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Steric and Electronic Substituent Effects on the Carbon-Carbon Bond

# Steric and Electronic Substituent Effects on the Carbon-Carbon Bond

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The factors influencing dissociation energies of C—C bonds have been investigated by thermochemical (ΔH_c°, ΔH_v, ΔH_{sub}) and kinetic methods and by molecular mechanics (MM2 force field). Quantitative analysis of the influence of strain H_s in 1 and in 2 and of the resonance energies H_r of the substituents X in 2 (X = C_6H_5, CN, OCH_3, COR, $COOCH_3$) has been successfully achieved.

$$X—CR^1R^2—CR^1R^2—X \quad 1 \rightarrow 2\,X-\overset{\cdot}{C}R^1R^2 \quad 2$$
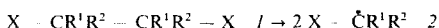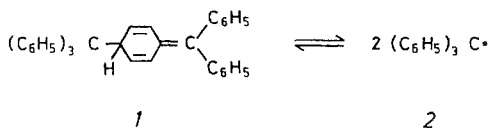
Enthalpy and entropy effects and their interrelationships are discussed. Resonance stabilization of radicals by more than one substituent (including capto-dative substitution) is frequently additive and in no example higher than this. A linear correlation is found between the central C—C-bond lengths in 1 and the strain enthalpies H_s, quite independent of the substituents X and their resonance contribution H_r.

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1 Introduction

The Carbon—Carbon Bond is the backbone of Organic Chemistry. For a covalent bond between two like atoms its strength is exceptional, a phenomenon which is pointed out in most beginners' text books of Organic Chemistry. Due to this exceptional bond energy and due to their chemical inertness C—C bonds in carbon structures have been ideally suited for the storage of solar energy of past times in primary fossil fuels as well as in renewable feedstocks such as cellulose, starch and fat.

From information related to linear saturated hydrocarbon structures bond strengths of about 80 kcal · mol⁻¹, bond lengths of about 154 pm and bond angles of about 109° are quoted as standard reference values for C—C bonds.

However, with the exception of small ring compounds, much too little is known about the range of these dimensions in different carbon structures and even less about the factors responsible for observed variations. The dimension of this question is recognized immediately when the C—C bond strength in ethane (88.2 kcal · mol⁻¹)[1] is compared with that of the central bond in the Gomberg dimer 1 (12 kcal · mol⁻¹)[2,3].

$$(C_6H_5)_3\ C \overset{H}{-} \hspace{-0.5em} \underset{}{\bigcirc} \hspace{-0.5em} = C \underset{C_6H_5}{\overset{C_6H_5}{<}} \quad \rightleftharpoons \quad 2\ (C_6H_5)_3\ C\cdot$$

<div align="center">

1 2

</div>

This difference of 76 kcal · mol⁻¹ in bond strength is translated into a rate factor of $1:10^{30}$ (at 300 °C) for the thermal cleavage of ethane into methyl radicals (at ∼700 °C) or 1 into trityl radicals 2[2] (at ∼25 °C). This is an incredible factor[4] for such a simple and basic phenomenon as the substituent effect on the C—C bond strength. Therefore it is even more astonishing that the traditional hyphen between two C's is considered to be a satisfactory symbol for this bond.

The enthalpy required for the thermal cleavage of a C—C bond into two carbon radicals is the defining reaction for the bond dissociation enthalpy H_D[1,5,6]. The reaction coordinate of this process on the enthalpy scale (Fig. 1) generally has no separate transition state (enthalpy maximum), because it is known that the rate of the back-reaction, the dimerization of simple alkyl radicals, is a non-activated process controlled by diffusion (see later).

Therefore the bond enthalpy H_D and the activation enthalpy $\Delta H^{\neq}$ for the dissociation process are generally identical[6a]. Consequently, bond enthalpies H_D can be deduced from the temperature dependence of the rate constants k of thermal bond cleavage reactions with the aid of the Eyring equation

$$\ln k = \ln \frac{k_B T}{h} - \frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R}$$

The question as to which factors determine the dramatic substituent effect on the C—C bond strength mentioned above has been discussed since Gomberg's days. A particularly important contribution was made by Karl Ziegler in his pioneering work of the fourties[7]. In this early demonstration of the power of kinetics for the investi-
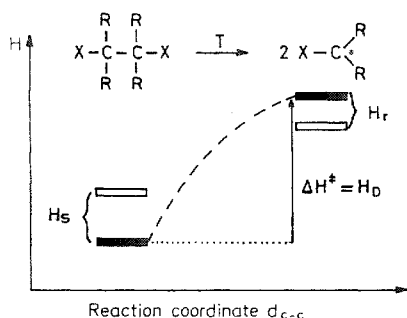
Fig. 1. Reaction coordinate of the bond dissociation process with non activated radical recombination; the influence of ground state strain H_s and of resonance stabilization H_r of the radical centers by the substituent X on the bond strength H_D is qualitatively indicated

gation of reaction mechanisms it was shown that the rate of $C-C$ bond dissociation (see Fig. 1) is increased by bulky substituents R and by X-groups such as phenyl which can conjugatively stabilize the radical being generated. In qualitative terms Ziegler recognized ground state strains H_s [8] and resonance stabilization of the carbon radicals H_r as the two factors contributing to the modification of $C-C$ bond strengths.
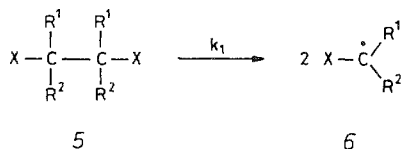
Work towards a quantitative analysis of these effects was initiated in our laboratory in the early seventies [9] when an unusually large ring size effects on the thermal cleavage reaction of 1,1'-diphenylbicycloalkyls *3* into 1-phenylcycloalkyl radicals *4* was observed; this was inexplicable by i-strain effects alone and pointed to the importance of f-strain in this phenomenon [10].
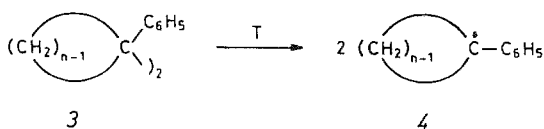
As a consequence, the aim of our own work was to attempt a quantitative analysis of the relationships between thermal stability, ground state strain and resonance effects of substituents and of the influence of strain on structure [9b]. The results were expected to be valuable not only as fundamental knowledge but were expected to contribute to fields of applied chemistry such as carbon initiators [11], coal pyrolysis [12] or thermal stabilities of polymers [13].

Models

With this aim in mind we began the investigation of the thermal stabilities, the thermochemistry and the structures of several series of compounds *5*. The substituents X and their characteristic resonance effects on the bond strengths are typical for each series (transition state effect). Within each series the bulk of the alkyl side chains R is changed in order to analyse the steric ground state effect.

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$$X-\overset{\overset{\displaystyle R^1}{|}}{\underset{\underset{\displaystyle R^2}{|}}{C}}-\overset{\overset{\displaystyle R^1}{|}}{\underset{\underset{\displaystyle R^2}{|}}{C}}-X \quad \xrightarrow{\;k_1\;} \quad 2\ X-\overset{\displaystyle\cdot}{C}\diagup^{\displaystyle R^1}_{\displaystyle R^2}$$

$$\mathbf{5} \hspace{8cm} \mathbf{6}$$

Additionally, results for some unsymmetrical compounds and the question of radical stabilization by more than one substituent will be discussed. Finally, some of the consequences of substitution and strain on structural parameters will be briefly addressed [9b]. The syntheses of all compounds referred to in this article and the determination of their structures and their configurations have been published or will be reported elsewhere [9b]. All compounds were obtained on at least a 100 mg scale and their purity was confirmed by standard analytical procedures.

2 Methods

The experimental approach to uncover relationships between bond strength, steric and resonance effects of substitutents and structure required the application of the broad methodology of Physical Organic Chemistry which can be outlined only briefly in this article [9a]. The thermolysis reactions were conducted in ampules with strict exclusion of oxygen but with the addition of good radical scavengers, such as mercaptans, tetralin or mesitylene [14-19]. At least 80–90 % of the products were derived from the radicals, e.g. 6 generated by homolysis of the weakest C—C bond in 5. Qualitative and quantitative analyses were performed by gc, capillary gc and coupled gc-MS-experiments. The products, generally obtained in high yield under proper conditions [14-18], are convincing evidence that induced decomposition is not a serious disturbing factor in the systems investigated.

The high selectivity for the cleavage of one C—C bond in preference to all others, which was observed almost without exception [20], is understandable in view of the enormous overall spread of the rate data mentioned above.

The kinetics of these pyrolysis reactions were followed by several complementary methods under conditions as close to the product studies as possible. The most frequently-used ampule technique [14-17] with gc analysis of 5 and the scavenger technique, with chloranil or Koelsch radical as scavenger [18], for very labile compounds 5 were complemented by the DSC method, in which the heat flow under conditions of linear temperature increase is analysed. It proved to be a particularly convenient and reliable technique [18, 21]. Rates were followed over a temperature span of at least 40 °C with temperature control of ± 0.1–0.2 °C. All rate data and activation parameters were subjected to a thorough statistical analysis including statistical weights of errors. The maximum statistical errors in k were $\pm 3\%$, in $\Delta H^{\neq} \leqq 1$ kcal $\cdot$ mol^{-1} in $\Delta S^{\neq}$ $\leqq 3$ e.u. and in $\Delta G^{\neq}$ (at the temperature of measurement) $\leqq 0.5$ kcal $\cdot$ mol^{-1}.

The question of cage recombination [22] merits special consideration in these systems. The most sensitive way to check for it was to test if meso/DL equilibrations occurred in the course of the thermolysis reaction of a pure diastereomer [18, 20]. Additional evidence for the unimportance of cage dimerizations are the high disproportionation-recombination ratios found for most of the radicals involved [9, 23] and the high fluid-
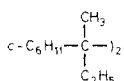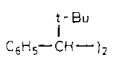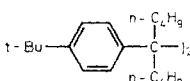
ities [23] of the medium at the high temperatures which were required for most reactions [9].

In a few cases the existence of intermediate radicals and their equilibrium constants with the dimers were established by esr. In a few instances rates of radical recombinations were measured by product-resolved kinetic esr experiments [24].

Thermochemical data were required for the estimation of ground state strain. Heats of formation $(\pm 0.5 \text{ kcal} \cdot \text{mol}^{-1})$ were obtained by the experimental determination of heats of combustion [25–27] using either a stirred liquid calorimeter [25] or an aneroid microcalorimeter [26]; heats of fusion and heat capacities were measured by differential scanning calorimetry (DSC), heats of vaporization [21, 25, 27] by several transport methods, or they were calculated from increments [28]. For the definition of the strain enthalpies Schleyer's single conformation increments [29] were used and complemented by increments for other groups containing phenyl [30] and cyano substituents.

Experimental thermochemical results were mainly required to extend the parametrization of the current force fields to highly strained compounds. Heats of formation calculated with Allinger's MM2 force field for alkanes [32] and its extension to alkylbenzenes [30] proved to be in by far the best agreement with the experimental results [27]. A few examples which demonstrate the quality of this agreement are shown in Table 1.

Table 1. A comparison of experimental and calculated strain enthalpies, $[\text{kcal} \cdot \text{mol}^{-1}]^a$ of some highly crowed hydrocarbons

	7	8	9	10
H_s (exp.)	66.3 ± 0.7^b	35.0 ± 0.7^b	17.8^c	$22.4^{c,\,d}$
H_s (MM2)^e	57.7	34.8	15.1	$\cdot$ 22.3
Ref.	33)	25)	15)	27)

^{a} $H_s = \Delta H_f^\circ(g) - \Delta H_f^N$; the strain free reference value ΔH_f^N is defined by group increments [29, 30].
^{b} heat of sublimation determined experimentally.
^{c} heat of vaporization calculated from increments [28].
^{d} corrected for strain introduced by the p-t-butyl substituent.
^{e} calculation of $\Delta H_f^\circ(g)$ using the MM2 force field, see Ref. [32c]

Only in the most extremely strained compound, tetra-t-butyl-ethane 7 [33], is an appreciable difference found between experiment and calculation. Even this can probably be overcome by a slight increase in the force constants for the van der Waals repulsion in the MM2 force field [34].

The quality of the MM2 force field was in addition tested for its ability to predict structural parameters. Comparison with X-ray data for many compounds [9, 31, 35], a few of which are shown in the last section of this article, indicated that the agreement was in general excellent.

An additional advantage of the force field method [32] is its power to predict the energy levels of conformations which are not populated and even complete rotational potentials of bonds. Again, statisfying agreement with results from dynamic nmr-measurements for a series of crowed hydrocarbons was found [36]. Knowledge of the shape of rotational potentials proved to be helpful for the interpretation of entropy effects in these series of compounds and in their thermolysis reactions.

3 The Steric Effect

To test the relationships between ground state strain and thermal stability independently of substituent effects several series of unsubstituted aliphatic model compounds are used.

In Fig. 2a the free enthalpies of activation $\Delta G^{\neq}$ (300 °C) of the thermolysis reactions of symmetrical hexaalkylethanes 11 (C_q—C_q series) — the weakest bond connects two quaternary carbons — are plotted against their ground state strain H_s as obtained from MM2 calculations [14,32,37]. The large range of stability differences encompassed by this series is easily judged from the scale on the right side of Fig. 2 in which is given for each compound the temperature at which the half-life is 1 h.

The high quality ($r = -0.987$) of the linear correlation in Fig. 2a, for which Eq. (1) is given in the caption, is quite surprising for several reasons. In particular, because free enthalpies of activation $\Delta G^{\neq}$ are correlated with strain enthalpies H_s despite the fact that there is neither an isoentropic ($\Delta S^{\neq} = $ const.) [41] nor an isokinetic relationship ($\Delta H^{\neq} \alpha \Delta S^{\neq}$) [41] within this series. Indeed $\Delta S^{\neq}$ varies from 13 to 26 entropy units [14]. In a kind of Exner test [42] it was shown, however, that the order of decreasing $\Delta G^{\neq}(T)$ values is independent of temperature and therefore significant for structural interpretation [14].

From the axis intercept in Fig. 2a, $\Delta G^{\neq}$ (300 °C) = 62.1 kcal · mol^{-1}, and from the mean entropy of activation, $\Delta S^{\neq} = 15$ e.u. [14], an activation enthalpy $\Delta H^{\neq}$ = 71 kcal · mol^{-1} is calculated for a hypothetical unstrained compound. This is in close agreement with the value for the bond dissociation energy expected from the literature values for this type of bond [1]. When the seemingly more proper $\Delta H^{\neq}$ values are plotted against H_s for this reaction a distinctly poorer correlation is found. It has, however, almost the same slope (-0.62) and an intercept corresponding to $\Delta H^{\neq} = 72$ kcal · mol^{-1} as in Fig. 2a [14].

The clue to an understanding of these unexpected phenomena is found in the "compensation effect" discussed by Benson [43]. $\Delta H^{\neq}$ is measured at much higher temperature — and for each member of the series in an individual temperature range — than the standard temperature 25 °C to which the strain enthalpy H_s corresponds. For a precise comparison $\Delta H^{\neq}$ values should be extrapolated over large temperature ranges down to 25 °C. This is not possible because $\Delta C_p^{\neq}$ values, the differences in heat capacity between ground and transition states, are not available. Benson points out [43] that the main factors determining $\Delta C_p^{\neq}$ are the changes in the degrees of freedom of translation, of internal and external rotation and of vibration. Just the same factors determine $\Delta S^{\neq}$. Therefore the temperature effects on $\Delta H^{\neq}(\Delta C_p^{\neq}$ dt) and on $T\Delta S^{\neq}$ are very similar. Due to the opposed signs of these two contributions to $\Delta G^{\neq}$ the temperature effect is largely compensated in $\Delta G^{\neq}$ [44], which is a term whose
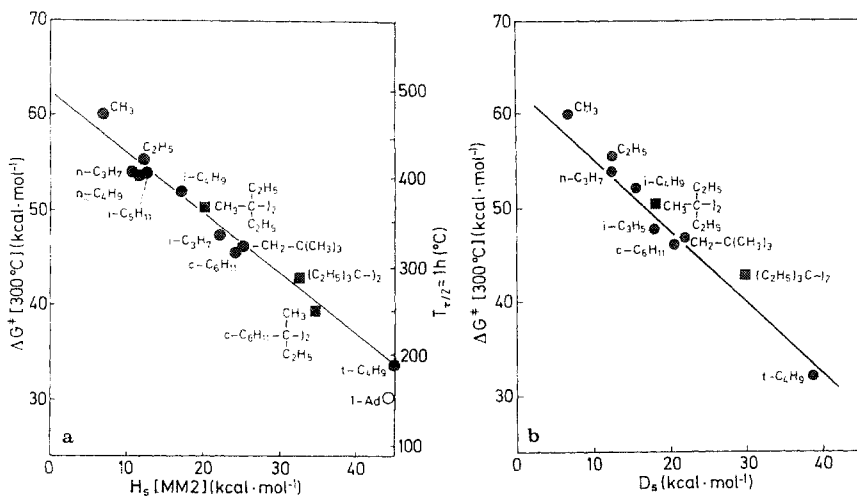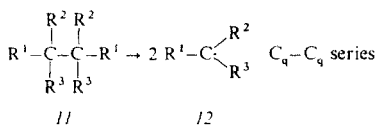
Fig. 2a and b. Relationships between $\Delta G^{\neq}$ (300 °C) of thermal decomposition of sym-hexyalkylethanes and
a ground state strain H_s (MM2 values) [32d]; b change in strain enthalpy during dissociation D_s (MM2 values) [32d]

$$R^1-\underset{\underset{R^3}{|}}{\overset{\overset{R^2}{|}}{C}}-\underset{\underset{R^3}{|}}{\overset{\overset{R^2}{|}}{C}}-R^1 \rightarrow 2\ R^1-C\overset{R^2}{\underset{R^3}{\diagdown}} \qquad C_q-C_q \text{ series}$$

$$\textit{11} \qquad\qquad \textit{12}$$

● R^1 indicated, $R^2 = R^3 = CH_3$
■ $R^1 R^2 R^3 C$ indicated
○ R^1 indicated, $R^2 = R^3 = CH_3$; H_s (MM2 value, 57.9 kcal · mol^{-1}) [39] corrected for inherent strain of adamantyl groups (7.9 kcal · mol^{-1}) [40].
Correlation equations:

Eq. 1. $\Delta G^{\neq}$ (300 °C) $= 62.1\ (\pm\ 0.7)\ -0.63\ (\pm\ 0.03)\ H_s$ [kcal · mol^{-1}] [14b, 37]
$r = -0.987$; $n = 13$
Eq. 2. $\Delta G^{\neq}$ (300 °C) $= 62.2\ (\pm\ 1.1)\ -0.72\ (\pm\ 0.05)\ D_s$ [kcal · mol^{-1}]
$r = -0.981$; $n = 10$

temperature dependence does not vary significantly within a reaction series. The correlations between $\Delta G^{\neq}$ and H_s are therefore better than those between $\Delta H^{\neq}$ and H_s and are more or less independent of temperature. We will take advantage of this in the following discussion.

An additional point of discussion is the slope -0.63 of the correlation in Fig. 2a. It suggests that $\sim 37\%$ of the ground state strain is still present in the radicals *12* being formed, as long as the reaction coordinate of Fig. 1 is valid. Figure 1 was based on the assumption of non-activated radical dimerization, which may no longer be the case for bulky radicals [45]. In order to get deeper insight into the situation the strain enthalpies of the radicals *12* involved were calculated by the MM2 force field which was extended to radicals for this purpose [46]. In Fig. 2b $\Delta G^{\neq}$ (300 °C)

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for the same series of compounds is therefore plotted against the change in strain D_s accompanying the dissociation process:

$$D_s = H_s \text{ (dimer)} - 2 H_s \text{ (radical)}$$

A correlation of similar quality as in Fig. 2a is obtained Eq. (2) ($r = -0.981$, $n = 10$) with almost unchanged intercept (62.2 ± 1.1 kcal $\cdot$ mol^{-1}). The slope is increased however to -0.72.

Very similar correlations Eq. (3 and 4) were found for a series of unsymmetrical C_q--C_q compounds *13* which dissociate into t-alkyl *14* and t-butyl radicals *15*

$$R^1R^2R^3C - C(CH_3)_3 \rightarrow R^1R^2R^3C \cdot + \cdot C(CH_3)_3 \qquad (n = 9)$$
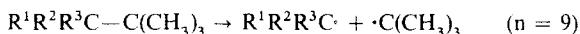
eq. (3) $\Delta G^{\neq}$ (300 °C) $= 64.4\ (\pm\ 0.4) - 0.67\ (\pm\ 0.02)\ H_s$
     [kcal $\cdot$ mol^{-1}]
     $r = -0.997$ [17]

eq. (4) $\Delta G^{\neq}$ (300 °C) $= 65.7\ (\pm\ 0.3) - 0.91\ (\pm\ 0.02)\ D_s^*$
   [kcal $\cdot$ mol^{-1}]
     $r = -0.998$ [17]

The change in strain is designated D_s^* in this case because the strain enthalpies of the radicals were estimated from the strain enthalpies of the corresponding hydrocarbons $R^1R^2R^3CH$ [47].

Summarizing, one can say that 75–90 % of the strain enthalpy released in the dissociation process is found as a reduction in $\Delta G^{\neq}$ or $\Delta H^{\neq}$. The missing 10–25 % is either a tribute to inadequacies of the compensation effect discussed before or also the recombinations of alkyl radicals pass, in contradiction to Fig. 1, a small activation barrier which is equal to 10–25 % of the strain enthalpy of the dimer [9].

Barriers to recombination have been observed for bulky persistent alkyl radicals like di-t-butylmethyl *16* or tri-isopropylmethyl *17* [45]. While *16* dimerized slowly but quantitatively [39,48–50a] to *7*, *17* decomposes in a unimoleculat process and its dimer remains unknown [45].
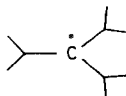
16   *17*

To obtain quantitative results the recombination and disproportionation rates of triethylmethyl radicals *19* were measured by kinetic esr spectroscopy [50]. The radicals *19* were generated by photolysis of *18*.

Despite the building up of 32.6 kcal $\cdot$ mol^{-1} of strain in the dimerization reaction its rate was independent of temperature. It is therefore a non-activated reaction. The order of magnitude of this rate is typical for a diffusion-controlled process. The selectivity for disproportionation to *21* and *22* as against dimerization to *20* and the

small rate retardation in comparison to t-butyl *15* [50b)] are therefore due to entropy control. This is probably quite generally the case for radical-radical reactions [17, 20)].

As suggested by Ingold [45,49,] and confirmed by independent rate data from our laboratory [50a)] only extremely crowded radicals like di-t-butylmethyl *16* have to pass an enthalpy barrier of recombination.

$$k_{dim,} \ (290-400 \ k) \sim 1.0 \cdot 10^8 \ l \cdot mol^{-1} \cdot s^{-1}$$

$$k_{dis,} \ (290-400 \ k) \sim 17 \cdot 10^8 \ l \cdot mol^{-1} \cdot s^{-1}$$

Very similar relationships were observed for other series of alkanes in which the weakest bond is that between two tertiary carbons (*23*, $C_t - C_t$ series) Eq. (5 and 6) [16)] or a tertiary and a quaternary carbon *25*, $C_t - C_q$ series) Eq. (7 and 8):

$$R^1R^2CH-CHR^1R^2 \rightarrow 2 \ R^1R^2CH \cdot \qquad C_t-C_t \ series \ [16)]$$
$$\qquad\qquad 23 \qquad\qquad\qquad 24$$

eq. (5) $\Delta G^{\neq} (300 \ ^\circ C) = 66.9 \ (\pm \ 1.0) - 0.65 \ (\pm \ 0.04) \ H_s$
$$[kcal \cdot mol^{-1}]$$
$$t = -0.975, n = 16$$

eq. (6) $\Delta G^{\neq} (300 \ ^\circ C) = 66.2 \ (\pm \ 1.5) - 0.79 \ (\pm \ 0.07) \ D_s$
$$[kcal \cdot mol^{-1}]$$
$$r = -0.97, n = 8$$

$$R^1R^2CH-C(CH_3)_3 \rightarrow R^1R^2CH \cdot + \cdot C(CH_3)_3 \qquad C_q-C_t \ series \ [17)]$$
$$\qquad 25 \qquad\qquad\qquad 26 \qquad\qquad 15$$

eq. (7) $\Delta G^{\neq} (300 \ ^\circ C) = 65.4 \ (\pm \ 1.1) - 0.70 \ (\pm \ 0.07) \ H_s$
$$[kcal \cdot mol^{-1}]$$
$$r = 0.971, n = 9$$

eq. (8) $\Delta G^{\neq} (300 \ ^\circ C) = 64.8 \ (\pm \ 1.5) - 0.82 \ (\pm \ 0.09) \ D_s^*$
$$[kcal \cdot mol^{-1}]$$
$$r = -0.97, n = 9$$

The axis intercept increases from the $C_q - C_q$ series (62.1 kcal $\cdot$ mol^{-1}) to the $C_q - C_t$ series (65.4 kcal $\cdot$ mol^{-1}) and the $C_t - C_t$ series (66.9 kcal $\cdot$ mol^{-1}), reflecting the known fact that the bond dissociation energies of carbon bonds decrease with increasing alkylation. This is frequently attributed to radical stabilization by hyperconjugation. This is not conclusive, however, and there is good evidence for an alternative

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interpretation of this difference in bond strength as a ground state phenomenon due to differences in the quality of overlap in these systems [16, 51, 52].

In the context of this work we investigated several pairs of $C_t—C_t$ diastereomers *23* which differed in their thermal stability.

Table 2. Differences in $\Delta H^{\ddagger}$ [kcal · mol^{-1}] and in $\Delta S^{\ddagger}$ [e.u.] of thermal cleavage for *D,L* and meso diastereomers $R^1 R^2 CH—CHR^2 R^1$ *23* and their comparison with corresponding differences[a] of ΔH^0 and ΔS^0 for the ground states

R^1	CH_3 [16]	CH_3 [16]	$c—C_6H_{11}$ [55]	C_6H_5 [54, 20]
R^2	$t—C_4H_9$	1-adamantyl	$t—C_4H_9$	$t—C_4H_9$
$\Delta\Delta H^{\ddagger}$ (D,L-meso)	6.3 ($\pm$ 1.1)	9.2 ($\pm$ 1.8)	4.3 ($\pm$ 1.0)	−1.5 ($\pm$ 1.2)
ΔH_s (meso-D,L)[a]	7.1	4.1	6.4	−3.2
$\Delta\Delta S^{\ddagger}$ (D,L-meso)	4.0 ($\pm$ 1.7)	13.0 ($\pm$ 2.3)	−0.4 ($\pm$ 1.6)	−7.6 ($\pm$ 2.1)
ΔS^0 (meso-D,L)[a, b]	2.9	3.2	0.3	−3.9

[a] force field calculations using the MM2 force field [30, 32b].

[b] the entropies were calculated [54a] by the program DELFI [53b], which calculates the full matrix of the second derivative of the energy

Because both diastereomers lead to the same radicals $R'R^2CH\cdot$ *24* on thermolysis this difference has to be due to differences in the ground state stability. This has been confirmed by EFF calculations and can be understood easily on conformational grounds [16, 56]. The minimum energy conformations of all members of the alkane series are gauche.

meso – *25*   D,L – *25*
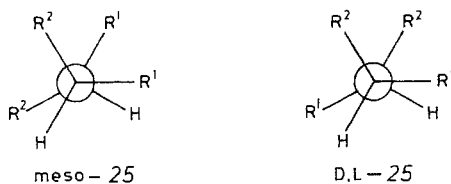
In the D,L-diastereomer D,L-*25* both bulkier R^1 groups can occupy the less hindered position opposite to hydrogen while in meso-*25* one R^1 group is in the less favorable position staggered with respect to two R groups; consequently D,L is more stable than meso. The conformational behaviour of the 1,2-diphenyl-1,2-dialkylethanes [15, 20] on the other hand is more complex due to the shape of the phenyl rings [9b, 54]. The diastereomers of di-t-butyldiphenylethane (see Table 2) show the reversed order in stability, because the meso isomer escapes strain by adopting the anti conformation.

This conformational situation is also responsible for entropy effects. It has been shown [16] that the entropy differences between two diastereomers in this series is mainly dependent on the shapes of the rotational profiles about the central bonds. The observed differences in $\Delta S^{\ddagger}$ (D,L-meso) for the thermolyses can be reproduced semiquantitatively by differences in ground state entropy (see Table 2) which were calculated by the force field method [53].

In summary, the relationship between ground state strain H_s and thermal stability of hydrocarbons which was suggested[1] in a qualitative manner by Ziegler [7], has now been successfully developed into a quantitative one. It is particularly satisfying that the slopes of the $\Delta G^{\neq}/H_s$ correlations of several series of hydrocarbons are very similar. This supports the assumption that the steric effect is acting in a quantitatively analogous manner in these series.

4 The Resonance Effect

As a next step in this analysis we investigated [18] a series of 1,2-diphenyl tetraalkyl ethanes 27 which generate resonance stabilized tertiary benzyl radicals 28 at elevated temperatures (Fig. 3). Having worked out a method for analysis of the steric effect we hoped to succeed also in quantitatively separating it from the resonance effect of substituents. It is immediately recognized from Fig. 3 and the related correlation Eq. (9 and 10) that thermolysis occurs at much lower temperatures ($100°-200 °C$) and with much lower activation enthalpies than in the aliphatic C_q-C_q series 11.

Again good linear correlations of $\Delta G^{\neq}$ (300 °C) and H_s [30, 32] Eq. (9) or D_s Eq. (10) are observed. The slopes of these correlations are very similar to those found for the aliphatic C_q-C_q series 11, supporting the assumption that the steric effect is the same in both cases. Therefore the difference in the axis intercepts (Fig. 3) of the correlations of the aliphatic C_q-C_q series 11 and the C_q-C_q phenyl series 27 must be ascribed to the action of the resonance substituent effect in 28. If the difference in mean entropy of activation in the two series ($\Delta S^{\neq} = 16$ [14b] and 20 e.u. [18] respectively) is taken into account it is calculated that the resonance energy H_r is $8.4 (\pm 1)$ kcal $\cdot$ mol^{-1} for each tertiary benzyl radical 28. This value corresponds numerically to the difference in bond dissociation energy of the tertiary $C-H$ bonds in 2-methyl propane $(93.2 \pm 0.2$ kcal $\cdot$ mol$^{-1})$ [57] and in cumene $(84.4 \pm 1.5$ [57] or 86.1 [58] kcal $\cdot$ mol^{-1}). Values for the benzyl resonance energy [59] quoted in the literature and obtained by other methods are in qualitative agreement but are quite scattered. The method we used has the unique advantage that H_r is evaluated from a whole series of compounds or reactions and that possible steric accelerations by phenyl are explicitly separated in this analysis.

A very similar result is obtained for sec-benzyl radicals 30 by the analysis of the C_t-C_t phenyl series [15] [20].

$$C_6H_5-CHR-CHR-C_6H_5 \longrightarrow 2\ C_6H_5-\dot{C}HR\ (C_t-C_t\ phenyl\ series$$
$$29 \hspace{4cm} 30$$
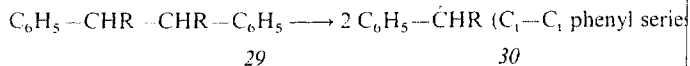
Eq. (11) $\Delta G^{\neq}$ (300 °C) $= 51.4 (\pm 1.4) - 0.48 (\pm 0.11)\ H_s$
[kcal $\cdot$ mol^{-1}]
$r = -0.86, n = 8$

In the manner discussed above, a resonance energy [59, 60] $H_r = 7.8 (\pm 1.5)$ kcal $\cdot$ mol^{-1} per secondary benzyl radical 30 is calculated by comparison of the axis intercept with that of the aliphatic C_t-C_t series 23 [20]. It is remarkable that in both
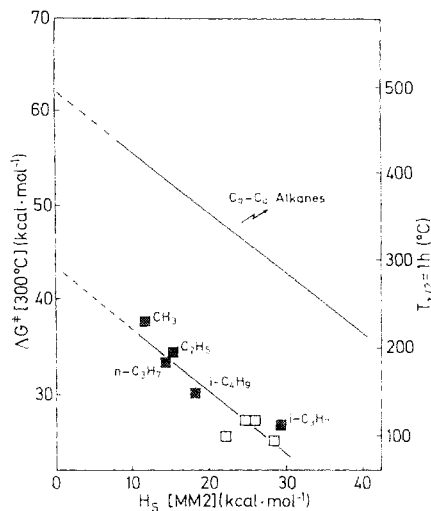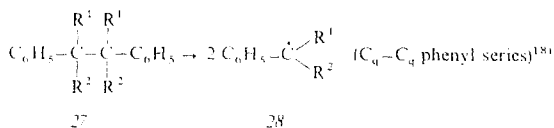
Fig. 3. Relationship between $\Delta G^{\neq}$ (300 °C) of thermolysis and ground state strain H_s for a series of 1,2-diphenyltetraalkylethanes (for comparison the correlation line for the thermolysis of *11* in fig. 2a is included)

$$C_6H_5-\overset{R^1}{\underset{R^2}{\overset{|}{\underset{|}{C}}}}-\overset{R^1}{\underset{R^2}{\overset{|}{\underset{|}{C}}}}-C_6H_5 \rightarrow 2\,C_6H_5-C\overset{R^1}{\underset{R^2}{\diagup}} \quad (C_9-C_9 \text{ phenyl series})^{[18]}$$

$$27 \qquad\qquad 28$$

■ R^1 indicated, $R^2 = CH_3$

☐ $R^1, R^2 = $ n-alkyl

Eq. **9.** $\Delta G^{\neq}$ (300 °C) = 43.3 ($\pm$ 2.3) – 0.64 ($\pm$ 0.11) H_s [kcal · mol^{-1}]

$r = -0.92, n = 9$

Eq. **10.** $\Delta G^{\neq}$ (300 °C) = 44.2 ($\pm$ 2.1) – 0.77 ($\pm$ 0.11) D_s [kcal · mol^{-1}]

$r = -0.93, n = 8$

series meso and D.L diastereomers of quite different thermal stability (see Table 2 and Ref. [20]) were included.

The correlations for the two phenyl-substituted series are, as seen from Fig. 3 and from the correlation coefficients of Eq. (9–11), of sowhat lower quality than those of the unsubstituted alkanes. This is probably due to the greater variations in $\Delta S^{\neq}$ in the two phenyl series. This variation has been ascribed mainly to two factors [18, 20, 61]. When frozen rotations around bonds in the ground state are set free on dissociation in the transition state an increase in $\Delta S^{\neq}$ results. This effect does not necessarily run parallel with the strain H_s, because rotational barriers of highly strained compounds are sometimes flatter than those of less strained ones [31, 35, 36]. The decisive question for estimating $\Delta S^{\neq}$ is the following: is there a rotamer of particular low energy, i.e. a steep minimum available? Due to the flat geometry of phenyl substituents this is the case in the phenyl series [35]. On the other hand, resonance

stabilized benzyl radicals are more restricted in their freedom for internal rotation than alkyl radicals [18]. A second effect influencing $\Delta S^{\neq}$ seems to be caused by very tight pairing of the radicals in the activated complex of bond dissociation [18]. The attractive forces responsible for this phenomenon could but need not lead to the formation of real tight radical pair intermediates. There is good evidence that benzyl type radicals form particularly tight radical pair complexes in which several of the internal rotations of the side chains cannot be set free [20, 62]. This has been discussed as the reason why the members with the ethyl side-chains in several of the investigated series have higher activation entropies $\Delta S^{\neq}$ than those with bulkier or longer side chains [18]. Whereas the small ethyl side-chains gains all its possible freedom of rotation even in a tight radical pair, this is not possible for larger groups.

At this point we conclude that our studies have led to a deeper understanding and a quantitative seperation of steric and resonance effects on $C-C$ bond strength a goal which has been discussed in the context of the hexaphenylethane story [2] for some decades.

Table 3. Resonance energies H_r [59] of substituted alkyl radicals
X $\dot{C}R^1R^2$ 6 ($\pm$ 1 kcal · mol^{-1})

X in 6	n^a	H_r [kcal · mol^{-1}]	Ref.
CH_3	13	$\equiv 0$	[14]
C_6H_5	17	8.4	[15, 18, 20]
$R^3-\underset{\overset{\|}{O}}{C}-$	3	6.5	[63]
$N\equiv C-$	7	5.5	[61]
CH_3OOC-	6	3.5	[64]
CH_3O-	7	1.3	[65]

^{a} number of compounds investigated in this series

A similar analysis. but not based on as extensive data in all examples, was consequently performed for other substituents. The results are reported in Table 3. The stabilizing effects of carbonyl, cyano and ester groups are in agreement with the most reliable literature references [1, 57, 61, 63-64]. The stabilization energies of Table should be particularly reliable, because they were obtained from reaction series and not from single experiments. The high stabilization by the keto function was somewhat surprising. The very small stabilizing effect of methoxy was not unexpected [66], even though alkoxy groups have frequently a large rate accelerating effect radical chemistry. particularly when radical centers are generated [67] α to alk groups, e.g. in autoxidations. These rates are usually, however, controlled by FMO interactions [68] and a large "α-methoxy effect" is a safe indicator of an early transition state in a reaction generating a radical center and of SOMO-HOMO control [67]

5 The Question of Additivity of Substituent Effects

This question has become particularly popular since Viehe [69] postulated that "cap-to-dative substitution", i.e. interaction of a radical center with a donor and an acceptor substituent, leads to stabilizing effects clearly exceeding additivity. In order to get deeper insight into this question, stabilizing effects of more than one substituent at the same time were determined for the series of radicals shown in Table 4. Their accuracy is lower than that of the data in Table 3, because several of these resonance effects H_r were obtained from the thermolysis data for a single compound.

Table 4. Resonance energies H_r[59] [kcal · mol^{-1}] of doubly and triply substituted radicals

Radical		n	H_r (exp)	H_r (calc)[a]	Ref.
$(CH_3)_3C\cdot$			$\equiv 0$	$\equiv 0$	
$(C_6H_5)_2\dot{C} \cdot R$	31	3	12[c]	16.8	[70]
$(C_6H_5)_3C^b$	2	2	19[c]	25.2	[70]
$R-\dot{C}(CN)_2$	32	5	8.5	11	[71]
$C_6H_5-\dot{C}\!\!<^{CH_3}_{CN}$	33	1	15	13.9	[61]
$C_6H_5-\dot{C}\!\!<^{CH_3}_{OCH_3}$	34	5	9.4	9.7	[66]
$(\triangleright)_3 C\cdot$	35	1	3.2	...	[21]
$(\triangleright)_2\dot{C}-CN$	36	1	8.5	7.7	[72]
$C_6H_5-\dot{C}\!\!<^{CN}_{OCH_3}$	37	1	14	15.2	[62]

[a] calculated by assuming additive stabilization by the susbstituents of Table 3.
[b] determined from thermolysis data for pentaphenylethane and 2,2-dimethyl-3,3,3-triphenylpropane [70].
[c] steric inhibition of resonance decreases H_r

The stabilization of benzhydryl *31* and triphenylmethyl *2* is less than additive, as expected for the non-planar propeller-like structures of these radicals, which do not allow the development of full conjugation. The angle of twist is probably very similar in benzhydryl and trityl radicals [73] and one is tempted to attribute to each twisted phenyl an additive stabilization of 6 kcal · mol^{-1}. On the other hand two cyano groups in *32* likewise stabilize a radical less than additively. Phenyl and cyano (*33*) and phenyl and methoxy (*34*) show additive stabilization. For one cyclopropyl group in *35* a little more than 1 kcal · mol^{-1} stabilization can be counted and additivity follows consequently for *36*. The captodative radical *37* is stabilized according to additivity

and not more. A similar, but still somewhat preliminary result has been found fc the α-cyano-α-methoxy-neopentyl radical *38*. Therefore a leveling effect by the phen; substituent is not responsible for the failure to observe a larger capto-dative effect i *37*.

The data in Table 4 are not yet sufficient to give a final answer as to when additivit is to be expected and when not. They clearly show however that additivity of subst tuent effects definitely is not the exception.

The 1-cyano-1-methoxybenzyl radical *37* and its dimers *39* were investigated wit particular care[62] in order to test the reliability and the persuasive power of the method used and the results discussed so far.

D,L — *39*   *37*   meso — *39*
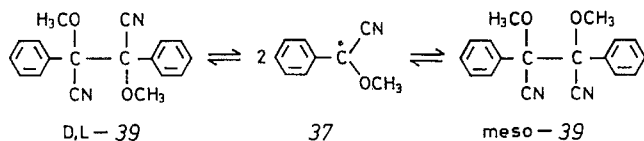
Meso- and D,L-2,3-dimethoxy-2,3-diphenylsuccinonitrile *39* were obtained in a 1: ratio by a preparative dimerization procedure. Their configurations were assigne by crystal structure analysis[74]. According to nmr both diastereomers have a conf guration with the phenyl groups in the anti position. From a conformational analys by the force field method it was concluded that these conformations remain the prefe red ones also for the isolated molecules; meso-*39* was calculated to be 1.2 kcal · mol¯
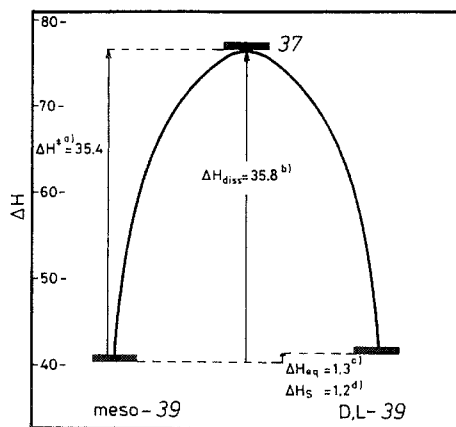
Fig. 4. Enthalpy diagram for the reversible dissociation of meso- and *D,L-39* [kcal · mol¯¹]. The numerical values in the Fig. are from the following sources:
a) from the kinetics of the thermal equilibration of meso-*39* and D,L-*39* (nmr method)[75]
b) from measurements of the equilibrium constant K_{diss} between *39* and *37* by esr[62];
c) from measurements of the equilibirum constant K_{eq} between meso-*39* and D,L-*39* by gc and nmr[62, 75];
d) from EFF calculations[62]

more stable than D,L-*39*. Figure 4 shows the complete reaction coordinate of the system which was constructed by independent determination of

1) the equilibirium constant K_{eq} over a temperature range of 40 °C by gc,
2) the equilibirum constant K_{diss} over a temperature range of 60 °C by esr [62] and
3) the activation enthalpies $\Delta H^{\neq}$ for the thermal dissociation of the two diastereomers independently [62, 75].

Figure 4 shows that the enthalpy difference between the two stereoisomers ΔH_{eq} is in excellent agreement with the prediction of the force field calculations.

The close agreement between ΔH_{diss} and $\Delta H^{\neq}$ in Fig. 4 allows the conclusion that the dimerization of the radicals *37* is a non-activated process. It has been confirmed independently by direct kinetic experiments [76] that $\Delta H^{\neq}$ of recombination for radicals *37* is similar to or smaller than their barrier for diffusion. Capto-dative substituted radicals accordingly have no kinetic stabilization.

Quite remarkable is the low entropy of activation $\Delta S^{\neq}$ of 10.9 e.u. for the dissociation of meso-*39* in contrast to ΔS_{diss} (31.1 ± 0.8 e.u.) for the complete dissociation into free radicals. In the activated complex of the dissociation of *39* the central $C-C$ bond is no doubt almost completely broken but the system has gained only little additional freedom of mobility as compared to the ground state dimer. This strongly supports the formation of a sandwich-like arrangement of the two radicals in the activated complex as discussed above [20, 77]. According to the principle of microscopic reversibility, the dimerization reactions of radicals of this type should proceed via the same sandwich-like alignement and, therefore, may have to pass a barrier in $\Delta G^{\neq}$ due to the loss of entropy complex formation. Among all possible encounter pairs those which are sandwich like oriented should be favoured by secondary valence interactions [50a, 77]. They are therefore more populated than differently oriented pairs e.g. those leading to disproportionation. This could explain the high dimerization/ disproportionation ratios which are found for benzyl type radicals [20] as well as for cato-dative radicals [69]. Hence simple steric effects may be responsible for the observed high regiospecificities of the termination of benzyl type radicals.

6 Strain, Structure and Bonding

The relationships between structure and strain constitute a very complex story which cannot be dealt with comprehensively in this context [9b]. For this reason only a few selected points of interest will be addressed briefly here:

1) the reliability of the force field method to predict structures of highly strained compounds and
2) the relationships between bond length, bond strength and strain.

In Fig. 5 the X-ray structure of *40*, the most highly strained member of the C_q-C_q alkane series is shown [39, 74] and in parentheses the predictions of MM2 force field calculations are given [39].

Despite the fact that in this compound the three central carbon bonds are 164 pm or longer and, therefore, are among the longest known bonds of this kind the predictions by the force field method are exceedingly precise. The very good agreement between experimental and calculated bond angles and torsional angles is even more impressive since these are controlled by much weaker force constants. A similar
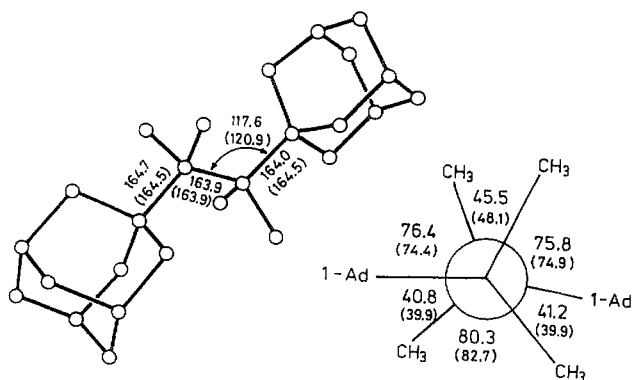
Fig. 5. Crystal structure of 3.4-di-(1-adamantyl)-2,2,5,5-tetramethylhexane 40[39, 74]. Results of for field calculations [32] in parentheses
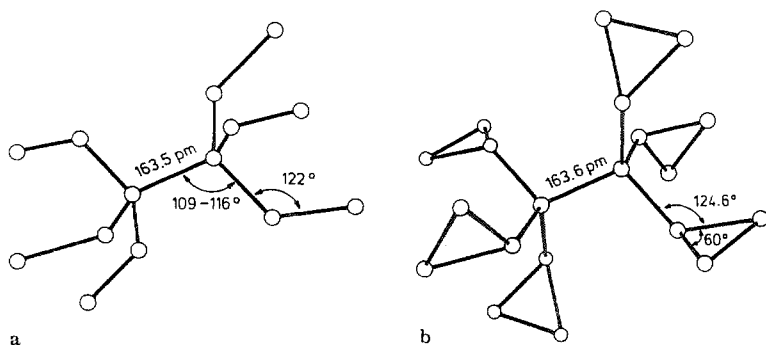

Fig. 6. Crystal structure of hexycyclopropylethane 41 [21] and force field structure [32] of hexyeth ethane 43

agreement has been found for many other highly strained compounds of the differe series discussed in this review [20,25,31,55,56,78,79].

The structure of hexacyclopropylethane 41 which decomposes at ~ 305 °C w $t_{1/2} = 1$ h, and its comparison with hexaisopropylethane 42 which is too unsta[to be isolated (see above) is of particular interest. A comparison of the X-ray structu of hexacyclopropylethane 41 [21] with the EFF structure of hexaethylethane 43[1] is shown in Fig. 6. It reveals that in the latter the preferred way of escaping strain to increase the bond angles at the α positions of the side-chains to values higher th 120°. In hexycyclopropylethane 41 the corresponding twelve bond angles are larg than 124° anyway as a consequence of the small inner angles of the cyclopropa rings. Therefore the cyclopropyl rings behave sterically more like ethyl side-chai than like isopropyl groups in which bond angle deformation is even more difficu
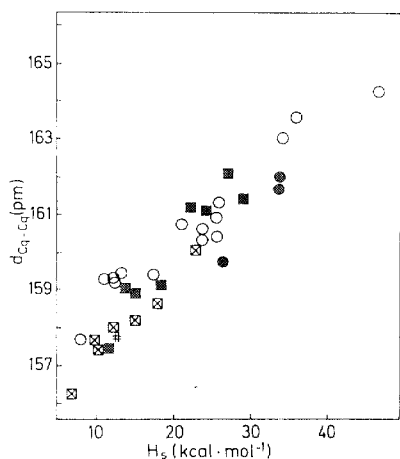
Fig. 7. Relationship between the central C_q-C_q bond lengths and the strain enthalpies in several C_q-C_q series; ○ C_q-C_q alkanes *11*, ⊠ C_q-C_q dinitriles, ■ C_q-C_q phenyl series *27*, ● C_q-C_q tetraphenylethanes ✠ captodative dimer *39*

The final point of interest, the relationship between bond lengths and bond strengths or ground state strain H_s, is shown in Fig. 7.

A reasonably good direct correlation between the length of the central $C-C$ bond and the ground state strain is observed for a large number of substituted C_q-C_q systems, including those of the benzhydryl type [70] and the capto-dative system *39* [74]. It is remarkable that the bond-weakening effect of the resonance stabilizing substituents has no effect on the bond length. Bond lengths are apparently a ground state phenomenon as is the strain enthalpy H_s, while the resonance effect of the substituents is a transition state effect as suggested long ago [7]. On the other hand the relationship in Fig. 7 is certainly partly fortuitous. It requires that in all series included in Fig. 7 the distribution of strain into angle deformation and bond streching must be very similar. For this reason it was not unexpected that compounds of the C_t-C_t series, which allow much better angle deformation [9b] in the central region of their structures [16, 20, 49, 54, 55, 79], do not obey the simple correlation of Fig. 7. It is restricted to the C_q-C_q compounds.

Despite this better mode of strain dissipation in the C_t-C_t series the central $C-C$ bond length in 2,3-dimethylbutane, the parent compound, is shorter than the extrapolated bond length of a hypothetical strainless parent C_q-C_q compound [79]. This supports the proposal made before, that C_i-C_i bonds are intrinsically stronger than C_q-C_q bonds. If the difference in resonance stabilization of tertiary and secondary alkyl radicals was the dominating factor determining these bond strengths it should have no consequences for the bond lengths [80].

The separate and quantitative evaluation of accelerating steric effects on the homolytic cleavage of $C-C$-bonds allowed the definition of intrinsic barriers for the bond dissociation reaction, i.e. $\Delta G^{\neq}$ or $\Delta H^{\neq}$ at $H_s = 0$ in Fig. 2 or 3 or in Eq. (1–11) in general. $\Delta H^{\neq}$ is equal to or slightly than the corresponding bond dissociation energy (BDE) [6a, 81] as pointed out earlier.

Intrinsic BDE's can be determined alternatively from appropriate group increments,

which define strain free heats of formation of educts and radical products. Using Schleyer's increments for alkanes [29] (CH_3 $\cdot$ 10.05; CH_2 5.13; CH -2.16 and C -0.30 kcal $\cdot$ mol^{-1}) and increments for radicals obtained by the same formalism [46] (CH_3 34.3; CH_2 36.6; CH 37.7 and C 38.6 kcal $\cdot$ mol^{-1}) the following two equations give numerical values for the bond energies of strain free C_t—C_t and C_q—C_q bonds:

eq. (12) $BDE(C_t C_t) = 2\,(37.7 + 2.16) = 79.7$ kcal $\cdot$ mol^{-1}

eq. (13) $BDE(C_q—C_q) = 2\,(38.6 + 0.30) = 77.8$ kcal $\cdot$ mol^{-1}

Obviously there are, by definition, no individual contributions of alkyl side chains in the educt molecules because they remain unchanged in the radicals. The difference in energy of these two bonds calculated in this way

$$\Delta BDE = 1.9 \text{ kcal} \cdot \text{mol}^{-1}$$

is in reasonable agreement with the difference in activation enthalpy for the C—C cleavage reaction.

$$\Delta\Delta H^{\neq}\,(H_S = 0) = 3.2 \pm 1.7 \text{ kcal} \cdot \text{mol}^{-1}\,.$$

$\Delta\Delta H^{\neq}$ is obtained from Fig. 2a and Eq. (5) when the difference in mean entropy of activation of the C_q—C_q series (16.2 e.u.) and the C_t—C_t series (13.2 e.u.) is taken into account.

The group increment analysis, in addition, suggests an explanation for the difference in BDE for C_q—C_q and C_t—C_t bonds. The exchange of hydrogen for alkyl at a C—C bond lowers the enthalpy considerably (going from a C_q—C_q bond to C_t—C_t to $-CH_2$—CH_2— and finally to ethane in steps, the change in ΔH is -1.8, -3.0 and -4.9 kcal $\cdot$ mol^{-1}, respectively). The energies of carbon radicals in contrast are decreased much less, if one goes from a tertiary to a socondary (-0.9 kcal $\cdot$ mol^{-1}) from there to a primary (-1.1 kcal $\cdot$ mol^{-1}) and finally methyl (-2.3 kcal $\cdot$ mol^{-1}). The large difference of these increments for secondary and tertiary hydrocarbon fragments in alkanes, mentioned above, is also the main reason for the large difference in BDE between tertiary and secondary C—H bonds.

$$BDE\,(C_{sec}—H — C_{tert}—H) = 2.1 \text{ kcal} \cdot \text{mol}^{-1}$$

This difference is therefore mainly due to a ground state phenomenon as pointed out earlier [51]. Clearly, therefore, $BDE\,(C_{sec}—X — C_{tert}—X)$ depends very much on the C—X bond being broken [51].

7 Acknowledgement

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