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Synthetic Organic Chemistry

With Contributions by

H.-D. Beckhaus, J. Collard-Motté, B. Czochralska,
R. S. Dhillon, Z. Janousek, J. Jurczak, M. Pietraszkiewicz,
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With 18 Figures and 23 Tables



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Table of Contents

Steric and Electronic Substituent Effects on the Carbon-Carbon Bond	
Ch. Rüchardt, H.-D. Beckhaus	1
Selective Hydroboration and Synthetic Utility of Organoboranes Thus Obtained	
A. Suzuki, R. S. Dhillon	23
Synthesis of Ynamines	
J. Collard-Motte, Z. Janousek	89
Electrochemically Reduced Photoreversible Products of Pyrimidine and Purine Analogues	
B. Czochralska, M. Wrona, D. Shugar	133
High-Pressure Synthesis of Cryptands and Complexing Behaviour of Chiral Cryptands	
J. Jurczak, M. Pietraszkiewicz	183
Author Index Volumes 101-130	205

Steric and Electronic Substituent Effects on the Carbon-Carbon Bond

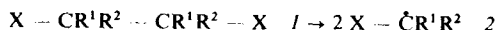
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Table of Contents

1 Introduction	2
2 Methods	4
3 The Steric Effect	6
4 The Resonance Effect	11
5 The Question of Additivity of Substituent Effects	14
6 Strain, Structure and Bonding	16
7 Acknowledgement	19
8 References	20

The factors influencing dissociation energies of C—C bonds have been investigated by thermochemical (ΔH_c° , ΔH_r , 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 = C₆H₅, CN, OCH₃, COR, COOCH₃) has been successfully achieved.



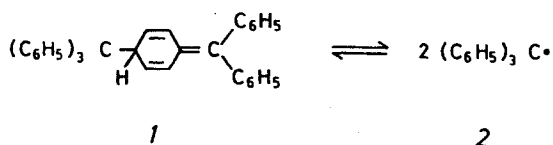
Enthalpy and entropy effects and their interrelationships are discussed. Resonance stabilization of radicals by more than one substituent (including captodative substitution) is frequently additive and in no example higher than this. A linear correlation is found between the central C—C bond lengths in 1 and the strain enthalpies H_s , quite independent of the substituents X and their resonance contribution H_r .

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 $80 \text{ kcal} \cdot \text{mol}^{-1}$, 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 ($88.2 \text{ kcal} \cdot \text{mol}^{-1}$)¹⁾ is compared with that of the central bond in the Gomberg dimer **1** ($12 \text{ kcal} \cdot \text{mol}^{-1}$)^{2, 3)}.



This difference of $76 \text{ kcal} \cdot \text{mol}^{-1}$ 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 $\sim 700^\circ\text{C}$) or **1** into trityl radicals **2**²⁾ (at $\sim 25^\circ\text{C}$). This is an incredible factor⁴⁾ 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 ΔH^\ddagger 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

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

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 forties⁷⁾. In this early demonstration of the power of kinetics for the investi-

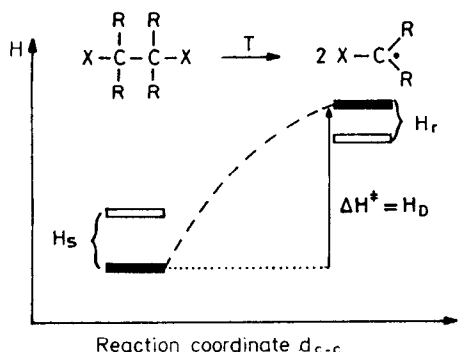
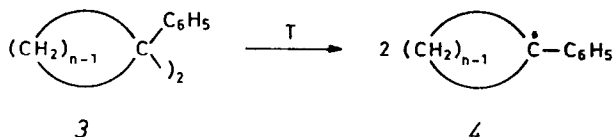


Fig. 1. Reaction coordinate of the bond dissociation process with non activated radical recombination; the influence of ground state strain H_s and of resonance stabilization H_r of the radical centers by the substituent X on the bond strength H_D is qualitatively indicated

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.

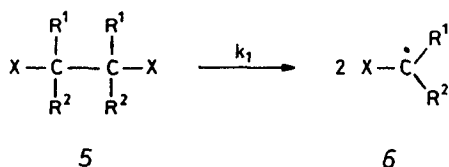
Work towards a quantitative analysis of these effects was initiated in our laboratory in the early seventies⁹⁾ when an unusually large ring size effects on the thermal cleavage reaction of 1,1'-diphenylbicycloalkyls **3** into 1-phenylcycloalkyl radicals **4** was observed; this was inexplicable by i-strain effects alone and pointed to the importance of f-strain in this phenomenon¹⁰⁾.



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 initiators¹¹⁾, coal pyrolysis¹²⁾ or thermal stabilities of polymers¹³⁾.

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.



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 substituents 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 $\Delta H^\ddagger \leq 1$ kcal \cdot mol⁻¹ in $\Delta S^\ddagger \leq 3$ e.u. and in ΔG^\ddagger (at the temperature of measurement) ≤ 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-

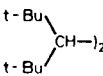
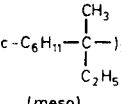
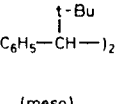
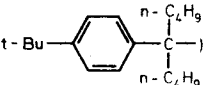
ities²³⁾ of the medium at the high temperatures which were required for most reactions⁹⁾.

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 experiments²⁴⁾.

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 combustion²⁵⁻²⁷⁾ using either a stirred liquid calorimeter²⁵⁾ or an aneroid microcalorimeter²⁶⁾; 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 increments²⁸⁾. For the definition of the strain enthalpies Schleyer's single conformation increments²⁹⁾ were used and complemented by increments for other groups containing phenyl³⁰⁾ 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 alkanes³²⁾ and its extension to alkylbenzenes³⁰⁾ proved to be in by far the best agreement with the experimental results²⁷⁾. 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 crowded 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	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 increments²⁸⁾.

^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-butylethane 7³³⁾, 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 field³⁴⁾.

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, satisfying agreement with results from dynamic nmr-measurements for a series of crowded 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 ΔG^* (300 °C) of the thermolysis reactions of symmetrical hexaalkylethanes // ($C_q - C_q$ 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 ΔG^* are correlated with strain enthalpies H_s despite the fact that there is neither an isoentropic ($\Delta S^* = \text{const.}$) ⁴¹⁾ nor an isokinetic relationship ($\Delta H^* \propto \Delta S^*$) ⁴¹⁾ within this series. Indeed ΔS^* varies from 13 to 26 entropy units ¹⁴⁾. In a kind of Exner test ⁴²⁾ it was shown, however, that the order of decreasing $\Delta G^*(T)$ values is independent of temperature and therefore significant for structural interpretation ¹⁴⁾.

From the axis intercept in Fig. 2a, ΔG^* (300 °C) = 62.1 kcal · mol⁻¹, and from the mean entropy of activation, $\Delta S^* = 15$ e.u. ¹⁴⁾, an activation enthalpy $\Delta H^* = 71$ 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 ΔH^* 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 $\Delta H^* = 72$ 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⁾. ΔH^* 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 ΔH^* values should be extrapolated over large temperature ranges down to 25 °C. This is not possible because ΔC_p^* values, the differences in heat capacity between ground and transition states, are not available. Benson points out ⁴³⁾ that the main factors determining ΔC_p^* are the changes in the degrees of freedom of translation, of internal and external rotation and of vibration. Just the same factors determine ΔS^* . Therefore the temperature effects on $\Delta H^*(\Delta C_p^* dt)$ and on $T\Delta S^*$ are very similar. Due to the opposed signs of these two contributions to ΔG^* the temperature effect is largely compensated in ΔG^* ⁴⁴⁾, which is a term whose

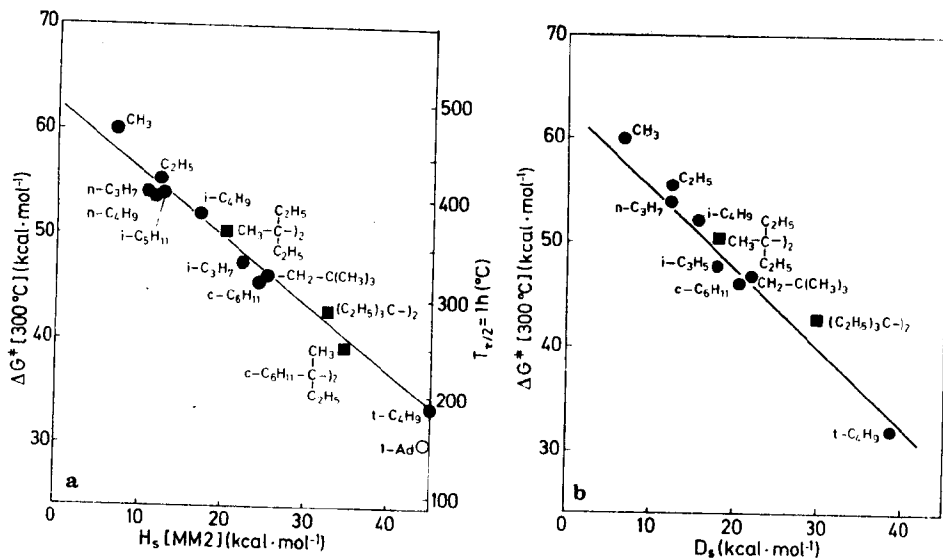
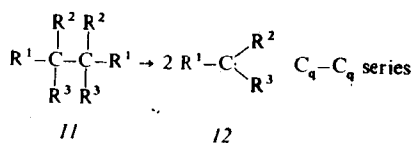


Fig. 2a and b. Relationships between ΔG^* (300 °C) of thermal decomposition of sym-hexyalkyl-ethanes and
 a ground state strain H_s (MM2 values)^{32d}; b change in strain enthalpy during dissociation D_s (MM2 values)^{32d}



● 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. ΔG^* (300 °C) = 62.1 (± 0.7) - 0.63 (± 0.03) H_s [kcal·mol⁻¹] ^{14b, 37}
 $r = -0.987$; $n = 13$

Eq. 2. ΔG^* (300 °C) = 62.2 (± 1.1) - 0.72 (± 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 ΔG^* and H_s are therefore better than those between ΔH^* 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 ~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 radicals⁴⁵. 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 purpose⁴⁶. In Fig. 2b ΔG^* (300 °C)

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 ($62.2 \pm 1.1 \text{ kcal} \cdot \text{mol}^{-1}$). 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



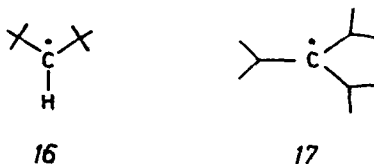
$$\begin{aligned} \text{eq. (3)} \quad \Delta G^\ddagger (300^\circ\text{C}) &= 64.4 (\pm 0.4) - 0.67 (\pm 0.02) H_s \\ &[\text{kcal} \cdot \text{mol}^{-1}] \\ r &= -0.997^{17)} \end{aligned}$$

$$\begin{aligned} \text{eq. (4)} \quad \Delta G^\ddagger (300^\circ\text{C}) &= 65.7 (\pm 0.3) - 0.91 (\pm 0.02) D_s^\ddagger \\ &[\text{kcal} \cdot \text{mol}^{-1}] \\ r &= -0.998^{17)} \end{aligned}$$

The change in strain is designated D_s^\ddagger 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 ΔG^\ddagger or ΔH^\ddagger . 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 dimer⁹⁾.

Barriers to recombination have been observed for bulky persistent alkyl radicals like di-t-butylmethyl 16 or tri-isopropylmethyl 17⁴⁵⁾. While 16 dimerized slowly but quantitatively^{39, 48–50a)} to 7, 17 decomposes in a unimolecular process and its dimer remains unknown⁴⁵⁾.



To obtain quantitative results the recombination and disproportionation rates of triethylmethyl radicals 19 were measured by kinetic esr spectroscopy⁵⁰⁾. The radicals 19 were generated by photolysis of 18.

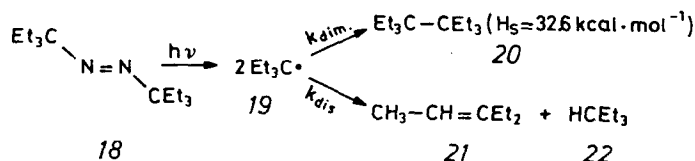
Despite the building up of $32.6 \text{ kcal} \cdot \text{mol}^{-1}$ of strain in the dimerization reaction its rate was independent of temperature. It is therefore a non-activated reaction. The order of magnitude of this rate is typical for a diffusion-controlled process. The selectivity for disproportionation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

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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)}.

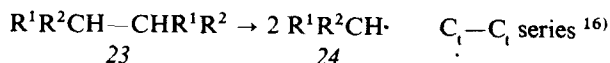
As suggested by Ingold^{45,49)} and confirmed by independent rate data from our laboratory^{50a)} only extremely crowded radicals like di-*t*-butylmethyl 16 have to pass an enthalpy barrier of recombination.



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

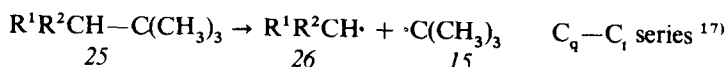
$$k_{\text{dis.}} (290-400 \text{ K}) \sim 17 \cdot 10^8 \text{ l}\cdot\text{mol}^{-1} \cdot \text{s}^{-1}$$

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):



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

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



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

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

The axis intercept increases from the C_q—C_q series (62.1 kcal·mol⁻¹) to the C_q—C_t series (65.4 kcal·mol⁻¹) and the C_t—C_t series (66.9 kcal·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

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_1-C_1 diastereomers 23 which differed in their thermal stability.

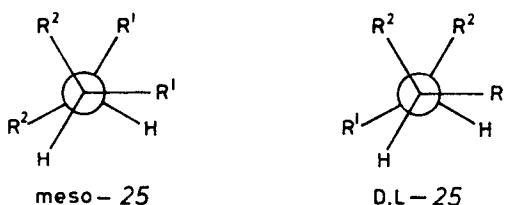
Table 2. Differences in ΔH^\ddagger [kcal \cdot mol $^{-1}$] and in ΔS^\ddagger [e.u.] of thermal cleavage for *D,L* and meso diastereomers $R^1R^2CH-CHR^2R^1$ 23 and their comparison with corresponding differences^a of ΔH^0 and ΔS^0 for the ground states

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_g (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^{53a)} 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 $R^1R^2CH\cdot$ 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.



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 shown¹⁶⁾ 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 ΔS^\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 method⁵³⁾.

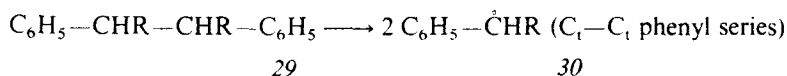
In summary, the relationship between ground state strain H_s and thermal stability of hydrocarbons which was suggested¹ in a qualitative manner by Ziegler⁷⁾, has now been successfully developed into a quantitative one. It is particularly satisfying that the slopes of the $\Delta G^*/H_s$ correlations 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 investigated¹⁸⁾ 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 ΔG^* (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 ($\Delta S^\ddagger = 16$ ^{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 · 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-methylpropane (93.2 ± 0.2 kcal · mol⁻¹)⁵⁷⁾ and in cumene (84.4 ± 1.5 ⁵⁷⁾ or 86.1 ⁵⁸⁾ kcal · mol⁻¹). Values for the benzyl resonance energy⁵⁹⁾ 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)}.



$$\text{Eq. (11)} \quad \Delta G^* (300^\circ\text{C}) = 51.4 (\pm 1.4) - 0.48 (\pm 0.11) H_s$$

[kcal · 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 · 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

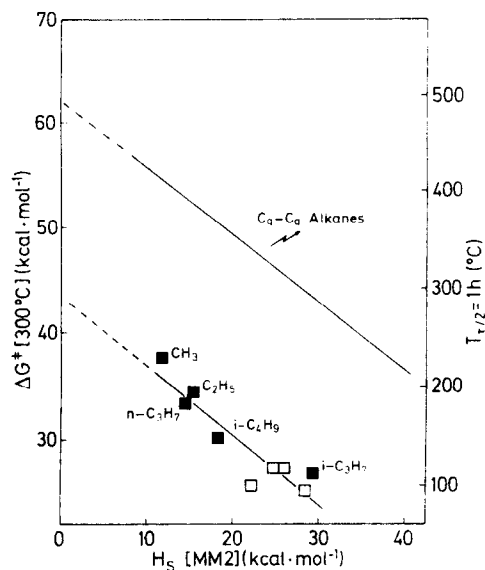
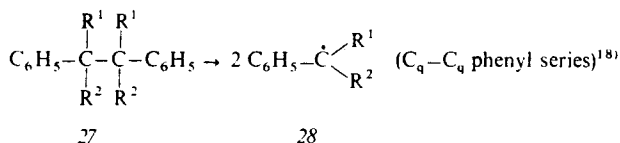


Fig. 3. Relationship between ΔG^* (300 °C) of thermolysis and ground state strain H_1 for a series of 1,2-diphenyltetraalkylethanes (for comparison the correlation line for the thermolysis of *II* in fig. 2a is included)



■ R¹ indicated, R² = CH₃

□ $R^1, R^2 = n\text{-alkyl}$

$$\text{Eq. 9. } \Delta G^* (300^\circ\text{C}) = 43.3 (\pm 2.3) - 0.64 (\pm 0.11) H_u [\text{kcal} \cdot \text{mol}^{-1}]$$
$$r = -0.92, n = 9$$
$$\text{Eq. 10. } \Delta G^* (300^\circ \text{C}) = 44.2 (\pm 2.1) - 0.77 (\pm 0.11) D, [\text{kcal} \cdot \text{mol}^{-1}]$$
$$r = -0.93, n = 8$$

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 somewhat lower quality than those of the unsubstituted alkanes. This is probably due to the greater variations in ΔS^\ddagger 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 ΔS^\ddagger 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 ΔS^\ddagger 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 series³⁵. On the other hand, resonance