polarity in the transition state, then there is a direct relationship between the strength of the bond being broken and the activation energy of the abstraction step.

This relationship between activation energy and bond strength is usually called the Evans–Polanyi equation:

$$E_{act} = \alpha[D(R-H)] + \beta.$$

Not only does the relationship hold when there is no polarity in the transition state, but it also holds when the polarity is constant (i.e. the same for each reaction).

$$RH + X^{\cdot} \rightarrow R^{\cdot} + HX$$
$$(E_{act} = \alpha[D(R-H)] + \beta).$$

Table 1. The Arrhenius parameters for hydrogen abstraction from methane[6,7]

	$CH_4 + R\cdot \longrightarrow CH_3\cdot + RH$		
R·	log A ($l\ mol^{-1}\ s^{-1}$)	E k cal mol^{-1}	D(R-H) k cal mol^{-1}
H·	11.1	11.9	104
F·	11.1	1.2	136
Cl·	10.4	3.9	103
Br·	11.0	18.6	87
I·	11.7	34	71
CH_3·	8.8	14.3	104
CF_3·	9.2	11.5	106
CH_3O·	8.8	11.0	104
C_2H_5·	8.7	17.7	98
$(CH_3)_2CH$·	8.7	19.6	94.5
$(CH_3)_3C$·	8.9	21.0	92

Table 2. Arrhenius parameters for hydrogen abstraction from branched alkanes by methyl radicals[6b]

	log A $l\ mol^{-1}\ s^{-1}$	E k cal mol^{-1}	log $k^{164°}$ $l\ mol^{-1}\ s^{-1}$
$\overset{*}{C}H_4$	8.76	14.23	1.65
$CH_3\overset{*}{C}H_3$	8.83	11.83	2.96
$CH_3\overset{*}{C}H_2CH_3$	8.82	10.13	3.75
$(CH_3)_3\overset{*}{C}H$	8.38	8.03	4.36

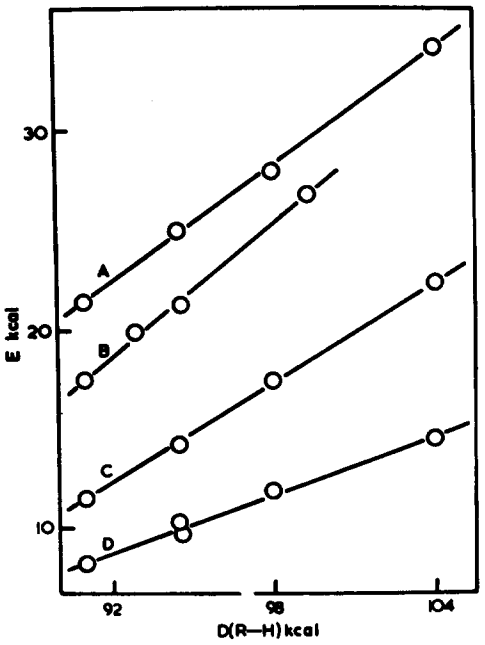


Fig. 1. Polanyi plots of E vs D (R-H) for reactions X+RH=XH+R: A, iodine atoms; B, difluoroamino radicals; C, bromine atoms (E displaced by +4 kcal); D, methyl radicals (see Ref. 7*a*).

Table 3. The Evans-Polanyi equation[7a]

$$RH + X\cdot \longrightarrow R\cdot + HX$$

$$(E_{act} =. \alpha\,[D(R\text{-}H)] + \beta)$$

X	α	β (k cal mol^{-1})
$CH_3\cdot$	0.49	74
$CF_3\cdot$	0.53	84
Br·	0.86	83
I·	0.91	69
$NF_2\cdot$	1.1	76

The existence of Evans–Polanyi relations emphasises the importance of the strength of the bond being broken. However it is very necessary to appreciate that no relationship of the Evans–Polanyi type is observed when the polarity changes from reaction to reaction. Indeed the importance of polarity is apparent even from the data in Table 1. It would be expected that the more endothermic the reaction the larger the constant α and, in conformity, α for iodine atoms is larger than for Br atoms. However, H abstraction by trifluoromethyl radicals is exothermic while H abstraction by Me radicals is close to thermoneutral and yet α for trifluoromethyl radicals is the larger. The difference is that the trifluoromethyl radicals are relatively "electrophilic" and therefore H abstraction is facilitated at the more nucleophilic centres (i.e. tert > sec > prim > CH_4). Evidence for this polarity is also demonstrated by the large value of α for the electrophilic difluoroamino radicals.

The strengths of the new bond formed

If the strength of the bond broken is important the strength of the bond being formed must also be important. The halogen atoms abstract H from alkanes but the new bond formed (i.e. the halogen hydride) varies from D(H − F) = 136 k cal mol^{-1} to D(H − I) = 71 k cal mol^{-1} and the reaction rate and selectivity varies enormously (see Table 1 for relative rate $k_F^{150°} = 10^{10}$, $k_I^{150°} = 10^{-5}$ l mol^{-1} s^{-1} and Table 4 for selectivity).

Table 4. Relative selectivities for hydrogen atom abstraction from alkanes by halogen atoms in the gas phase

Atom	Temp °C	CH_3-	$CH_2<$	$CH\equiv$
F·	25	1	1	2
Cl·	25	1	4	7
Br·	150	1	80	2,000
I·	150	1	1,000	97,000

The selectivity is also affected by polarity (see below) but the halogens are all electronegative species and polarity only makes a very small contribution to the change in selectivity illustrated in Table 4.

Evidence for the importance of polarity in radical transfer reactions

It is interesting to compare the activation energies for H abstraction reactions involving small heats of reaction and non-polar transition states.

Table 5. Activation energies for nearly thermoneutral hydrogen atom transfer reactions involving small non-polar molecules (k cal mol^{-1})[6,7]

	E_1	E_2	ΔH_1
$H\cdot + H_2 \underset{2}{\overset{1}{\rightleftharpoons}} H_2 + H\cdot$	9.0	9.0	0
$H\cdot + CH_4 \underset{2}{\overset{1}{\rightleftharpoons}} H_2 + CH_3\cdot$	11.5	12.5	-1.0
$H\cdot + CF_3H \underset{2}{\overset{1}{\rightleftharpoons}} H_2 + CF_3\cdot$	11.0	10.0	+1.0
$CH_3\cdot + CH_4 \underset{2}{\overset{1}{\rightleftharpoons}} CH_4 + CH_3\cdot$	14.0	14.0	0
$CH_3\cdot + CF_3H \underset{2}{\overset{1}{\rightleftharpoons}} CH_4 + CF_3\cdot$	11.5	11.2	+0.3
$CH_3O\cdot + CH_4 \underset{2}{\overset{1}{\rightleftharpoons}} CH_3OH + CH_3\cdot$	11.0	10.5	+0.5

The very striking feature of Table 5 is the small range of activation energies. The activation energy for H atom exchange with H_2 molecules is relatively small and the H atom transfer between Me radicals and methane is relatively large. For the rest it is noticeable that the reactions which have some polarity in the transition state (i.e. those involving $CF_3^{\cdot}$ and $CH_3O^{\cdot}$) tend to have the lowest activation energies. However the significance of polarity is demonstrated far more effectively in Table 6.

Table 6. Activation energies for nearly thermoneutral hydrogen atom transfer reactions involving small polar molecules (k cal mol^{-1})[6,7]

	E_1	E_2	ΔH°_1
$H\cdot + HCl \underset{2}{\overset{1}{\rightleftharpoons}} H_2 + Cl\cdot$	4.0	5.0	-1.0
$CH_3\cdot + HCl \underset{2}{\overset{1}{\rightleftharpoons}} CH_4 + Cl\cdot$	2.5	3.5	-1.0
$CF_3\cdot + HCl \underset{2}{\overset{1}{\rightleftharpoons}} CF_3H + Cl\cdot$	5.0	8.0	-3.0

All the activation energies in Table 6 are lower, and most are substantially lower than those in Table 5. This is because the height of the energy barrier is lowered by polar forces in the transition state. The lowest energy barrier in Table 6 is that between methane and hydrogen chloride. It is particularly striking that H abstraction from hydrogen chloride by trifluoromethyl radicals is the most exothermic of the forward reactions and yet has the highest activation energy. This is because the "electronegative" trifluoromethyl radical will resist the formation of a polar transition state, while the "electropositive" Me group will facilitate the formation of a polar transition state.

$$CH_3^{\cdot} + H\text{–}Cl \rightarrow [\overset{\rightarrow}{CH_3^{\delta+}} \cdots \vec{H} \cdots {}^{\delta-}Cl]^{\ddagger} \rightarrow CH_3^{\cdot} + \overset{\delta+}{H}\text{–}\overset{\delta-}{Cl}.$$

[Electron releasing Me group facilitates the formation of the polar "activated complex"]

$$CF_3^{\cdot} + H\text{–}Cl \rightarrow [\overset{\leftarrow}{CF_3} \cdots \overset{\delta+}{H} \cdots \overset{\rightarrow}{\overset{\delta-}{Cl}}]^{\ddagger} \rightarrow CF_3^{\cdot} + \overset{\delta+}{H} - \overset{\delta-}{Cl}.$$

[Electron seeking trifluoromethyl group resists the formation of the polar "activated complex".]

In conformity with this picture the energy barrier for the exchange of H atoms with hydrogen chloride is intermediate between that for the transfers involving Me and trifluoromethyl radicals.

In Tables 5 and 6 both the forward and the backward reactions are listed and the effect of polarity in Table 6 is to lower the energy barrier. In thermoneutral reactions or in reactions with small heats of reaction, polarity can be the governing effect and even in reactions with substantial positive heats of reaction, polarity is a contributing factor (see Table 7).

Table 7. Activation energies for hydrogen transfer reactions with large heats of reaction and polar transition states (k cal mol^{-1})[6,7]

	E_1	E_2	ΔH°_1
$CH_3\cdot + HBr \underset{2}{\overset{1}{\rightleftharpoons}} CH_4 + Br\cdot$	3	19	-16
$CF_3\cdot + HBr \underset{2}{\overset{1}{\rightleftharpoons}} CF_3H + Br\cdot$	3	22	-19

When we have data for the reaction in one direction only it is necessary to distinguish between the effect polar substituents have on the strengths of the bonds being broken and formed, from polarity in the transition state. If we do not know anything about the bond strength from other sources but observe that a polar substituent has opposite effects on the H abstraction reactions of Me and trifluoromethyl radicals, we can attribute this to polarity in the transition state. The abstraction of H from the silanes is exothermic for both Me and trifluoromethyl radicals. There is only data for these reactions in the forward direction but the fact that polar substituents have opposite effects on the activation energy of H abstraction by $CH_3\cdot$ and $CF_3\cdot$ radicals confirms that polarity is affecting the height of the energy barrier.

Table 8. Activation energies for hydrogen abstraction from substituted silanes by $CH_3\cdot$ and $CF_3\cdot$ radicals (k cal mol^{-1})[6]

Radical	SiH_4	$(CH_3)_3SiH$	Cl_3SiH
$CH_3\cdot$	6.9	7.8	4.3
$CF_3\cdot$	5.1	5.6	6.0

The comparatively large differences in activation energy observed with polar bonds like those in the hydrogen halides are not to be expected in reactions involving substituted hydrocarbon derivatives. Nonetheless clear evidence of polarity is apparent. If we compare the relative rates of H abstraction from iso-butane and ethane by trifluoromethyl and Me radicals, we find both react faster with iso-butane, $CF_3\cdot$ relatively the more so. On the other hand the relative rate of H abstraction from acetone by $CH_3\cdot$ radicals is greater while the relative rate of H abstraction by $CF_3\cdot$ radicals is less than H abstraction for ethane. Trifluoromethyl radicals are much more reactive and therefore normally less selective, but in the

Table 9. Relative rates of hydrogen abstraction by $CH_3\cdot$ and $CF_3\cdot$ radicals at sites of differing polarity ethane taken as standard[6b]

	D(R - H) k cal mol^{-1}	$k^{164}_{rel}(CH_3\cdot)$	$k^{164}_{rel}(CF_3\cdot)$
$(CH_3)_3C$-D	91	14	60
CH_3COCH_2-H	92	2.1	0.5

transition states the iso-Bu group enhances the polarity due to the trifluoromethyl group:

$$(\overset{+}{C}H_3)_3C\cdots H\cdots \overset{+}{C}F_3$$

whereas the CO group opposes the polarity of the trifluoromethyl group:

$$CH_3\overset{+}{C}OCH_2\cdots H\cdots \overset{+}{C}F_3.$$

In H abstraction from acetone by a Me radical the polarity of the Transition State is enhanced and the reaction is facilitated:

$$CH_3\overleftrightarrow{C}OCH_2\cdots H\cdots\overleftrightarrow{C}H_3.$$

(N.B. These results are in direct contradiction of the Reactivity Selectivity Principle)

The inductive effect of successive substituent Me groups in the alkanes e.g. [CH_3CH_2–H; $(CH_3)_2CH$–H; $(CH_3)_3C$–H] is too small to control the rate constant ratio for H abstraction by $CF_3^{\cdot}$ and $CH_3^{\cdot}$. However in ammonia and the corresponding amines [e.g. H_2N–H; CH_3HN–H; $(CH_3)_2N$–H] the electronegativity of the nitrogen accentuates the opposing inductive effect of the methyl groups so that the rate constant ratio k_{CF_3}/k_{CH_3} does illustrate the polar effect:[6b]

$$CF_3^{\cdot}(CH_3^{\cdot}) + \rangle N\text{–}H \longrightarrow CF_3H(CH_4) + \rangle N^{\cdot}$$

k_{CF_3}/k_{CH_3}	H_2N–H	CH_3NH–H	$(CH_3)_2N$–H
	3.1	9.3	16

The most common approach to establish the importance of polarity in a reaction used by physical organic chemists is the Hammett $\sigma\rho$ replation. It was first used by Kooyman[8] and shortly after by Walling.[9] The subject has been excellently reviewed by Russell.[3] Figure 2 (taken from Ref. 2) shows Hammett (Brown) σ^+ correlations for the chlorination[10] and bromination[11] of substituted toluenes.

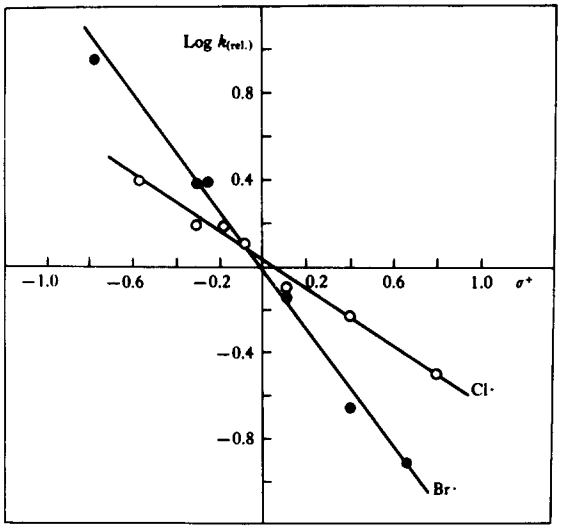


Fig. 2. Hammett (Brown) $\sigma^+\rho$ plot for the chlorination (*) and bromination (·) of substituted toluenes.[10,11] (see Ref. 2).

The ρ values were −0.7 and −1.8 for chlorination and bromination respectively. Bromination being endothermic and therefore having a late transition state, has the larger ρ value even though bromine is less electronegative than chlorine. The studies are complicated by the fact that the values of ρ depend on concentration and in the case of bromination on the concentration of HBr. Van Helden and Kooyman also compared the rate of chlorination of 2-X-2-methylpropanes [$(CH_3)_3C-X$] with the dissociation constants of the corresponding carboxylic acids (XCH_2CO_2H).[8] None of these kinds of studies can lead to a quantitative interpretation of the importance of polarity in radical transfer reactions. They do however confirm that such an effect exists and are important in showing that these procedures developed for heterolytic reactions can be usefully applied to radical reactions.

Reversal of the polar effect

We can generalise the "polar effect" observed in halogenation (esp. chlorination) reactions. If we have a molecule R–H in which R contains electronegative substituents close to the H being abstracted, the

R–H bond will become polarised ($\overleftrightarrow{R\text{–}H}$) and thus will oppose the formation of polar hydrogen chloride ($\overleftrightarrow{H\text{–}Cl}$).

$$\overleftrightarrow{R\text{–}H} + Cl^{\cdot} \rightarrow R^{\cdot}\cdots H\cdots\overleftrightarrow{Cl} \rightarrow R^{\cdot} + H\text{–}\overleftrightarrow{Cl}.$$

If the polarity of the bond being formed can be reversed the effect of the substituents should be reversed. Unfortunately halogen abstraction by H atoms is very difficult to study kinetically. However, halogen abstraction by trimethyltin and trimethylgermanium radicals can conveniently be studied in the gas phase.

$$(CH_3)_3M^{\cdot} + R\text{–}Cl \rightarrow (CH_3)_3MCl + R^{\cdot}$$
$$R^{\cdot} + (CH_3)_3MH \rightarrow RH + (CH_3)_3M^{\cdot}$$

[where M = Sn or Ge].

The new bond formed, a metal-halogen bond, is very polar so that electronegative groups in R will facilitate halogen abstraction.

$$\overleftrightarrow{R\text{–}Cl} + (CH_3)_3M^{\cdot} \rightarrow R^{\cdot}\cdots\overleftrightarrow{Cl}\cdots M(CH_3)_3 \rightarrow R^{\cdot} + \overleftrightarrow{Cl\text{–}M}M(CH_3)_3.$$

Table 10. The relative rates of chlorine abstraction by $(CH_3)_3Ge$ and $(CH_3)_3$ Sn radicals[12,13]

R-Cl	$(CH_3)_3Ge^{\cdot}$	$(CH_3)_3Sn^{\cdot}$
RCH_2-Cl (1°)	1	1
R_2CH-Cl (2°)	2.5	3.6
R_3C-Cl (3°)	4.0	8.1

Since the Ge–H bond is probably weaker than the Sn–H bond, trimethylgermanium radicals would be expected to be more selective than trimethyltin radicals. However, the expected polar effect will be in direct opposition to normal bond strength order (3° < 2° < 1°). In other words trimethylgermanium radicals appear less selective in Table 10 because they are more affected by polarity. This is confirmed by Table 11 in which the relative rates of Cl atom abstraction from R–CCl_3 molecules is compared.

Table 11. Relative rates of chlorine atom abstraction from R–CCl_3 molecules by trimethylgermanium and trimethyltin radicals in the gas phase at 25°[12,13]

$(CH_3)_3M^{\cdot} + R\text{-}CCl_3 \longrightarrow (CH_3)_3MCl + RCCl_2^{\cdot}$

	Relative Rates	
$R\text{-}CCl_3$	$(CH_3)_3Ge^{\cdot}$	$(CH_3)_3Sn^{\cdot}$
$H\text{-}CCl_3$	1	1
$F\text{-}CCl_3$	9.1	1.5
$Cl\text{-}CCl_3$	41.6	2.8
$CH_3\text{-}CCl_3$	3.6	1.5
$ClCH_2\text{-}CCl_3$	10.0	2.0
$Cl_2CH\text{-}CCl_3$	26.9	4.7
$CF_3\text{-}CCl_3$	33.1	3.7

As we shall see below release of steric compression plays an important part in determining the ease of atom abstraction so that to determine the magnitude of the "reverse" polar effect we should compare

pairs of compounds where the steric compression is similar. Comparison of the rates of Cl abstraction from chloroform (H–CCl_3) and trichlorofluoromethane (F–CCl_3) shows that abstraction by trimethylgermanium radicals is nearly an order of magnitude faster from trichlorofluoromethane and the same applies to the pair, 1,1,1-trichloroethane (CH_3CCl_3) and 1,1,1-trichloro-trifluoroethane (CF_3CCl_3), where Cl abstraction from CF_3 CCl_3 is almost ten times the faster. Cl abstraction by trimethyltin radicals is much less affected by polarity but again abstraction is fastest from the molecules containing the most electronegative substituents.

The difference the effect substituents have an H abstraction by Br, and Cl abstraction by trimethylgermanium is well illustrated in Table 12.

Table 12. Reversal of the substituent effects on hydrogen abstraction and halogen abstraction[12]

$$X\text{-}CCl_2\text{-}H + Br\cdot \xrightarrow{\text{"A"}} XCCl_2\cdot + HBr$$

$$X\text{-}CCl_2\text{-}Cl + (CH_3)_3Ge\cdot \xrightarrow{\text{"B"}} XCCl_2\cdot + (CH_3)_3GeCl$$

Relative Rates (X=H unity)		
X	"A"	"B"
H	1	1
F	0.04	9.1

Just as polarity can override bond strength in H abstraction reactions so the "reverse" polar effect observed in halogen abstraction can be the controlling factor.

Steric effects in radical transfer reactions and their effect on bond strength

We can distinguish between three types of steric effect which are likely to be important in radical transfer reactions. Steric hindrance which inhibits the radical approaching the reaction site,[14] steric inhibition of resonance which prevents the incipient radical from being stabilised by electron delocalisation[15] and finally steric compression which is partly released in forming the new radical.[16] All three types of steric effect are important in free radical reactions but it is the last, the release of steric compression which must occur in every abstraction reaction. Thus the familiar decreasing order of carbon hydrogen bond strengths in alkanes, primary, secondary and tertiary, Rüchardt attributes to increasing release of steric strain (rather than increasing stabilisation of the incipient radical by hyperconjugation). His arguments are clearly set out in his original paper. Strong evidence for the importance of the release of torsional strain comes from the reactions of cyclic compounds. Table 13 shows that hydrogen abstraction from the strainless cyclohexane is invariably the slowest. This is because in forming the cyclopentyl and cycloheptyl radicals the torsional strain is released. The effect is small which is to be expected since the amount of strain (deduced from the relative heats of combustion) is small, but if release of torsional strain is

Table 13. Hydrogen abstraction from cyclopentane, cyclohexane and cycloheptane[17] (E in k cal mol^{-1}, log A in mol^{-1} s^{-1})

	$Br\cdot$		$CF_3\cdot$		$C_2F_5\cdot$		$CH_3\cdot$		$CCl_3\cdot$	
	log A	E	log A	E	log A	E	log A	E	log A	E
Cyclopentane	11.6	9.4	9.3	6.2	8.6	5.7	8.9	9.5	9.0	10.7
Cyclohexane	12.2	11.5	9.1	6.3	8.6	5.8	9.1	9.9	8.8	10.7
Cycloheptane	11.4	8.0	9.4	6.0	9.0	5.7	9.1	9.3	9.1	9.9

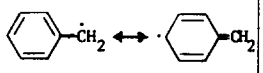
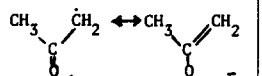
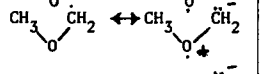
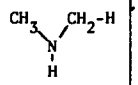
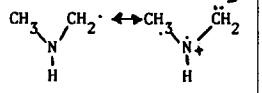
cycloheptyl radicals the torsional strain is released. The effect is small which is to be expected since the

detectable in the unsubstituted cycloalkanes, how much greater will the effect be when a hydrogen atom is abstracted from iso-butane. This results in a tertiary radical which is not constrained in a strictly planar conformation.

The importance of electron delocalisation in determining bond strength

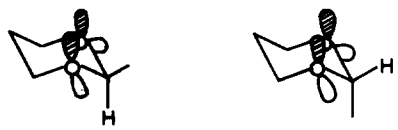
Steric compression is undoubtedly one of the important factors affecting the bond strengths; however delocalisation of the odd electron (resonance stabilisation) in the incipient radical is also important and will be manifest when the reaction is endothermic and the transition state late. Table 14 lists the Arrhenius Parameters for hydrogen abstraction from substituted methanes ($R\text{–}CH_3 + CH_3^{\cdot} \rightarrow RCH_2^{\cdot} + CH_4$) where the substituent E provides varying opportunities of delocalising the unpaired electron. At one time hyperconjugation loss was believed to be important in determining the bond strengths of

Table 14. Hydrogen abstraction from substituted methanes by methyl radicals[60]

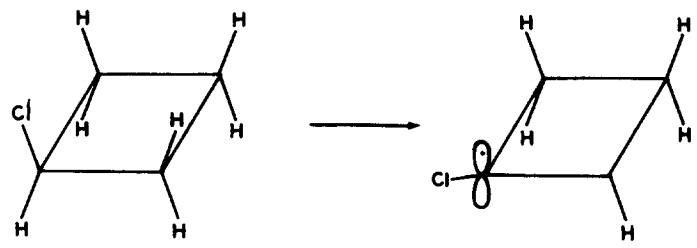
RCH_2–H	Resonance	log A ($l\ mol^{-1}\ s^{-1}$)	E (k cal mol^{-1})	$k^{164°}$ ($l\ mol^{-1}\ s^{-1}$)
CH_3CH_2–H	$H\text{–}CH_2CH_2\cdot \leftrightarrow H\cdot CH_2{=}CH_2$	8.1	10.4	1×10^3
$C_6H_5CH_2$–H		8.6	9.5	6.3×10^3
CH_3COCH_2–H		8.5	9.7	2.3×10^3
CH_3OCH_2–H		8.6	10.0	2.0×10^3
		8.4	8.9	8.9×10^3

branch chain alkanes. Evidence now seems to suggest that it is only of minor significance, and release of steric compression is the major effect.

Resonance stabilisation of the unpaired electron depends on the half filled orbital having symmetry such that it can overlap well with the adjacent p-atomic orbital or π-orbital. Such overlap may be restricted by steric factors, e.g. in a ring where both "steric inhibition of resonance" and "stereo-electronic" effects are possible. An example of stereo-electronic effects is the H abstraction from cyclic ethers.[18]



When the axial H atom and the shaped sp^3 hybrid orbitals of the O atoms are triperiplanar and H abstraction is favoured (abstraction by t-BuO$^{\cdot}$ radicals $k_a/k_e = 11.2$). The chlorination of chlorocyclobutane provides an example where release of steric strain and stereo-electronic effects work together.[19]



The rate of H abstraction (at 25°) from the α-position in chlorocyclobutane is five times faster than abstraction from a normal secondary aliphatic H atom not withstanding the effect of Walsh orbitals which lead to a strengthening of cyclobutane exo-cyclic bonds. The Cl atom will adopt a coplanar position to minimise steric compression and to have one of its 3p-atomic orbitals eclipsed with the half filled 2p-atomic orbital of the ring carbon.

The combination of steric and polar effects

The normal order of radical attack on an alkane of tertiary > secondary > primary can be interpreted in terms of release of steric compression. An electron repelling inductive effect will augment the effect of steric compression when the attacking atom or radical is "electrophilic". We can compare the selectivity of Br atoms with Me radicals. Attack by the Br atoms will be enhanced by the inductive effect of adjacent alkyl substituents whereas the attack by Me radicals (if polar at all) will be retarded. Table 15 shows that the polar effect is very much greater than might have been expected. H abstraction by Me radicals is slightly exothermic whereas H abstraction by Br atoms is endothermic (even for iso-butane).

Table 15. Arrhenius parameters for hydrogen abstraction by $Br^{\cdot}$, $CH_3^{\cdot}$ and $CF_3^{\cdot}$[6]

	$Br^{\cdot}$		$CH_3^{\cdot}$		$CF_3^{\cdot}$		log	log
	log A	E_{act}	log A	E_{act}	log A	E_{act}	$k_{Br^{\cdot}}/k_{CH_3^{\cdot}}$	$k_{CF_3^{\cdot}}/k_{CH_3^{\cdot}}$
H-H	10.7	17.5	8.6	10.5	9.3	8.5	-2.4	+1.7
CH_3-H	10.6	18.6	8.8	14.2	8.9	11.3	-0.5	+1.5
CH_3CH_2-H	10.9	13.4	8.8	11.8	8.4	6.9	+1.3	+2.0
$(CH_3)_2CH$-H	10.7	10.1	8.8	10.1	8.1	6.5	+1.9	+1.1
$(CH_3)_3C$-H	10.3	7.5	8.3	8.0	7.7	4.9	+2.25	+1.2

We would thus expect Br to be more selective, but because of the higher "A"-factors for atom reactions the difference in rate constant might not be large. Table 15 shows however that the rate of H abstraction by Br atoms from molecular H_2 is two orders of magnitude slower than that for abstraction by Me radicals, but for H abstraction from iso-butane it is two orders of magnitude the faster. Indeed the activation energy for H abstraction from iso-butane by Br atoms is less than that for Me radicals (in spite of the adverse thermochemistry). Once again this is a polar effect overriding bond strengths.

$$(CH_3)_3CH + Br^{\cdot} \rightarrow (CH_3)_3\overset{+\rightarrow}{C}\cdots H\cdots\overset{+\rightarrow}{Br} \rightarrow (CH_3)_3C^{\cdot} + HBr.$$

Table 15 also demonstrates that although trifluoromethyl radicals show weakly "electrophilic" properties these are too weak to greatly influence the course of a reaction which is only slightly polar.

As reagents, i.e. as attacking atoms, the halogens are "electrophilic" species, but as substituents in addition to being "electronegative" they also can behave as electron donors.

$$\ddot{X}\text{-}\dot{C}HR \longleftrightarrow \overset{+}{\ddot{X}}\text{-}\ddot{\overset{-}{C}}HR.$$

Exactly the same is true for OMe both as a radical ($CH_3O^{\cdot}$) and as a substituent. There are comparatively little data about ethers or OMe radicals but there are good kinetic data about F and Cl substituents (Table 16).

Table 16 shows that the electron donating properties of substituent halogen atoms outweighs their electron attracting properties for these nearly thermoneutral or endothermic reactions. H abstraction from the halogenomethanes by Me and trifluoromethyl radicals and by Br atoms is enhanced by the introduction of one or two halogen atoms and indeed dichloromethane and difluoromethane are more reactive than chloromethane and fluoromethane respectively. Three F atoms in fluoroform are necessary for the polar effect (supplemented by the bond strength) to inhibit attack by electronegative Br atoms. In contrast however the three chlorine Cl atoms of chloroform greatly enhance the rate of H abstraction by Br atoms and trifluoromethyl radicals presumably because release of steric strain overcomes the polar effect of the Cl atoms.

Table 16. Hydrogen abstraction from the halogenomethanes (gas phase)

	Br·		CF_3·		CH_3·	
R-H	log A	E	log A	E	log A	E
CH_3-H	11.0	18.6	9.2	11.5	8.8	14.2
FCH_2-H	10.7	16.1	9.1	11.2	8.2	11.8
$ClCH_2$-H	10.9	14.7	9.1	10.6	8.9	9.4*
F_2CH-H	10.4	15.6	8.9	11.2	8.0	10.4
Cl_2CH-H	10.0	10.9	9.1	10.6	8.5	7.2
CF_3-H	10.1	22.3	-	-	7.4	13.6
CCl_3-H	9.4	9.3	8.1	6.6	7.8	10.8

Direct effects of substituents I

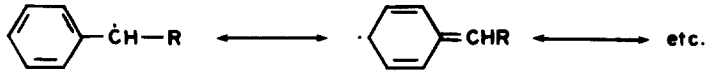
Halogenation. The effect of substituents is better investigated by the study of larger molecules than substituted methanes, not only to investigate the influence of the substituents on non-adjacent atoms but also because small differences in rates of attack are more easily confirmed. The results are best expressed in terms of relative selectivity (RS_x^y) where superscript y denotes the atom in question and x denotes the atom taken as standard and the ratio is corrected for the number of H atoms at each site.

Table 17. The relative selectivities RS_3^y for the chlorination of 1-substituted butanes at 50° in the gas phase*

X	α CH_2	β CH_2	γ CH_2	δ CH_3	Ref.
X=H	1	3.6	3.6	1	(24)
F	0.9	1.7	3.7	1	(4)
Cl	0.8	2.1	3.7	1	(4)
Br	0.4	-	3.6	1	(4)
CF_3	0.04	1.2	4.3	1	(29)
FOC	0.08	1.6	4.2	1	(26)
ClOC	0.2	2.1	3.9	1	(26)
CH_3O_2C	0.4	2.4	3.6	1	(26)
HCO_2	-	1.5	4.1	1	(27)
CH_3CO_2	0.7	2.2	4.3	1	(27)
CF_3CO_2	0.2	1.4	4.0	1	(27)
N≡C	0.2	1.7	3.9	1	(30)
O_2N	<0.01	-	3.9	1	(31)
CH_3O	3.5	0.7	4.4	1	(26b)
$(CH_3)_3C$	2.9	3.7	5.3	1	(28)
C_6H_5	6.5	1.3	(4)	1	(27)

*Rounded off values

The most evident feature of Table 17 is that the relative selectivities for attack at the γ and δ-positions are very similar no matter what the substituent. This suggests that in gas phase chlorination a substituent has little effect beyond the second carbon atom. This conclusion may need some modification when bulky groups are involved, but polar effects are definitely too attenuated at the γ-position to have a significant effect on the rate of H abstraction by halogen atoms *in the gas phase.* At the α-position only three of the sixteen different substituents accelerate hydrogen abstraction by Cl atoms. The phenyl group undoubtedly stabilises the incipient radical by delocalising the unpaired electron:



With the OMe group such delocalisation requires contribution from a polar structure, and it is perhaps surprising that the

$$CH_3O\dot{C}HC_3H_7 \leftrightarrow CH_3\overset{+}{\dot{O}}\text{–}\overset{-}{\ddot{C}}H\text{–}O_3H_7$$

rate of attack is so high especially as ester groups are strongly deactivating. Clearly the adjacent CO bond of the ester prevents the alkyl oxygen acting as a donor at all. The activating properties of the *t*-Bu group could be attributed to polarity or to release of steric strain overcoming the steric hindrance which obstructs the approach of the Cl atom. The electronegativity of the substituent halogens almost exactly counterbalances their ability to delocalise the unpaired electron. It is noticeable that the trifluoromethyl group which cannot delocalise the unpaired electron is the most deactivating substituent at the α-position, in sharp contrast to the F atom which has similar electronegativity but which can delocalise the unpaired electron (see above). With the exception of the *t*-Bu group all the other groups are electronegative and slightly retard abstraction from the β-position.

Table 18. The relative selectivities RS_δ^γ for the bromination of 1-substituted butanes at 160° in the gas phase*

X	α CH_2	β CH_2	γ CH_2	δ CH_3	Ref.
H-	1	80	80	1	(4)
F-	9	7	80	1	(4)
Cl-	35	30	80	1	(4)
CF_3-	<1	7	80	1	(29)
FOC-	35	25	80	1	(25)
ClOC-	30	30	80	1	(25)
CH_3O-OC-	40	35	80	1	(25)
CH_3COO-	20	30	80	1	(26)
CF_3COO-	2	7	80	1	(26)
N≡C	25	8	80	1	(30)
O_2N-	2	?	70	1	(31)

* Rounded off values (α and β to the nearest whole number, γ to nearest multiple of 10)

Table 18 confirms that any polar effect of the substituent is too attenuated at the γ-position to have a significant effect on hydrogen abstraction by Br atoms in the gas phase. The most significant feature of Table 18 is however that every substituent except the trifluoromethyl group enhances H abstraction by Br atoms at the α-position, in sharp contrast to Table 17 where all the same substituents inhibit H abstraction by Cl atoms. Thus in the exothermic chlorine reaction polarity governs the reaction, while in endothermic bromination the polar effect, although still present, is completely overruled by the influence of bond strength, which is controlled in this case by the release of steric compression.

The relative selectivities for the chlorination of 2-substituted butanes are listed in Table 19. It shows that H abstraction from the substituted site (β) is only slightly retarded by all the electronegative

Table 19. Relative selectivities RS_δ^γ for the chlorination of 2-substituted butanes at 60° in the gas phase

X	α CH_3	β CHX	γ CH_2	δ CH_3*	Ref.
H-	1	3.6	3.6	1	
F-	<0.1	4.7	2.7	1	(32)
Cl-	0.2	4.2	4.1	1	(32)
FOC-	0.2	2.0	4.8	1	(33)
ClOC-	0.2	1.8	4.0	1	(33)
$CH_3CO{\cdot}O$-	0.3	2.1	2.8	1	(33)
$CF_3CO{\cdot}O$-	0.2	1.3	3.9	1	(33)
N≡C-	0.2	2.6	3.6	1	(33)
C_6H_5-	0.8	2.7	3.0	1	(33)
O_2N-	0.04	0.15	1.8	1	(33)

* α-position taken as 1, all values rounded off

substituents (except NO_2). In the secondary position the presence of a substituent will increase the steric strain. The α-position in the 2-substituted butane is much more deactivated by a particular substituent than the β-position in the 1-substituted butane is deactivated by the same substituent. This is because the release of steric compression when a hydrogen is abstracted from the primary α-position in the 2-substituted butane is small.

In bromination of 2-substituted butanes the reaction is almost entirely restricted to attack at the substituted 2(β)-position, for all but the most polar substituents. Only the nitro-group (O_2N–) and the trifluoroacetoxy group ($CF_3CO{\cdot}O$–) are sufficiently polar to reduce the rate of hydrogen abstraction from the substituted site below that of the 3(γ)-position.[30]

Direct effect of substituents II

Radicals. So far our discussion of free radical substitution of longer chain substituted alkanes has been restricted to halogenation because this is the easiest to study. The ideal system incorporates a chain mechanism:

$$X-Y \rightarrow X^{\cdot}+Y \qquad \text{initiation}$$

$$\left.\begin{aligned} X^{\cdot}+RH &\rightarrow HX+R^{\cdot} \\ R^{\cdot}+X-Y &\rightarrow R-Y+X^{\cdot} \end{aligned}\right\} \text{chain propagation.}$$

Unfortunately many obvious chain carrying steps are endothermic or almost thermoneutral so that the second atom transfer step becomes too slow and the radicals disappear in radical-radical or radical-wall reactions. For example X–Y could be methyl iodide (CH_3–I), but iodine abstraction by alkyl radicals ($R^{\cdot}$) is endothermic and therefore so slow that almost no chain reaction is observed. For this reason the data relating to Me radicals in Tables 20 and 21 are only approximate.

Table 20. The relative selectivities RS_δ^α of different atoms and radicals from 1-fluorobutane in the gas phase

Atom or Radical	Temp	$\overset{\alpha}{F\text{-}CH_2}—\overset{\beta}{CH_2}—\overset{\gamma}{CH_2}—\overset{\delta}{CH_3}$				(Ref)
F·	<25	0.3	0.8	1	1	(24)
Cl·	25	0.9	2	4	1	(24)
tBuO·	25	7	3	8	1	(34)
CF_3·	150	2	2	14	1	(35)
CH_3·	150	8	10	10	1	(35)
CCl_3·	150	7	--	90	1	(36)
Br·	150	10	9	90	1	(24)

Table 20 shows that the four radicals fall into the same overall pattern as the halogen atoms. The β-position is deactivated to all the electrophilic radicals, but not to Me radicals. On the other hand the combination of delocalisation of the unpaired electron and the release of steric compression is sufficient to ensure that H abstraction by all the atoms and radicals except the electronegative F and Cl atoms is actually enhanced at the 1 (α)-position.

Table 21 shows that the deactivating polar effect of the trifluoromethyl group completely overcomes any effect due to the release of steric strain and only Me radicals show enhanced attack at the 1(α)-position (the low reactivity of the β-position to methyl radical attack is probably due to a poor iodine transfer step as discussed above). The relatively high rate of Me radical attack at the α-position is significant (poor iodine transfer would lead to an under-estimate) since there is good evidence to suggest that C–H bonds adjacent to a powerful electronegative group are strengthened, i.e. some of the lack of reactivity of the other radicals and atoms at the α-position is due to the strength of the C–H bonds adjacent to the CF_3– group as well as unfavourable polarity in the transition state. The bulk of the CF_3– group may also hinder the approach of the incoming radical.

Table 21. The relative selectivities R_s^x of different atoms and radicals in abstracting hydrogen from 1,1,1-Trifluoropropane in the gas phase

Atom or Radical	Temp	$\overset{\alpha}{CF_3}\overset{}{CH_2}-\overset{\beta}{CH_2}-\overset{\gamma}{CH_2}-\overset{\delta}{CH_3}$				(Ref)
Cl·	25	0.03	1	4	1	(29)
CF_3·	150	0.1	2	14	1	(35)
CH_3·	150	1.3	3	10	1	(35)
CCl_3·	150	0.6	11	90	1	(36)
Br·	150	<0.5	7	90	1	(29)

CONCLUSIONS

Free Radical Substitution is a two stage process involving two discrete atom (or group) transfers. In the examples discussed in the article the course of the overall reaction is determined by the initial atom transfer. The rate is governed by two terms, the pre-exponential term (or "A"-factor) and the activation energy.

$$R\text{–}H + X^{\cdot} \rightarrow R^{\cdot} + HX.$$

The "A"-factor varies by nearly three orders of magnitude depending on whether the initial species X· is an atom or a radical. [See Table 1.] However the "A"-factors vary very little from radical to radical [see Table 1] or to changes in the attacked molecule (RH). [See Table 2.] We can thus reduce the factors which control Free Radical Substitution Reactions to two, the relative strengths of the bonds being broken and formed, and to polarity in the transition state. We can express the effect of these factors as a set of qualitative rules:

(i) If there is little polarity (or if the polarity is constant) the relative rate of atom transfer by a particular radical will depend on the strength of the bond being broken. This finds expression in the Evans–Polanyi equation which applies when X· is constant and R varies:

$$E_{act} = \alpha[D(R-H)] + \beta.$$

The strength of the bond being broken can be regarded as being affected by two factors (apart from polarity)

(a) resonance stabilisation of the incipient radical (normally unimportant).

$$:\ddot{\underset{\cdot\cdot}{Cl}}\text{–}\dot{C}HR \longleftrightarrow :\overset{+}{\ddot{Cl}}\text{–}\bar{\ddot{C}}HR$$

(b) the extent to which steric strain is released in forming the new radical.

(ii) The strength of the bond being formed is equally important. If there is no polarity in the transition state (or polarity is constant) the selectivity of radical X· for different sites will depend on the heat of reaction (ΔH large and positive a very selective reaction: ΔH large and negative a very unselective reaction.)

	R–H(1°)	R–H(2°)	R–H(3°)	ΔH k cal mol^{-1}
X = F	1	1	2	−36
X = I	1	1000	97000	+27

(iii) In thermoneutral transfer reactions the activation energy is dependent on the degree of polarity in the transition state (the greater the polarity the lower the activation energy).

$$\text{NON-POLAR: } H^{\cdot} + CH_4 \rightarrow H_2 + CH_3^{\cdot} \quad E_{act} = 11.9 \text{ k cal mol}^{-1}$$
$$\Delta H \simeq -1 \text{ k cal mol}^{-1}$$

$$\text{POLAR: } \overset{+\rightarrow}{CH_3}^{\cdot} + \overset{+\rightarrow}{HCl} \rightarrow CH_4 + Cl^{\cdot} \quad E_{act} = 2.5 \text{ k cal mol}^{-1}$$

$$\Delta H \simeq -1 \text{ k cal mol}^{-1}.$$

Even in reactions which are not thermoneutral, polarity can be the controlling factor, overriding the effect of bond strength if the reactions are slightly exothermic, e.g.

$$\overset{\leftarrow+}{CF_3}^{\cdot} + \overset{+\rightarrow}{HCl} \rightarrow CF_3H + Cl^{\cdot} \quad E_{act} = 5.0 \text{ k cal mol}^{-1}$$

$$\Delta H = -3 \text{ k cal mol}^{-1}$$

(less polar transition state than Me and slower in spite of a more negative heat of reaction).

In a series of reactions involving atom transfer from similar sites (e.g. H atoms from the Me group of substituted toluenes) polarity can be observed in Free Energy Relations of the Hammett type (Fig. 2)

$$Y\text{-}C_6H_4CH_3 + X^{\cdot} \rightarrow YC_6H_4CH_2^{\cdot} + HX$$

$$X = Cl \text{ Hammett } \rho = 0.66 \quad X = Br \text{ Hammett } \rho = 1.76.$$

(iv) In exothermic reactions the transition state is early and although polarity may be significant (retarding "a" and accelerating "b"), neither release of steric strain nor delocalisation of the unpaired electron in the incipient radical are important, while in endothermic

$$\left.\begin{array}{rcl} Cl^{\cdot} + CCl_3H & \overset{a}{\rightarrow} & HCl + CCl_3^{\cdot} \quad \Delta H = -6 \text{ k cal mol}^{-1} \\ Cl^{\cdot} + CH_4 & \overset{b}{\rightarrow} & HCl + CH_3^{\cdot} \quad \Delta H = +1 \text{ k cal mol}^{-1} \end{array}\right\} \frac{k_a}{k_b} = 1.0 \ (164°C)$$

reactions the transition state is late, polarity has less effect but both release of steric compression and delocalisation of the unpaired electron in the incipient radical are important.

$$\left.\begin{array}{rcl} Br^{\cdot} + CCl_3H & \overset{a}{\rightarrow} & HBr + CCl_3^{\cdot} \quad \Delta H = +10 \text{ k cal mol}^{-1} \\ Br^{\cdot} + CH_4 & \overset{b}{\rightarrow} & HBr + CH_3^{\cdot} \quad \Delta H = +17 \text{ k cal mol}^{-1} \end{array}\right\} \frac{k_a}{k_b} \ (164°C) \quad 1{,}000$$

(v) Radicals (or atoms) which lead to polar transition states can be regarded as "electronegative" (e.g. the halogens) or "electropositive" (e.g. trialkyl germanium radicals). Electron withdrawing substituents will enhance transfer reactions by electropositive radicals and retard reactions with electronegative radicals.

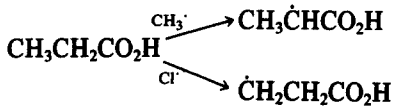
$$XCCl_2\text{–}H + Br^{\cdot} \rightarrow XCCl_2^{\cdot} + HBr$$

$$XCCl_2\text{–}Cl + Me_3Ge^{\cdot} \rightarrow XCCl_2^{\cdot} + Me_3GeCl$$

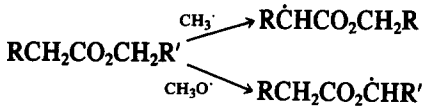
$$X = H \text{ or } F$$

$$k^F_{Br}/k^H_{Br} = 0.04 \quad k^F_{Me_3Ge}/k^H_{Me_3Ge} = 9.1.$$

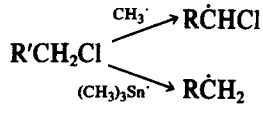
In more general examples this can lead to different radicals attacking different sites in the same molecule:



Similarly:



or abstracting a different atom:



Polarity and bond strength have been treated above as though they were independent variables. It is important to remember that this is an approximation and polarity and bond strength are necessarily intimately related and cannot be completely separated. However, much of mechanistic organic chemistry is built on qualitative theory employing the concept of polarity as an independent phenomenon. The success of this approximation speaks for itself and the whole purpose of the present article is to provide an account of free radical substitution reactions in these terms. Most of the work described is in the gas phase because the effect of the solvent on free radical reactions is very little understood and deserves an article on its own. This means that much important work (notably the amino-radical cation[34]) has been omitted. However if a comprehensive theory is to be constructed we must understand the reaction in the gas phase first before we tackle the problem in solution.

This report attempts to summarise the current position in free radical substitution reactions and to provide a qualitative picture for organic chemists not working in the field. It is not a comprehensive review and indeed wherever possible the data have been taken from compilations (e.g. Refs. 6 and 7). Otherwise the Tables are compiled from the work of one laboratory wherever possible, in the belief that any systematic error due to the experimental methods employed will be constant. It is important to acknowledge that this has meant that there are many workers in laboratories across the world who have contributed to the conclusions drawn in this article and yet whose names do not appear in the references.

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