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88

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Organic Chemistry
Syntheses and Reactivity

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Organic Chemistry
Syntheses and Reactivity

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Steric Effects in Free Radical Chemistry

Christoph Rüchardt*

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

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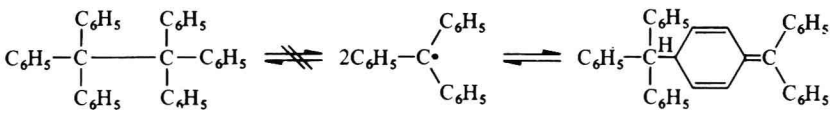
* This review is an extended version of an article in „Zeitschrift der Sowjetischen Chemischen Mendelejew-Gesellschaft", April 1979.

I Introduction

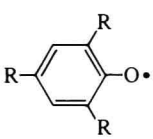
Steric effects have been discussed in free radical chemistry ever since the discovery of the first free radical, triphenylmethyl *1* by M. Gomberg in 1900[1]. To what extent is the dissociation of its dimer, which was believed to be hexaphenylethane *2*[3] till 1968[2], determined by electronic stabilization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

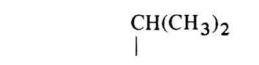
The recognition[2] that the α, p-dimer *3* is formed in equilibrium with *1* and not the α,α-dimer *2* was interpreted as a result of the smaller steric strain in *3* than in *2*[3]. Also the known strong influence of p-substituents on the equilibrium constants between substituted trityl radicals and 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



4

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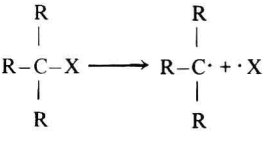
Since these developments became known the importance of steric effects on the reactivity of free radical reactions has also been more clearly recognized and more thoroughly investigated[11]. Some more important and more recent results along these lines are the topic of this review.

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].

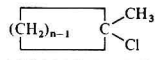
Table 1. Relative rates of formation of cyclic carbenium ions and free radicals from precursors *10–19*[a]

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	0.009
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	$3.5 \cdot 10^{6}$	>4000
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	–	–

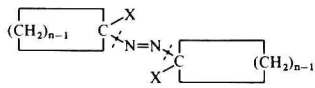
[a] The bonds cleaved in the rate determining step of homolytic decomposition of *11–19* are indicated in the formula.

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



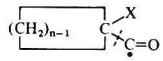
10[15] 80% EtOH, 25°C



11[19] X = CN, toluene, 80°C

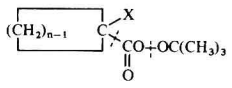
12[20] X = C_6H_5, benzene, 60°C

13[21] X = CH_3, benzene, 200°C



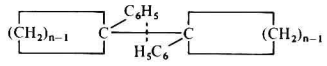
14[22] X = H, 125°C

15[22] X = CH_3, 135°C

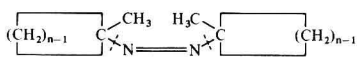


16[25] X = CH_3, benzene, 80°C

17[25] X = H, ethylbenzene, 110°C



18[24] Octane, 220°C

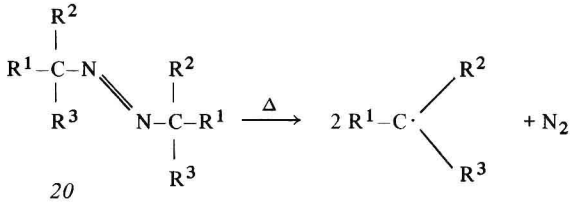


19[26] Ethanol, −28°C

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].



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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

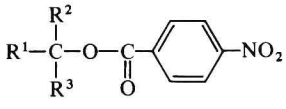

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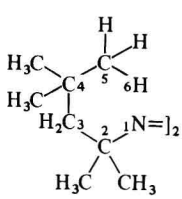
Table 2. Rate Constants k_{rel} and activation parameters for the thermolysis of azoalkanes $R^1R^2R^3C-N=)_2$ *20* in hydrocarbon solvents

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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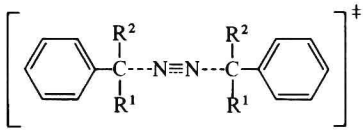
and the nitrogen atoms are acting as shown in *22*. The same extraordinary rate enhancing effect of neopentyl side chains was observed for the thermolysis rates of azonitriles *20* (R^1, R^2 = alkyl, R^3 = CN)[29a] and α-carbomethoxy-azoalkanes *20* (R^1, R^2 = alkyl, $R^3 = COOCH_3$)[32]. For α-phenyl 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-



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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-

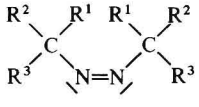

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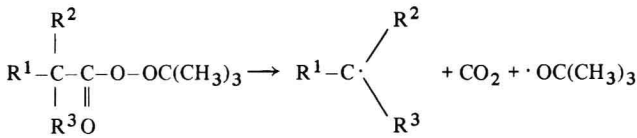
Table 3. Steric acceleration of thermolysis of *trans*-azoalkanes *20* (180 °C, ethylbenzene) and *cis*-azoalkanes *24* (−28 °C, ethanol)

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



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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].

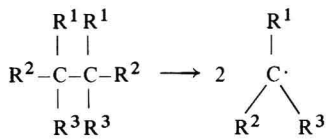
[b] a statistical correction $k_1 = k_{exp.}/2$ was introduced because this molecule has two equivalent bonds which can be cleaved on thermolysis.

[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.

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

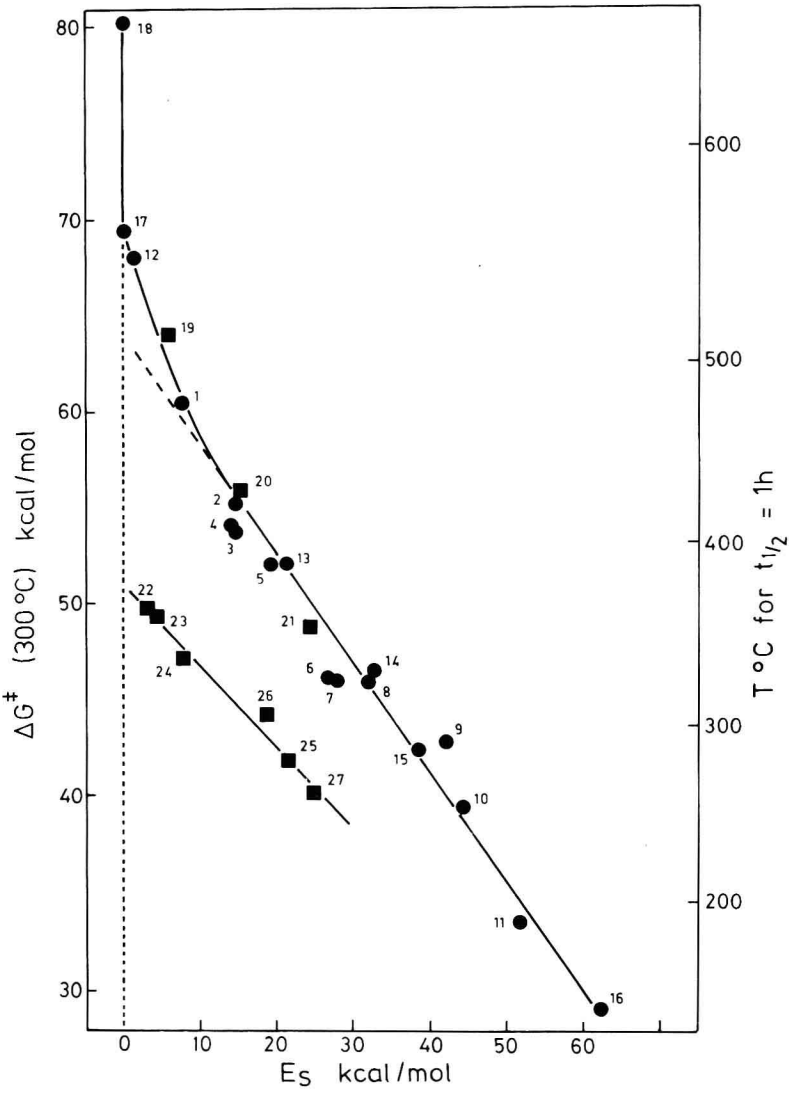


Fig. 1. Correlation between Thermal Stability and Ground State Strain E_S for hydrocarbons *26* (results from Table 5)

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?

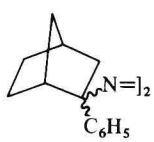
$$\Delta G^{\ddagger}\,(300\,^{\circ}C) = 51 - 0.41\,E_{Sp}\,[kcal/mol]$$

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].

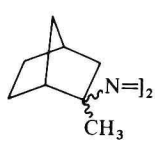
It has to be pointed out, however, that these considerations suffer somewhat from the fact that up to now it was necessary to calculate the strain energies of the phenyl substituted alkanes by a different force field[40] than those of the alkanes[39].

3 Further Steric Effects

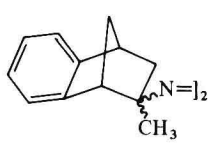
When 2-norbornyl type radicals are generated from exo/endo isomeric precursors differences in rate are generally observed. The higher rate of decomposition of the exo-isomer is usually explained on steric grounds[12, 18]. This phenomenon is demonstrated by the following examples:



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



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



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

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