CHRISTOPH RÜCHARDT

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Steric Effects in Free Radical Chemistry

Christoph Rüchardt*

Chemisches Laboratorium der Universität Freiburg, Albertstr. 21, D-7800 Freiburg i. Br., Federal Republic of Germany

Dedicated to Professor H. Pommer on the occasion of his 60th birthday.

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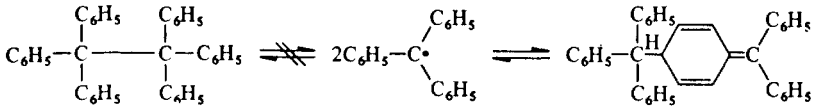
* This review is an extended version of an article in „Zeitschrift der Sowjetischen Chemischen

I Introduction

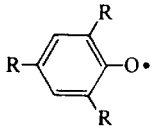
Steric effects have been discussed in free radical chemistry ever since the discovery of the first free radical, triphenylmethyl *1* by M. Gomberg in 1900[1]. To what extent is the dissociation of its dimer, which was believed to be hexaphenylethane *2*[3] till 1968[2], determined by electronic stabilization of triphenylmethyl *1*[4] or by steric strain in its dimer?



2 *1* *3*

The opinion that stabilization of *1* by resonance was decisive, predominated for a long time and mastered the discussion of the relationship between structure and reactivity in free radical chemistry till quite recently[5]: Accordingly selectivity in free radical reactions was assumed to be mainly due to differences in the thermodynamic stability of the radicals taking part in a reaction or a potential competing reaction.

The recognition[2] that the α, p-dimer *3* is formed in equilibrium with *1* and not the α,α-dimer *2* was interpreted as a result of the smaller steric strain in *3* than in *2*[3]. Also the known strong influence of p-substituents on the equilibrium constants between substituted trityl radicals and their dimers[6] found an obvious explanation in this way. The earlier observation that not only those phenoxy radicals *4* carrying three conjugating phenyl substituents *4* (R = C_6H_5)[7a] are persistent[8] but also their



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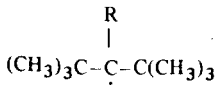
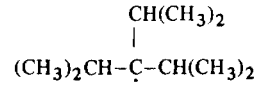
t-butylated counterparts *4* (R = t–C_4H_9)[7b] pointed to the predominating influence of steric effects. Similar results have been obtained in other classes of persistent radicals[7c, 8]. The most convincing evidence for the prime importance of steric effects for the persistence of radicals was provided by the observation of a large series of crowded alkyl radicals like *5*–*7* over longer periods of time by esr. They do not dimerize for energetic reasons[9, 10].



5 R = H
6 R = $C(CH_3)_3$



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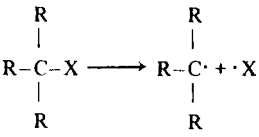
Since these developments became known the importance of steric effects on the reactivity of free radical reactions has also been more clearly recognized and more thoroughly investigated[11]. Some more important and more recent results along these lines are the topic of this review.

Finally it has to be remarked briefly that the reactivity and selectivity of free radicals is certainly not only determined by steric and bond energy effects or by the thermodynamic stability of these transients. Polar effects are also important, in particular in those reactions which have "early" transition states e.g., the steps of free radical chain reactions[12]. They are either due to dipole interactions in the ground state or to charge polarization at transition states. FMO-theory apparently offers a more modern interpretation of many of these effects[13].

II Steric Effects in Homolytic Decomposition Reactions

When an alkyl free radical *9* is generated by homolytic cleavage of a C–X bond in its precursor *8*



8 *9*

hybridization at the central C-atom changes simultaneously from sp^3 towards sp^2 [14]. All repulsive forces between the substituents R decrease when the bond angles are increased accordingly. Therefore conformational effects can also influence the ease of generation of alkyl radicals.

1 Ring Size Effects

As a model system for demonstrating conformational effects on the rate of radical generation the determination of the influence of the ring size on the rate of formation of cycloalkyl radicals was chosen. Ring size effects on the rate of generation of cycloalkyl carbenium ions were known from the works of Prelog and Brown[15] and were explained by the I-strain[15] i.e., on conformational grounds. During carbenium ion formation the five-ring system loses conformational strain relative to the six-ring system. Cyclopentyl esters therefore solvolyze faster than their cyclohexyl counterparts. Particularly high rate constants were observed for the medium-ring systems. The large transannular nonbonded interactions are partially relieved on ionization due to the formation of planar or nearly planar carbenium ions[16]. When cycloalkyl radicals are generated both effects are also found, in fact the more distinctly, the closer the transition state geometry is approaching the sp^2-state of the radicals[5, 12, 17, 18].

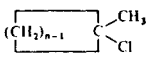
Table 1. Relative rates of formation of cyclic carbenium ions and free radicals from precursors *10–19*[a]

n	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*
4	2.77	0.03	0.03	0.06	0.297	0.084	0.12	0.23	$1.86 \cdot 10^{-5}$	–
5	124.9	11.5	70.5	2.75	1.18	0.787	0.33	0.47	5.43	0.00
6	≡1.00	≡1.00	≡1.00	≡1.00	≡1.00	≡1.00	≡1.00	1.00	≡1.00	≡1.00
7	108.6	194.0	190	42.8	–	–	1.68	2.27	$2.2 \cdot 10^{4}$	65
8	285.7	1325	–	187	–	–	2.46	4.27	$3.5 \cdot 10^{6}$	>400(
9	44.0	–	–	–	–	–	2.05	4.02	–	–
10	17.8	292	–	–	–	–	1.93	3.26	–	–
11	12.0	–	–	–	–	–	1.89	2.77	–	–
12	–		–	–	–	–	1.76	1.92	–	–

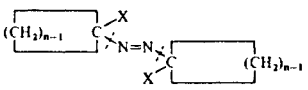
[a] The bonds cleaved in the rate determining step of homolytic decomposition of *11–19* are indicated in the formula.

The five-ring – six-ring effect is larger for the endothermic azo decompositions of *11–13* ($\Delta H^{\ddagger} \approx 20$–$50$ kcal/mol)[19–21] than for the decarbonylation of *14* and *15*[22] ($\Delta H^{\ddagger} \approx 9$–$15$ kcal/mol)[23]. The five membered cyclic hydrocarbon *18* ($\Delta H^{\ddagger} \approx 50$ kcal/mol)[24] also decomposes faster than the six membered. The effect is, however, smaller in this example than for the thermolysis of the corresponding azo compounds *12*. This is probably due to the grossly different decomposition temperatures of *18* and *12* and to the overlapping influence of F-strain for *18* (see below). One recognizes from the data in Table 1 that the five-ring – six-ring effect is generally the largest, when α-phenyl- or α-cyano-conjugated radicals are generated. Conjugated radicals require a more strictly planar geometry than unconjugated alkyl radicals[14] (cf. *11–13*). The rate of generation of secondary alkyl radicals from *14* or *17* also responds more strongly to ring size effects than the rate of generation of tertiary radicals from *15* and *16*[25]. The formation of secondary radicals is a more endothermic process. The smallest ring size effect and even an inverse five-ring – six-ring effect is observed in the thermolysis reactions of the peresters *16* and *17*, although all evidence points to a concerted homolytic fragmentation mechanism for these reactions[25]. Apparently, at the transition state of this endothermic reaction the peroxide bond is nearly broken, while the stronger C_{α}-CO-bond is stretched only to a relatively small extent. Therefore, hybridization and geometry at C_{α} have hardly changed. This interpretation is supported by the study of α-CH_3O-[12c], α-CN-[12c] and α-phenyl-substituent effects and by other criteria[5, 12, 18].

Exceptional behavior among the reactions of Table 1 is shown by the thermolysis reaction of *18*. While the direction of the five-ring – six-ring effect is normal, a particular large rate enhancement (10^4–10^6) is found for the thermolysis of the seven and eight membered compounds and an unexpected high thermal stability for the four membered one. Apparently the thermolysis rates of *18* are not only determined by the change in the I-strain but much more by the strong repulsive Van der Waals interactions across the central C-C-bond which are revealed on bond homolysis. A smaller effect of similar nature is recognized in the decomposition rates of *cis*-1-methyl-1-azocycloalkanes *19*[26]. Because of the low activation enthalpies of *cis*-azo decompositions ($\Delta H^{\ddagger} \approx 10$–$15$ kcal/mol)[26] the small five-ring – six-ring effect was



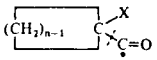
10[15] 80% EtOH, 25°C



11[19] X = CN, toluene, 80°C

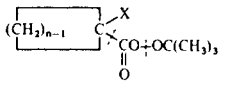
12[20] X = C_6H_5, benzene, 60°C

13[21] X = CH_3, benzene, 200°C



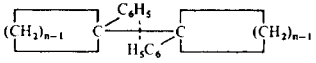
14[22] X = H, 125°C

15[22] X = CH_3, 135°C

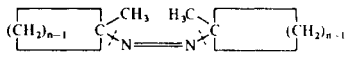


16[25] X = CH_3, benzene, 80°C

17[25] X = H, ethylbenzene, 110°C



18[24] Octane, 220°C

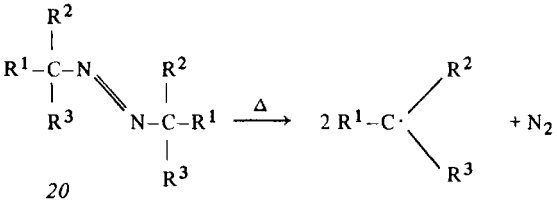


19[26] Ethanol, −28°C

expected because the C-N-bonds are stretched much less at transition state than in the *trans*-azo series. The particularly high rates of thermolysis of *19* (n = 7–8) most probably are due to the release of Van der Waals repulsive interactions between the *cis*-oriented 1-methyl-cycloalkyl groups.

2 Group Size Effects

The influence of the group size on the rate of generation of alkyl radicals has been investigated for the same reactions as mentioned in Table 1 [12a, 27]. Most information is available on the thermolysis of t-azoalkanes *20* (R^1–R^3 = alkyl)[28].



20

Qualitatively the same reactivity pattern was observed for the decomposition of *sym.* azonitriles *20* (R^1 = CN, R^2, R^3 = alkyl)[29] and several symmetrically and unsymmetrically substituted azo compounds[30]. A selection of these results is found in Table 2. It is apparent from these data that the thermal stability of *20* decreases as the size of the groups R^1–R^3 increases. Rüchardt et al. have observed that a linear relationship exists between the thermolysis rates of Table 2 and the S_N1-solvolysis rates of corresponding *t*-alkyl-p-nitrobenzoates *21* in 80% acetone-water[28d]. The

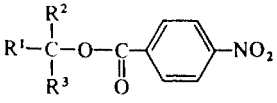


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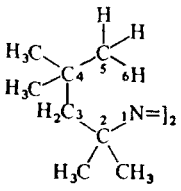
Table 2. Rate Constants k_{rel} and activation parameters for the thermolysis of azoalkanes $R^1R^2R^3C-N=)_2$ *20* in hydrocarbon solvents

R^1	R^2	R^3	$k_{rel.}$ (180 °C)[a]	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$ e. u.
CH_3	CH_3	CH_3	≡1.00	43.2[b]	17.7[b]
CH_3	CH_3	C_2H_5	1.19	–	–
CH_3	CH_3	1-C_3H_7	[3.3[c]]	40.7[b]	14.2[b]
CH_3	CH_3	1-C_8H_{17}	2.27	–	–
CH_3	CH_3	2-C_3H_7	3.00	–	–
C_2H_5	C_2H_5	C_2H_5	3.65	–	–
CH_3	CH_3	*t*.But.	5.30 [7.7[c]] [13[d]]	40.9[b]	16.3[b]
CH_3	CH_3	*i*-But.	7.51	–	–
CH_3	2-C_3H_7	2-C_3H_7	23.0	–	–
CH_3	C_2H_5	*t*.-But.	36.5	–	–
C_2H_5	C_2H_5	*t*.But.	107	–	–
2-C_3H_7	2-C_3H_7	2-C_3H_7	206	–	–
CH_3	CH_3	neo-Pentyl	247 [480[c]] [1320[d]]	35.6[a]	11.9[a]
CH_3	2-C_3H_7	neo-Pentyl	453	33.8[a]	9.4[a]
CH_3	CH_3	neophyl	[706[c]]	35.0[b]	11.4[b]
CH_3	neo-Pentyl	neo-Pentyl	[57000[d]]	30.0[e]	5.2[e]

[a] Ref.[28d] [b] Ref.[28c] [c] at 150 ° see Ref.[28c] [d] at 100 °C see Ref.[28a] [e] Ref.[28a]

slope of this correlation is approximately 1. Because both series respond in the same way to group size, steric acceleration by relieve of back strain was proposed as common interpretation[28]. During homolysis of *20* as well as heterolysis of *21* the repulsive Van der Waals interactions between the side chains R^1-R^3 are continuously reduced because the bond angles between these groups are increased during the change of hybridization from sp^3 towards sp^2. Interestingly those examples in Table 2 which carry a neopentyl side chain deviate from the observed correlation. It is assumed that the particularly fast thermolyses rates of neopentyl substituted azo compounds like *22* are due to another type of ground state strain which is releaved on homolysis. It was proposed that due to γ-branching and according to Newman's rule six[31] heavy Van der Waals repulsions between the methyl hydrogens of the neopentyl groups



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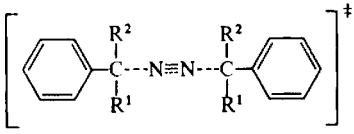
and the nitrogen atoms are acting as shown in *22*. The same extraordinary rate enhancing effect of neopentyl side chains was observed for the thermolysis rates of azonitriles *20* (R^1, R^2 = alkyl, R^3 = CN)[29a] and α-carbomethoxy-azoalkanes *20* (R^1, R^2 = alkyl, $R^3 = COOCH_3$)[32]. For α-phenyl substituted azoalkanes *20* (R^1, R^2 = alkyl, $R^3 = C_6H_5$) the relationship between thermal stability and size of the groups R^1 and R^2 is more complex, apparently because the resonance stabilization of the developing radical center at the transition state *23* decreases with increas-



23

ing group size[33]. This could be partly due to steric hindrance of resonance[34]. In addition, however, the transition state *23* is probably reached earlier on the reaction coordinate when the group size of R^1 and R^2 is increased. According to the Hammond principle[17] this means less C-N-bond stretching and less radical character in *23*. For symmetrical azo compounds *20* (R^1, R^2 = alkyl, R^3 = alkyl, CN, $COOCH_3$, C_6H_5) there is good evidence that both C-N-bonds are cleaved more or less simultaneously in the rate determining step[35]. This is not generally so for unsymmetrical azo compounds $R^1N_2R^2$ [36].

In comparison with the decomposition of *trans*-azoalkanes *20* a much larger group size effect has been found for the thermolysis rates of a few *cis*-azoalkanes *24*. Due to the repulsion of the free electron pairs on the two nitrogen atoms and due to steric interaction between the *cis* oriented alkyl groups *cis* azoalkanes *24* decom-

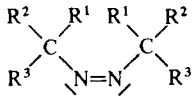


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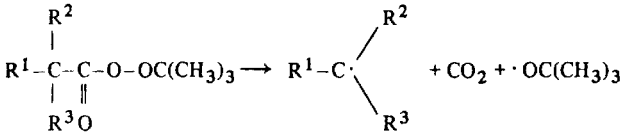
Table 3. Steric acceleration of thermolysis of *trans*-azoalkanes *20* (180 °C, ethylbenzene) and *cis*-azoalkanes *24* (−28 °C, ethanol)

R^1	R^2	R^3	$k_{rel}(20)$	$k_{rel}(24)$[37]
CH_3	CH_3	CH_3	≡1.00	≡1.00[a]
CH_3	CH_3	C_2H_5	1.19	4.4
CH_3	CH_3	i-C_3H_7	3.00	64
CH_3	CH_3	i-C_4H_9	7.51	153
CH_3	C_2H_5	C_2H_5	1.87	37
C_2H_5	C_2H_5	C_2H_5	3.65	1428
CH_3	CH_3	t-C_4H_9	5.30	>1600

[a] $k_1 = 0.615 \cdot 10^{-4}\ s^{-1}$

pose at much lower temperatures into radicals[35c, 37]. Although the transition state of this much less endothermic reaction should be located earlier on the reaction coordinate than for the thermolysis of *20*[12a, 17], rates are subject to larger steric acceleration. In addition to the relief of back strain, front strain between the to groups $R^1R^2R^3C$ also becomes important (cf. Table 3).

The rates of homolytic fragmentation of peroxyesters *25* are also enhanced when the size of the side chains R^1-R^3 = alkyl is increased. This is shown for several examples in Table 4. The rate enhancing effect is smaller than for the azoalkane thermolyses



25

discussed above. Taking into account, however, the multiplicative back strain effect in both alkyl parts of azoalkanes, then the effect of steric acceleration becomes comparable for the thermolysis of *20* and *25*. The different temperature of these two thermolyses reactions may partly be responsible for this. The data of the two series even show a linear correlation with the slope ~ 1 on a logarithmic scale[38b]. Again only the neopentyl substituted compounds deviate from this correlation as discussed previously.

It is somewhat contradictory and not yet fully understood why the back strain effect on the rate of perester decompositions is so large. We had reasoned before from the discussion of conformational effects that the C_α-CO-bond of *25* is only stretched to a small extent at transition state. From an analysis of bond energies[5, 18] it becomes questionable if the homolysis of C-N-bonds (as in *20*) and C-C-bonds (as in *25*) is likely to be directly comparable[5, 12a, 18]. In addition the extent of C_α-CO-cleavage at the transition state of fragmentation of *25* may well be itself dependent on the

Table 4. Steric acceleration of thermolysis of peroxyesters *25* in ethylbenzene at 60 °C[38]

R^1	R^2	R^3	k_1(rel) (60 °C)	$\Delta H^\ddagger$ kcal/mol	$\Delta S^\ddagger$ e.u.
CH_3	CH_3	CH_3	≡1.00	28.3	5.3
CH_3	CH_3	C_2H_5	1.29		
CH_3	CH_3	1-C_8H_{16}	1.73		
CH_3	CH_3	$(CH_3)_2CHCH_2$	2.30		
C_2H_5	C_2H_5	C_2H_5	3.19		
C_2H_5	C_2H_5	2-C_3H_7	6.50		
CH_3	CH_3	$(CH_3)_3C$	3.4	27.2	4.6
CH_3	CH_3	$(CH_3)_3CCH_2$	2.6	26.5	2.0
2-C_3H_7	2-C_3H_7	2-C_3H_7	32	26.6	6.7

size of the groups R^1-R^3 in *25*. This is indicated e.g., by the small steric acceleration observed when the rates of decomposition of a series of peresters *25* (R^1,R^2 = alkyl, $R^3 = C_6H_5$) with alkyl side chains of different bulk are compared[33].

Table 5. Thermal decomposition of hydrocarbons $R^1R^2R^3C\text{-}CR^1R^2R^3$. Temperature T for $t_{1/2}$ = 1 h, free enthalpy of activation $\Delta G^{\ddagger}$ at 300 °C and strain enthalpy E_S[a]

No.	R^1	R^2	R^3	T[°C] ($t_{1/2}$ = 1 h)	$\Delta G^{\ddagger}$(300 °C) [kcal/mol]	E_S[a] [Kcal/mol]	Ref.
1	CH_3	CH_3	CH_3	490	60.5	7.8	39b, 42)
2	CH_3	CH_3	C_2H_5	420	55.3	14.9	43, 45)
3	CH_3	CH_3	1-C_3H_7	411	53.6	14.8	44)
4	CH_3	CH_3	1-C_4H_9	412	53.9	14.5	44)
5	CH_3	CH_3	i-C_4H_9	384	51.9	18.7	45)
6	CH_3	CH_3	2-C_3H_7	329	46.4	26.3	45)
7	CH_3	CH_3	$(CH_3)_3CCH_2$	321	46.3	27.8	45)
8	CH_3	CH_3	c-C_6H_{11}	315	45.8	32.1	43, 45)
9	C_2H_5	C_2H_5	C_2H_5	285	43.1	42.4	43, 45)
10	CH_3	C_2H_5	c-C_6H_{11}	250	39.6	44.3	43, 45)
11	CH_3	CH_3	*t*-C_4H_9	195	33.7	51.8	45)
12	CH_3	CH_3	H	565	68	2.0	46)
13	C_6H_{11}	C_6H_{11}	H	384	52.1	22.8	45, 47)
14	C_6H_{11}	*t*-C_4H_9	H(D, L)	329	46.7	32.6	45, 48)
15	C_6H_{11}	*t*-C_4H_9	H(meso)	285	42.6	38.5	45, 48)
16	*t*-C_4H_9	*t*-C_4H_9	H	141	29.6	62.7	45, 49)
17	CH_3	H	H	590	69	0	50)
18	H	H	H	695	79	0	51)
19	2.2.4.4 Tetramethylpentane[b]			502	63.9	6.4	45)
20	2.2.3.4.4 Pentamethylpentane[b]			415	55.8	15.1	45)
21	2.2.3.3.4.4 Hexamethylpentane[b]			350	48.8	24.9	45)
22[c]	CH_3	C_6H_5	H	365	50.0	2.8	41)
23[c]	C_2H_5	C_6H_5	H	363	49.7	4.0	41)
24[c]	i-C_3H_7	C_6H_5	H	335	47.4	7.6	41)
25[c]	*t*-C_4H_9	C_6H_5	H	289	42.1	21.4	41)
26[d]	*t*-C_4H_9	C_6H_5	H	303	44.6	18.5	41)
27[c]	*t*-C_5H_4	C_6H_5	H	259	40.3	24.6[e]	41)

[a] Difference in heat of formation as calculated by the force fields according to Ref.[39] (for *1–21*) and Ref.[40] (Set B) for *22–27* and the hypothetical heat of formation of the unstrained molecules[39b, 41].

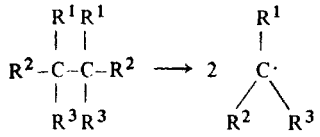
[b] a statistical correction $k_1 = k_{exp.}/2$ was introduced because this molecule has two equivalent bonds which can be cleaved on thermolysis.

[c] meso-diastereomer

[d] racem.diastereomer

[e] experimental value from heat of combustion

As previously pointed out in the discussion of ring size effects on bond homolyses the largest steric acceleration by bulky substituents is expected for the thermal cleavage of C-C-bonds in tetra- or hexasubstituted ethanes *26*. Im comparison to azoal-



26

kanes the N_2-group separating the two alkyl fragments is missing in *26*. Therefore much stronger front strain interaction across the central C-C-bond is expected in *26* than was found between the alkyl groups in *20* or *24*. This is verified by the results in Table 5. The temperature at which the hydrocarbons recorded in the table decompose with a half time $t_{1/2}$ = 1h varies between 695 °C for ethane and 141 °C for sym. tetra-*t*-butylethane. The difference in free enthalpy of activation is almost 50 kcal/mol in this series! It has been shown that this extremely large rate effect is due to steric acceleration. When the rate constants were correlated with the Taft-Hancock steric substituent constants E_s^c [82] for the halves of the molecules *26* two separate linear correlations were found: one for the compounds *1–11* in Table 5[43] in which the central C-C-bond connects two quaternary centers, the second correlation line is followed by the rate data of a large group of compounds[52] with a central C-C-bond between two tertiary carbons e.g., the compounds *12–16* in Table 5. This separation into two separate correlations is due to differences in structure. The C_t–C_t compounds *12–16* have a gauche ground state conformation which allows for much larger angle deformations in order to escape the building up of ground state strain than anticonformations[47–49].

It was all the more satisfying to find a linear correlation (Fig. 1) between the thermal stability of most aliphatic compounds of Table 5 as expressed by $t_{1/2}$ = 1h or by $\Delta G^{\ddagger}$ (300 °C), and their ground state strain. The strain energies were obtained by force field calculations[39, 40, 51] and confirmed for a selected number of examples by the determination of heats of combustion[48, 49, 52, 53]. This proves that C-C-bond strengths of branched alkanes are mainly influenced by Van der Waals repulsions acting in the ground state of hydrocarbons which are released on bond dissociation. The exponential increase of bond strength for those hydrocarbons *26* with particularly small strain energies (no. 12 and 17–19 in Table 5) is still unexplained[5]. The correlation of Fig. 1 allows the prediction of thermal stabilities of many aliphatic hydrocarbons by force field calculations. It is particularly interesting to note that the diastereomeric compounds no. 14 and 15 of Table 5 have distinctly different stabilities. This was explained on conformational grounds[48]. Another interesting phenomenon is the observation that the slope of the correlation for the aliphatic compounds in Fig. 1 is not –1 but –0.6 as shown by the equation derived from Fig. 1.

$$\Delta G^{\ddagger}\ (300\ ^{\circ}C) = -0.6\ E_S + 65.6\ \text{kcal/mol}.$$

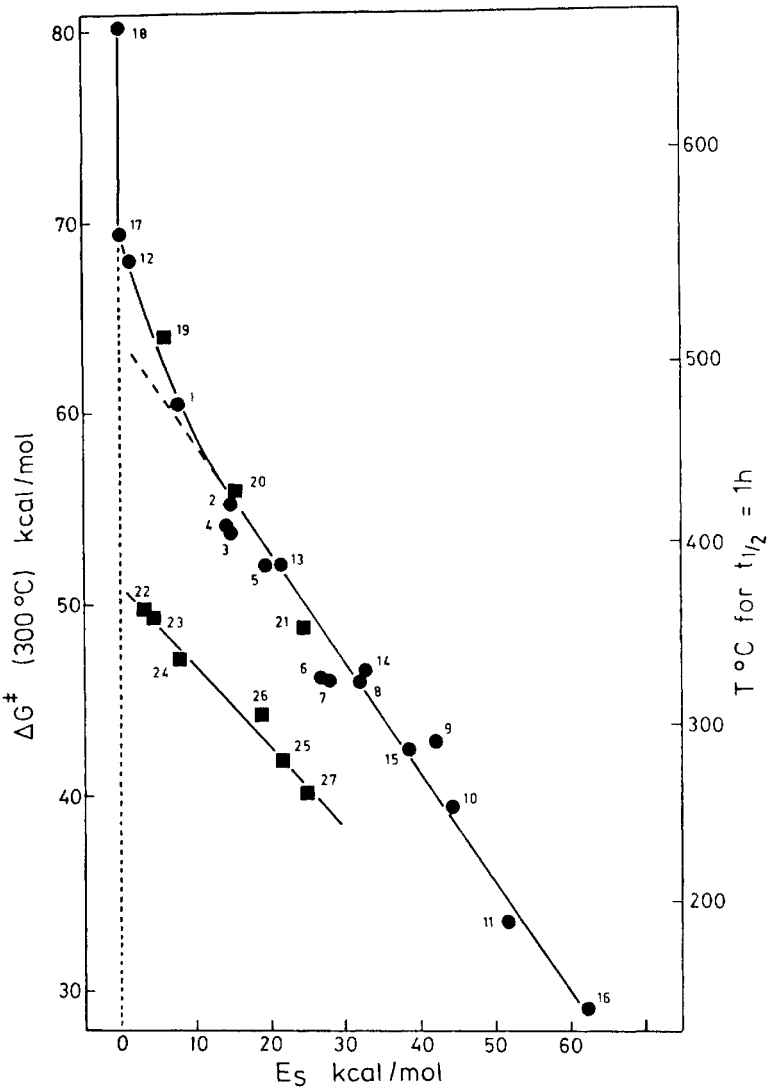


Fig. 1. Correlation between Thermal Stability and Ground State Strain E_S for hydrocarbons *26* (results from Table 5)

This suggests that at the transition state of this homolytic cleavage reaction 40% of the ground state strain is still present. Under the reasonable assumption that the radicals, which are the cleavage products, are more or less strain-free[10b,49], this means that the recombination of bulky alkyl radicals has an activation barrier of corresponding magnitude. A bond dissociation enthalpy $D_H \sim 76$ kcal/mol is calculated for the C-C-bonds in almost unstrained branched aliphatic hydrocarbons by this correlation in good agreement with the literature value for the central bond of 2.3-dimethyl butane[45].

A corresponding correlation is obtained for the rate constants of α,α'-phenyl substituted alkanes *26* ($R^1 = C_6H_5, R^2 = H, R^3 = alkyl$) (see Fig. 1)[41]. It has, however, a different slope and a different axis intercept. When both correlations are extrapolated to $E_{Sp} = 0$, a difference of about 16 kcal/mol in $\Delta G^{\ddagger}$ is found. This value is not unexpected because in the decomposition of α,α'-phenyl substituted ethanes (Table 5, no. 22–27) resonance stabilized secondary benzyl radicals are formed. From Fig. 1 therefore a resonance energy of about 8 kcal/mol for a secondary benzyl radical is deduced. This is of the expected order of magnitude[54].

What is the reason for the smaller slope of this correlation?

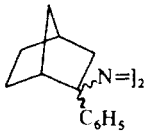
$$\Delta G^{\ddagger}\,(300\,^{\circ}C) = 51 - 0.41\,E_{Sp}\,[kcal/mol]$$

Two factors are probably contributing: On increasing the strain by increasing the group R^3 in *26* benzyl type radicals are generated which could deviate from planrity and therefore suffer from steric hindrance of resonance[34]. Alternatively, the more strained *26* is, the more the transition state of dissociation of *26* will be shifted in the direction of the hydrocarbon. Its radical character will decrease accordingly and therefore also the size of the resonance effect on the rates[41].

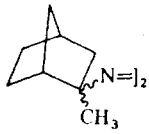
It has to be pointed out, however, that these considerations suffer somewhat from the fact that up to now it was necessary to calculate the strain energies of the phenyl substituted alkanes by a different force field[40] than those of the alkanes[39].

3 Further Steric Effects

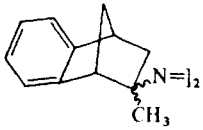
When 2-norbornyl type radicals are generated from exo/endo isomeric precursors differences in rate are generally observed. The higher rate of decomposition of the exo-isomer is usually explained on steric grounds[12, 18]. This phenomenon is demonstrated by the following examples:



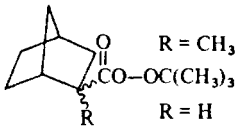
$k_{exo(Azo)}/k_{endo} = 116$ (200 °C)[18]



$k_{exo(Azo)}/k_{endo} = 68$ (200 °C)[18]

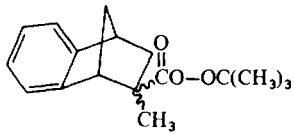


$k_{exo(Azo)}/k_{endo} = 99$ (200 °C)[55]



$k_{exo(CO_2OtBut)}/k_{endo} = 6.4$ (80 °C)[18, 55]

$k_{exo(CO_2OtBut)}/k_{endo} = 4.1$ (80 °C)[18, 56]



$k_{exo(CO_2OtBut)}/k_{endo} = 2.9$ (80 °C)[55]

The torsional effect as propsed by Schleyer[57] and steric hindrance of the departing group according to Brown[57] both have been discussed as interpretations of these reactivity series.

The rate of homolytic decomposition of bi- and polycyclic bridgehead azo compounds[18, 58] and peroxyesters[18, 59] decreases with increasing strain of the polycyclic system, because internal ring strain increases further on dissociation. This view is supported by the observation of a linear correlation between the rates of radical generation and the change in strain energy on dissociation as estimated by force field calculations according to Schleyer[58, 59]. For the perester decomposition again a polar effect probably is superimposed.

III Steric Effects in Aliphatic Substitution Reactions

When alkyl radicals take part in atom transfer reactions as acceptors

$$R\cdot + X\text{–}Y \longrightarrow R\text{–}X + Y\cdot$$

or as donors

$$R\text{–}H + Y\cdot \longrightarrow R\cdot + HY,$$

a change in hyridization between the sp^2 and the sp^3 state of the central carbon atom is involved, even though the transition states of these reactions are usually found to be placed early on the reaction coordinates[5, 12, 18]. Because of the different steric interactions of substituents at the central carbon atom and because of the different shielding of the reaction center by these groups in the two hybridization states, steric effects on reactivity are expected in addition to electronic[13] and polar effects[13].

A conformational effect was detected for the H-transfer reactions from cycloalkanes to a series of attacking radicals. The data of Table 6 show that cyclopentane is generally a better H-donor than cyclohexane. The rate ratio is generally largest for the least reactive radicals because the change in hybridization at transition state

Table 6. Relative Rates of H-transfer from cyclopentane (k_5) and cyclohexane (k_6) to radicals X·[60]

X·	Cl· CCl_4, 0 °C	*t*-ButO· CCl_4, 0 °C	C_6H_5· CH_3CN, 75 °C	·CCl_3 $BrCCl_3$-CCl_4, 75 °C	Br CH_3CN, 75 °C
k_5/k_6	1.0	1.0	2.8	4.0	3.1

has progressed to the farthest extent in these cases. Increased reactivity is also observed for cycloalkanes of the medium-ring size (C_8–C_{10})[60].

The well known difference in reactivity in transfer reactions of primary, secondary and tertiary hydrogens is most probably neither due to steric acceleration nor to a difference in electronic stability of primary, secondary and tertiary radicals[5, 12, 18]. This latter interpretation was favored in the literature until quite recently[5] because H-transfer reactivity of primary, secondary, and tertiary hydrogens decreases parallel with an increase in the C-H-bond dissociation energy. The suggestion that the drastic change in C-H bond energies is due to a ground state effect[5, 12] was recently supported by McKean[61], who observed an interesting correlation between bond dissociation energies and infrared stretching frequencies ν_{CH} for a large group of compounds. Hydrogen bound to carbon atoms which carry good conjugating groups like phenyl or CN deviate distinctly from this correlation. Using the PMO-theory Boldt et al.[13c] recently recognized fairly good correlations between activation energies of some H-transfer reactions and the superdelocalizabilities $S_r^{(R)}$ [13a, b]. They point out that the principle of maximum overlap, using MINDO-3 data, may serve well in predicting relative rates of H-transfer reactions. Apparently the C-H bond energies are directly related to $S_f^{(R)}$.

Bartlett et al.[62] on the other hand have found that mainly exo-2-norbornyl halides *28* are obtained from 2-norbornyl radicals *27* and halogen transfer agents. The product ratio of exo-halide *28* and endo-isomer *29* was largest for large halogen transfer agents XY. XY apparently approaches *27* preferentially from the less shielded exo-side. The torsional effect[57] discussed before is probably also of importance. Similar results were obtained more recently for the transfer of hydroxy groups from peracids to *27*[63].

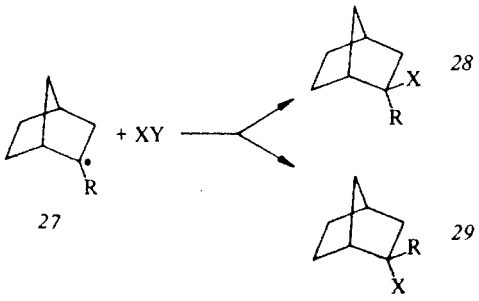
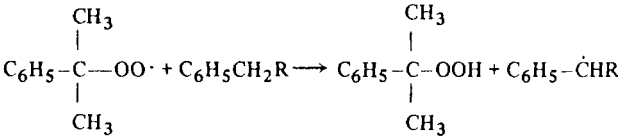


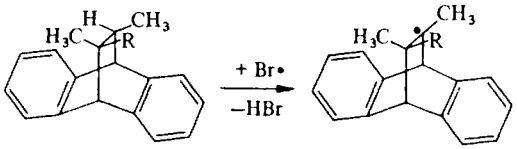
Table 7. Relative rates of H-transfer from the 2-position (k_2) and the 1-position (k_1) of adamantane to attacking radicals X· [65, 66]

X·	Cl·	Br·	·CCl_3	O O ‖ ‖ [CH_3–C–C–CH_3]*	C_2H_5O–CO–ṄCl
k_1/k_2	2–6	9	24	∞	∞

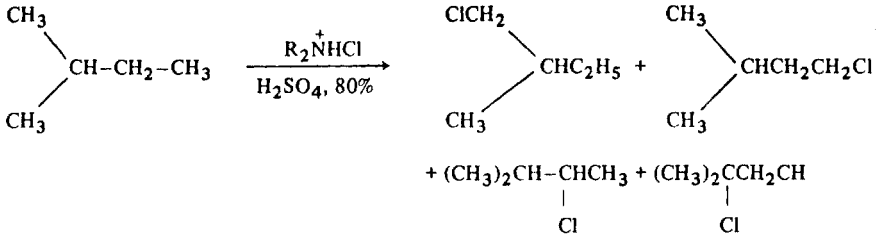
The well known decreased reactivity of hydrogen bound to the bridgehead position of small polycyclic hydrocarbons in transfer reactions is in accord with the steric bridgehead effect[64] discussed above. Although this position usually is shielded to a comparatively low extent an increase in internal strain is expected on bond dissociation. The 2-position of adamantane is more shielded than the 1-position. The ratio of products obtained by radical attack at the 1-position (k_1) and the 2-position (k_2) therefore increases with the size of the attacking radical species[64, 65] as shown by the data of Table 7. Steric hindrance of H-transfer has also been observed in autoxidation reactions. An example is the decreasing reactivity of hydrogens in benzyl position towards attacking cumylperoxy radicals[67] with increasing size of R. In other



cases, however, steric acceleration of H-transfer due to relief of back strain was postulated as in the bromination of a series of dibenzo-bicyclooctanes[68]. For example



the compound with R = CH_3 is more reactive than the corresponding compound with R = H because the steric interaction between *vic.* eclipsed methyl groups decreases in the process of H-transfer. Steric hindrance to H-transfer becomes more pronounced, the bulkier the attacking radical is. This has been favorably used in preparative free radical halogenations for increasing selectivity[69]. The best known examples are the chlorinations with N-chloramines in sulfuric acid. Aminium radical cations $R_2NH^{+\cdot}$ are the H-transfer agents in these reactions[70] and their size can be systematically changed by ranging the groups R. An example is the chlorination of isopentane[71]:



R	Relative rate of *prim.*,	*sec.*, and	*tert.* hydrogens[a]
CH_3	0.32	0.93	≡1
i-C_3H_7	0.25	0.70	≡1
neo-C_5H_{11}	0.71	2.70	≡1
t-C_4H_9	1.70	6.00	≡1

[a] statistically corrected.

In the product determining chain transfer step[70]

$$R_2NH^{+}\cdot + R'H \rightarrow R_2NH_2^{+} + R'\cdot$$

of di-*tert.*-butylaminium radical cation the secondary hydrogen is more reactive than the primary and both exceed the reactivity of the tertiary hydrogen, quite in contrast to the usual reactivity order in other hydrogen transfer reactions[5]. For the same reason an unusual product composition of heptylchlorides is obtained in the chlorination of n-heptane using N-chlor-diisobutylamine in H_2SO_4 as chlorinating agent.

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

1.3 69.4 22.9 11.3 isomer distribution of chloroheptanes (%)

The high yield of 2-chloroheptane is again due to the least steric shielding of the methylene group in the 2-position from attack by the bulky diisobutyl aminium radical cation. This may be partly due to coiling of the alkane chain in the polar reaction medium. 99% 1-chloroadamantane is obtained by this procedure from adamantane and N-chloro dimethylamine. As the attacking radical has a positive charge this reaction also strongly responds to polar effects. Thus n-alkane derivatives carrying

Product distribution of chlorinations with N-chloro-diisopropylamine

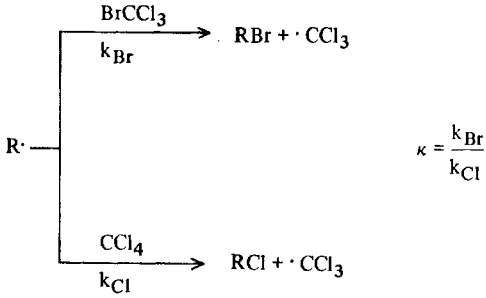
CH_3-	$-CH_2-$	$-CH_2-$	$-CH_2-$	$-CH_2-$	$-CH_2-X$	X
4	85	10	1	–	–	$-O-COCH_3$
6	90	2	2	–	–	$-OH$
4	83	11	1	–	1	$-OCH_3$
7	90	3				$-COOCH_3$

electronegative substituents in the 1-position are chlorinated with high selectivity in the ω-1-position[70]. Similar principles have been used with particular advantage for the selective halogenation of steroids. The bulky reagents

$BrCCl_3$[72, 73] $C_6H_5JCl_2$[73, 74] $C_2H_5-O-CO-NCl_2$[66]

allow in many instances a selective substitution of the most easily accessible 9-α- or 14-α-hydrogens, thus opening synthetic routes to the corticosteroids[74] and cardenolids[73]. Similar selective hydroxylations[75] and fluorinations[76] of steriods have been disclosed which probably also are free radical reactions[74]. A Completely different highly successful approach for selective free radical substitutions in the steriod field based on intramolecular H-transfer was introduced by the Barton Reaction and widely extended since[77]. The key idea was that 1.5-hydrogen transfer[78] is for steric reasons by far the preferred intramolecular mode of transfer. This principle has been elegantly extended in recent years by R. Breslow[73] to "template directed" reactions in which the reagent, e.g., the aryl iodine dichloride moiety, is bound to the steriod substrate *via* alkyl chains of different chain length. A particular advantage has been worked out in the so-called "relay mechanism" in which the substrate bound reagent – e.g., aryliodine dichloride – is generated *in situ* by an external reagent – e.g., SO_2Cl_2 – and a substrate bound precursor of the reagent – e.g., aryliodine[73]. All these reactions will not be discussed in more detail in this review.

An investigation of the competing halogen transfer from $BrCCl_3$ and CCl_4[5, 79] has shown that steric effects are also of importance in atom transfer reactions to alkyl and aryl radicals. Giese[80] investigated very carefully the temperature depen-



pendence of the selectivity κ of this reaction for a large series of alkyl and aryl radicals. Linear Eyring plots of log κ vs. 1/T were obtained over a large temperature range (0 °C–130 °C). Two types of radicals had to be distinguished according to this plot, however, because two separate sheafs of straight correlation lines with intersecting points (isoselective temperature) in the range of 60 ± 20 °C and 50 ± 10 °C, respectively, were observed. The two types of radicals were classified as π-radicals and σ-radicals, respectively[80], but probably a more operational distinction as "flexible" (π) and "nonflexible" (σ) may be preferable[81]. Above and below the isoselective temperature the selectivity series are reversed. There exists therefore no simple structure selectivity relationship. In contrast, however, the scale of differences in activation enthalpies $\Delta H^{\ddagger}_{Cl} - \Delta H^{\ddagger}_{Br}$ of the two competing halogen transfer reactions

is independent of temperature. A good linear correlation is obtained, when $\Delta H^{\ddagger}_{Cl} - \Delta H^{\ddagger}_{Br}$ is plotted *vs.* the steric substituent constants E_s^c[82] as shown in Fig. 2 for a series of alkyl radicals.

$$\frac{\Delta\Delta^{\ddagger}_{R}}{\Delta\Delta H^{\ddagger}_{CH_3}} = \delta E_s^c$$

With increasing steric shielding of the radical center $\Delta H^{\ddagger}_{Cl} - \Delta H^{\ddagger}_{Br}$ also increases. This steric effect is explained by the difference in X-CCl_3 bond strengths which dominates to a greater extent the selectivity ($\Delta H^{\ddagger}_{Cl} - \Delta H^{\ddagger}_{Br}$) the later the transition state is reached on the reaction coordinate i.e., the more bulky the attacking alkyl radical is.

Because E_S^c-constants for complex groups are obtainable at present only by an empirical procedure[82] a corresponding analysis is not possible for aryl-, vinyl-, and other nonflexible σ-type radicals. This difficulty was overcome recently by the development of a new set of steric substituent parameters $\mathscr{S}_f$ for front strain phenomena. These constants are defined as the difference in heat of formation for the hydrocarbons *30* and *31*. The heats of formation are calculated for this purpose by

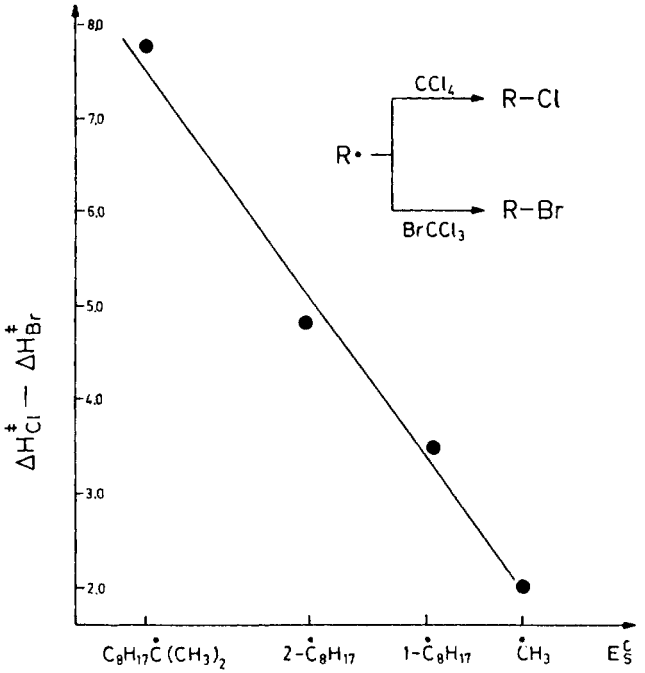


Fig. 2. Linear free enthalpy relationship between the difference in enthalpy of activation for the halogen transfer from CCl_4 and $BrCCl_3$ to alkyl radicals and the steric substituent parameters of alkyl radicals[83]

R-C(CH$_3$)$_3$ R-CH$_3$

30 *31*

molecular mechanics[84]. The plot of Fig. 3 shows that flexible and nonflexible radicals again give two separate correlation lines with $\mathcal{S}_f$ parameters[85]. The nonflexible σ-type radicals have the same geometry as the group R has in the model compounds *30* and *31* used for the computation of $\mathcal{S}_f$. The planar flexible π-type

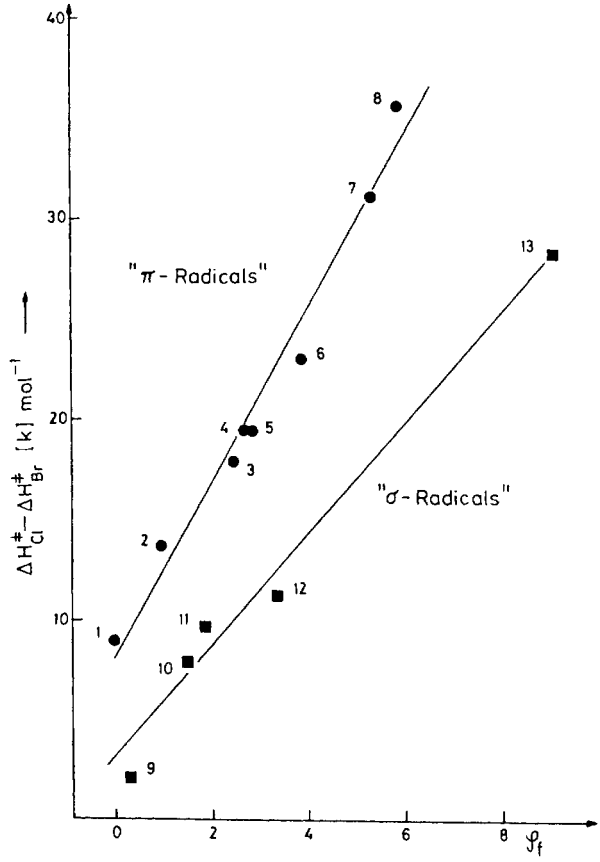
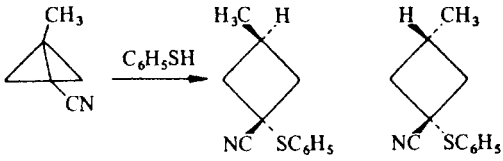


Fig. 3. Correlation of $\Delta H^{\ddagger}_{Cl} - \Delta H^{\ddagger}_{Br}$ [for the halogen transfer from CCl_4 and $BrCCl_3$ to radicals] and the steric substituent constants $\mathcal{S}_f$[84, 85]

No.	Radical	No.	Radical
1	CH_3	8	$CH_3C(C_2H_5)_2$
2	1-C_6H_{13}	9	CH_2=CH
3	c-C_6H_{11}	10	c-C_3H_5
4	2-Bicyclo[2.2.2]octyl	11	C_6H_5
5	2-C_8H_{17}	12	7-Norbornyl
6	$C_4H_9C(CH_3)_2$-CH_2	13	o-t-C_4H_9-C_6H_4
7	$C_8H_{17}C(CH_3)_2$		

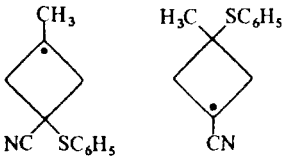
radicals on the other hand exert a larger front strain effect towards a reaction partner than predicted from the interaction of its bent analogue structure in *30* and *31*. Therefore the slope of the correlation for the flexible radicals in Fig. 3 is larger than for the nonflexible. This phenomenon supports the assumption of a planar geometry for the flexible π-type alkyl radicals[14]. In addition it stresses the importance of steric effects on free radical substitution reactions. Recently, in a similar analysis for bridgehead free radicals it was shown that $\Delta H^{\ddagger}_{Cl}$-$\Delta H^{\ddagger}_{Br}$ decreases with increasing internal strain of the polycyclic ring systems, although the front strain of these bridgehead radicals increases[86]. The position of the transition states on the reaction coordinate for halogen transfer to bridgehead radicals is apparently mainly determined by the change in i-strain and not so much by f-strain as expected.

Szeimies recently published an impressive example of a steric effect on a S_R2 reaction at carbon for the addition of thiols to the central bond of bicyclo[1.1.0]-systems[87]. From the radical chain addition of thiophenol to *32* the stereoisomeric cyclobutanes *33a* and *33b* are obtained exclusively in 56% yield. The thiylradical



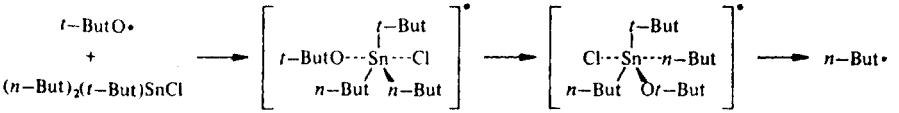
32 *33a* *33b*

attacks the central C-C-bond in *32* preferentially at the less hindered carbon, generating *34*, although this radical is less stabilized than *35* which would be generated by reversed regioselectivity of thiyl attack on *32*. Steric effects are also known for S_R2-



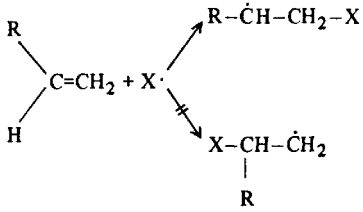
34 *35*

substitution at heteroelements. When t.-butyloxy radicals attack di-n-butyl-*t*.-butyl tinchloride a *n*-butyl group is expelled preferentially because it is the smaller ligand which prefers an apical position from which the leaving group usually departs from the addition complex[88].

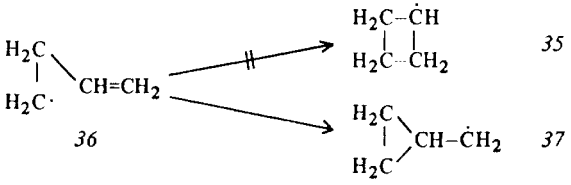


IV Steric Effects in Free Radical Addition Reactions

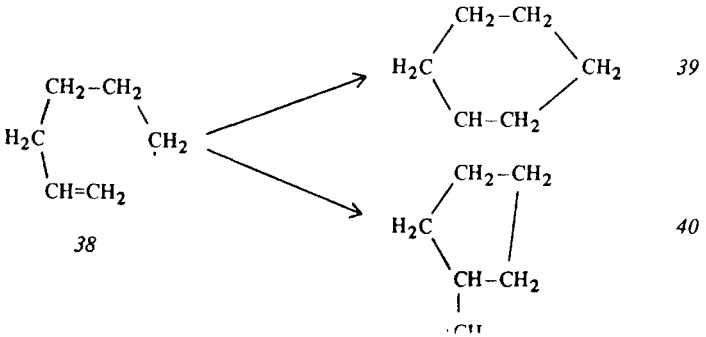
The recognition of anti-Markownikoff orientation when HBr was added to alkenes in the presence of traces of peroxides or air lead to the discovery of the large and important class of free radical addition reactions to unsaturated systems[89]. The anti-Markownikoff orientation of these reactions i.e., the preference of initial radical at-



tack at the less substituted carbon atom of the unsaturated system was interpreted for a long time by the stabilizing influence of α-substituents and in particular of α-alkyl groups at a radical center. As an alternative interpretation, the smaller steric repulsions during radical attack, a double bond at the less substituted end has been discussed[90]. Since the analysis of a large series of bond energies of primary, secondary and tertiary alkyl derivatives had lead to the conclusion that alkyl radicals are not particularly stabilized by α-alkyl substituents[5], the steric interpretation began to enjoy greater popularity[18]. This was supported by the results of intramolecular radical additions leading to cyclization. The homoallylic radical *36* or the 5-hexenyl



36 *35* *37*



38 *39* *40*

radical *38* cyclize exclusively or at least with high preference to the primary radicals *37* and *40*, respectively, and not or much slower to the secondary radicals *35* or *39*. This was no longer explainable on energetic grounds and a stereoelectronic interpretation was given. During cyclization bond formation by radical attack occurs preferentially at the end of the double bond which is more accessible on steric grounds[78, 91].

Because the addition steps are generally fast and consequently exothermic chain steps, their transition states should occur early on the reaction coordinate and therefore resemble the starting alkene. This was recently confirmed by *ab initio* calculations for the attack at ethylene[92] by methyl radicals and fluorene atoms. The relative stability of the adduct radicals therefore should have little influence on reactivity[12a]. The analysis of reactivity and regioselectivity for radical addition reactions, however, is even more complex, because polar effects seem to have an important influence. It has been known for some time that electronegative radicals X· prefer to react with ordinary alkenes[93] while nucleophilic alkyl or acyl radicals rather attack electron deficient olefins e.g., cyano or carbonyl substituted olefins[94, 95]. The best known example for this behavior is copolymerization[96]. This view was supported by different MO-calculation procedures[92, 97] and in particular by the successful FMO-treatment of the regioselectivity and relative reactivity of additions of radicals to a series of alkenes[13a, 98]. An excellent review of most of the more recent experimental data and their interpretation was published recently by Tedder and Walton[93].

Many examples of the influence of steric effects on reactivity and regioselectivity in free radical additions are known. The anti-Markownikoff regioselectivity apparently is smaller than originally assumed[5, 18, 93, 99] and frequently dependent on the size of the attacking radical[100] as shown by the following data[101]:

$\overset{1}{CH_3}-\overset{2}{CH}=CH-R$ Relative Reactivity for attack at C_1/C_2

R \ X·	n-C_4H_9S·	t-C_4H_9S·
C_2H_5-	1.08	1.10
2-C_3H_7-	1.30	2.55
t-C_4H_9-	1.91	>100:1

Particularly striking is the deactivation of the rate of radical addition by methyl groups at the center of primary attack as shown by the following data[102]:

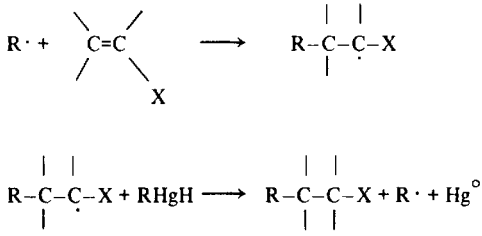
Relative rates of attack of alkenes by CF_3-radicals

$CH_2=CH_2$	$CH_2=CHCH_3$	$CH_2=C(CH_3)_2$	$CH_3CH=C(CH_3)_2$
↑	↑ ↑	↑ ↑	↑
≡1.0	2.3 0.2	6.0 0.5	2.80

While β-methyl groups excert a slight rate enhancing effect for attack by CF_3-radicals, α-methyl groups reduce it. The small changes in relative rate make it particularly difficult to propose a unique interpretation[93] for these and similar results, because high regioselectivity and low substrate selectivity cannot both be explained on the same energetic grounds e.g., by the different thermodynamic stability of primary, secondary and tertiary radicals[103]. This is even more contrasting for radicals other than CF_3. Ethylene and isobutene have comparable methyl affinities which are 5–10 times higher than those of *cis*- and *trans*-butene[18, 104]. Cyclopropyl radicals attack ethylene even three times faster than isobutene[105]. Similar trends have been observed in detailed investigations of halogenated alkenes[93].

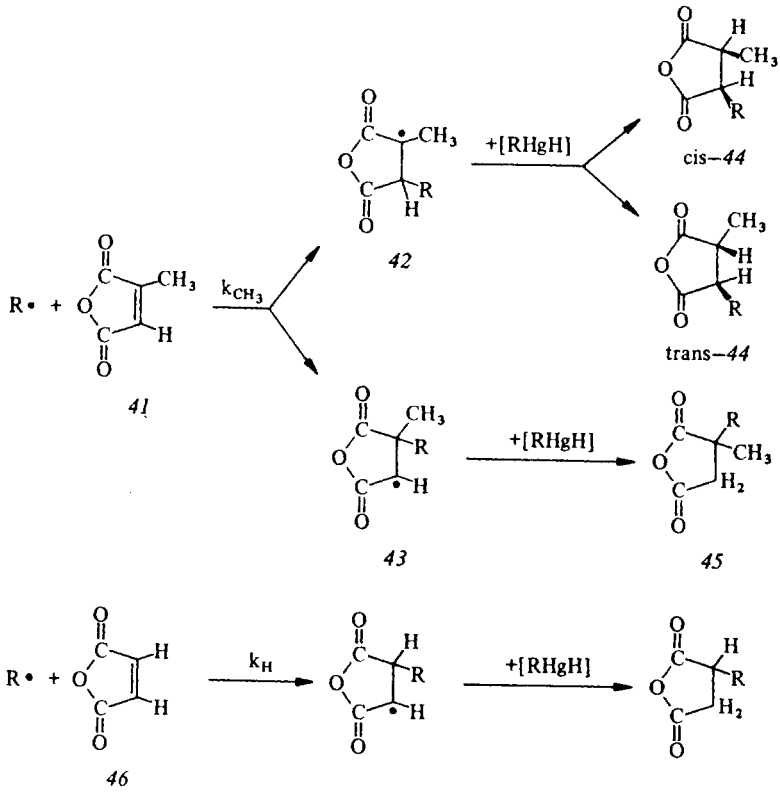
A further interesting example of a steric effect was recently published[106]. The sterically shielded 2.2.6.6-tetramethyl piperidinium radical cation adds to cyclohexene by almost three powers of ten slower than the piperidinium radical cation itself[107].

The combined influences of polar and steric effects and of the strength of the newly formed bond[93] was also recognized in the reaction of α,β-unsaturated carbonyl compounds and similar electron deficient alkenes[95] with organomercurials and $NaBH_4$. For the addition of alkyl radicals to substituted styrenes, ρ assumed a



$X = -CN; -COR; -COOCH_3$

small positive value which was, however, dependent on temperature. For the ρ-values of a series of alkyl radicals an isoselective temperature at 90 °C was noted[108]. For the addition of alkyl radicals of different size to maleic anhydride *46* and methylmaleic anhydride *41*, steric effects on the regioselectivity and stereoselectivity became apparent besides polar effects[99, 103]. The regioselectivity series *44*:*45* is in accord with an explanation by the steric effect in the addition step. The competition constants k_H/k_{CH_3} for the reaction of an alkyl radical with *41* and *46*, respectively, likewise show the influence of a steric effect, but a polar effect as described by the FMO-description could hardly be distinguished. The more nucleophilic attacking radical e.g., t.-butyl, is the more reactive and likewise the more selective[109]. Finally stereoselectivity in the formation of *cis*- and *trans-44* shows that in the second chain step, H-transfer from the less hindered side is prefered, although in this way the less stable *cis-44* is formed in preference to *trans-44*. It has been known for a long time that norbornene is also attacked by radicals from the exo-side[89, 110] with great preference.



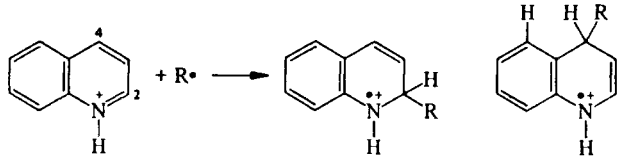
R·	*44:45*	*cis-44: trans-44*	k_H/k_{CH_3} (−10 °C)
$(CH_3)_3C$·	99:1	92: 8	13.6
c-C_6H_{11}·	97:3	89:11	9.8
1-C_6H_{13}·	97:3	62:38	6.5
CH_3·	98:2	43:57	–

The first step of a free radical aromatic substitution, the formation of the σ-complex, is also an addition step. The o,m,p-product ratio therefore also responds to steric effects. This is shown for the free radical phenylation and dimethylamination of toluene and *t.*-butylbenzene in Table 8. The larger the substituent on the aromatic system and the bulkier the attacking radical, the more p-substitution product is obtained at the expense of o-substitution. In the phenylation reaction the yield of m-product also increases in contrast to the dimethylamination reaction. The substitution pattern of this latter reaction is, in addition to the steric effect, governed heavily by polar effects because a radical cation is the attacking species[113].

Table 8. Steric substituent effects in free radical aromatic substitutions

R·	Toluene			t.-Butylbenzene		
	%o	%m	%p	%o	%m	%p
C_6H_5· [111]	63	21	16	24	49	27
$(CH_3)_2NH^+$· [112]	5.6	22.6	71.8	0	14.6	85.4

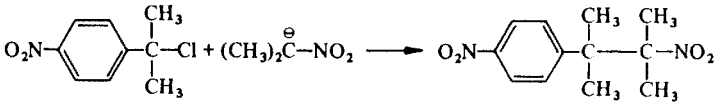
Even more pronounced steric effects have been observed for the free radical alkylation of protonated N-heterocyclic bases by the procedure of Minisci[69, b, d]. Quinoline is attacked selectively in the 2- and 4-position by nucleophilic alkyl radicals in sulfuric acid. The largest radicals, *t.*-butyl, react exclusively in the 2-position because of steric hindrance by the peri-hydrogen when attack occurs at the 4-position.



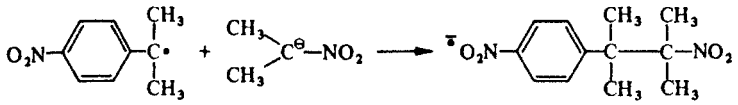
R·	% 2-alkylquinoline	% 4-alkylquinoline
CH_3·	23	25[a]
1-C_3H_7·	28	36[a]
2-C_3H_7·	13	26[a]
t-C_4H_9·	100	0

[a] besides 2.4-dinitroquinoline.

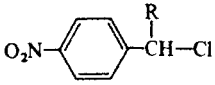
Steric effects, although clearly recognized, introduce relatively small rate retardations or increases in selectivity in all these examples, probably because the transition states of all these addition reactions are rather loose ones, i.e., they occur early on the reaction coordinate when the distances between the radical and the substrates are still rather large[92, 93, 97]. An extreme example of a free radical reaction which does not response heavily to steric effects, is the $S_{RN}1$-substitution reaction of Kornblum[114] by which bonds between two quaternary carbons can be formed with great ease and in good yield, as is shown by one of many published examples[114]. The decisive step



in the chain reaction is the attack of a p-nitrocumyl radical at the carbanion center generating a new aromatic radical anion. The rate of this new type of reaction is apparently extremely high and therefore does not respond strongly to steric effects



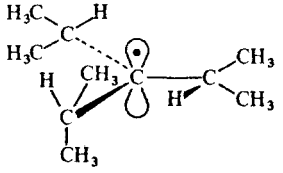
In a similar fashion therefore, quaternary substituents can also be introduced to aromatic ring systems by the aromatic counterpart $S_{RN}1$-procedure as investigated mainly by Bunnett[115]. In an extreme situation of steric shielding, however, a response



to steric effects has been detected. 1-alkyl-p-nitrobenzyl chlorides react with the anion of 2-nitropropene with C-alkylation when R = CH_3, C_2H_5, but with O-alkylation when R = i-C_3H_7 or t.-butyl[116].

V Steric Effects in Dimerization and Disproportionation Reactions

The unusual persistence of many highly branched alkyl radicals[9, 10] mentioned in the introduction proves that radical dimerizations can be hindered or even suppressed by the steric effect of bulky groups. For the dimerization of di-tert-butylmethyl e.g., an activation barrier of about 20 kcal/mol was estimated[49]. Most examples of persistent alkyl radicals, as e.g., *5* and *6*, have no β-hydrogens which are the prerequisite for disproportionation to occur. Triisoproplymethyl *7*, however, is also persistent although β-elimination of hydrogen should lead to destruction of this radical in the course of disproportionation with another radical. It is presumed[9] that *7* has a conformation *47* in which the β-hydrogens are arranged in the nodal plane of the SOMO. Therefore, H-transfer to an attacking radical and formation of a double bond cannot be a synchronous process. Very recently, however, Berndt et al.[10b] have



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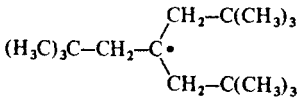


48

reported that trineopentylmethyl *48* and a few other neopentyl substituted methyl radicals also show remarkable persistence. It was not reported whether their decay is a unimolecular or bimolecular process.

In general, the rate ratio of the disproportionation k_d and dimerisation k_c increases with the bulk or size of the radicals concerned[117]. For simple alkyl radicals even a

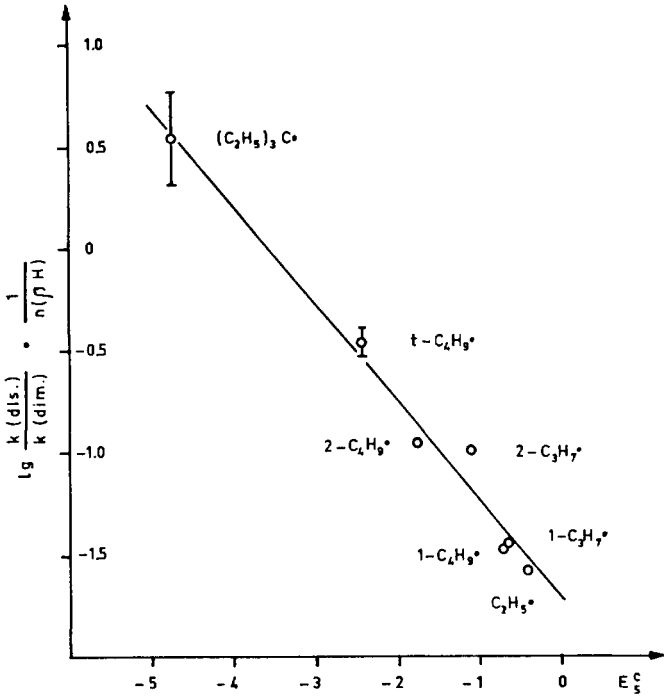
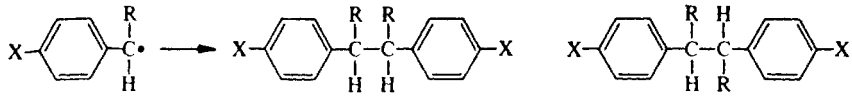


Fig. 4. Relation between the statistical corrected ratio of rates of disproportionation and dimerization of alkyl radicals and their E_s^c-constants[43] $\lg \frac{k_d}{k_c} \cdot \frac{1}{n_{\beta H}} = -0.48\ E_s^c - 1.73$ ($r = 0.9901$)
$n_{\beta H}$ = number of β-H-atoms in the radical

linear relation between $\log k_d/k_c$ (statistically corrected) and Taft's steric substituent constants E_s^c was found[43] (see Fig. 4). The interpretation of this steric effect is a more more subtile problem than recognized on first sight. Schuh and Fischer[118] have shown by an investigation of the influence of temperature and solvent viscosity on the termination constant, as well as k_d and k_c, for t.-butyl radicals that this effect cannot be explained simply by the greater steric hindrance of approach of the two radicals for dimerization than for disproportionation. The termination constant $2\,k_t$ of the self reaction of *t.*-butyl radicals is diffusion controlled and requires no activation. Observed large solvent and temperature dependences of k_d/k_c were ascribed to anisotropic reorientation motions of the radicals during their encounter in the solvent cage. This may also be the reason for the low probability of recombination of 2-cyano-2-propyl radicals as deduced from CIDNP-experiments[119].

Recently, an interesting example of stereoselective radical dimerization was described which awaits explanation. It was found that radical *49* (X = p-Cl; R = t-butyl) dimerizes diastereoselectively[120] to the more stable D, L-diastereomer in contrast to other radicals *49* with smaller side chains R. It has not been clearly decided so far



49 meso D, L

X·	R	Yield ratio D, L: meso
H	CH_3	1:1
H	C_2H_5	1:1
Cl	t-C_4H_9	1.66:1

whether the dimerization of this rather bulky radical is an activated process or a diffusion controlled one, and whether diastereoselectivity is due to a difference in free activation enthalpy for the two possible dimerization modes or due to anisotropic orientation motions as discussed by Schuh and Fischer[118]. The temperature dependence of the diastereoselectivity of this dimerization was found to be quite small. The influence of solvent[118] is actively being investigated at present at the author's laboratory.

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