erated during the pyrolysis of $Ba^{2+}(NH_3)_2(NP^{-}\cdot)_2$ originates from the naphthalene. This is consistent with the mechanism proposed in reaction 3. However, the deuteration studies do not eliminate the possibility that the H_2 comes from the ammonia in the final step. The fact that the amount of hydrogen produced varies dramatically with the choice of hydrocarbon supports the mechanism proposed in reaction 3.

It appears that significant amounts of hydrogen can be generated regardless of the polyacene used. Studies carried out with calcium and strontium serving as the metal yield very similar results. In fact, the yield of hydrogen from the $Ca^{2+}(NH_3)_2(AN^{-}\cdot)_2$ salt was indistinguishable from that of the analogous barium salt.

Experimental Section

The alkaline earth metal complexes were generated via the reduction of the polyaromatic hydrocarbons with 1 equiv of the alkaline earth metal in liquid ammonia in a manner that is identical with that previously described.[1] The pyrolysis studies were carried out by heating evacuated bulbs containing the solid salts in an oil bath. The evacuated bulbs were connected to a vacuum line through two U-tubes. The U-tube closest to the bulb containing the salt was kept under a dry ice–acetone bath at −78 °C, and the second U-tube was immersed in liquid nitrogen. After the vacuum line was pumped down to about 10^{-6} mmHg, a breakseal separating the bulb and the U-tubes and vacuum system was broken. The pressure in the vacuum system was monitored with a Fluid Precision Inc. capacitron pressure gauge to ±0.01 mm of Hg. From the known volume of the vacuum system, the number of mol of gas that passed through the two U-tubes was obtained. When these noncondensable gases were exposed to hot copper oxide, the pressure dropped to zero and a mole of water was condensed from the vacuum line for each mole of gas present. This coupled with the NMR analysis of liquid formed from the reaction of the gas with CuO confirms the fact that the gas was uncontaminated hydrogen.

The number of moles of liquid N_2 condensable gases emitted from the pyrolyzed salt was obtained by pumping the noncondensables from the system and then removing the liquid nitrogen bath from the second U-tube. Unpolymerized hydrocarbon was recovered from the U-tube immersed in the dry ice–acetone bath.

Mass spectral analyses were carried out with a HP 5790 mass selective detector, and the analytical samples were sent to Micro-Analysis, Inc. for elemental analyses. ESR spectra were recorded with a Bruker (IBM) E-2000 ESR spectrometer.

Conclusions

It has been found that heating solid samples of the alkaline earth metal–ammonia–polyaromatic anion radical complexes to temperatures above 60 °C yields significant amounts of hydrogen gas. This hydrogen gas appears to originate from the aromatic hydrocarbon anion radical and results in the subsequent polymerization of the polyaromatic. Simultaneously with this reaction, there is some degradation of the complex back to the metal, ammonia, and polyacene. This simple decomposition is favored by small polyacenes (those with low electron affinities), while the production of hydrogen is favored by the larger polyacene systems.

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Thermolysis of Highly Congested Tri-*tert*-alkylmethanols: Strain Energies of Bridgehead Alkyl Radicals

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The rate constants and the products of the thermolysis of tertiary alcohols, $R^1R^2R^3COH$, where R^i is *tert*-butyl, 1-adamantyl, 1-bicyclo[2.2.2]octyl, or 1-norbornyl, have been determined. Apart from the usual secondary alcohols and ketones, the products include new ketones, formed by ring-opening of the 1-norbornyl group, and solvent-incorporated alcohols. The activation energies for (*t*-Bu)–C, Ad–C, Oc–C, and, in one case, Nor–C cleavage are compared with the molecular mechanics calculated strain-energy changes, Δstrain. These latter are based on a simple model of the reaction intermediate where the bridgehead radicals are represented by the corresponding alkanes. Taking the $\Delta G^{\ddagger}(200\ °C)/\Delta$strain correlation for *t*-Bu· formation as a reference, one can show that the deviations, ΔΔstrain, of the data for the formation of the other radicals (Ad, 2.4; Oc, 4.0; Nor, 7.7 kcal mol^{-1}) indicate the real difference between the strain energies of the radicals and the alkanes. Analogous $\Delta\Delta G^{\ddagger}$ data for other reactions considered to involve rate-determining radical formation correlate with ΔΔstrain, the slopes ranging from 0.16 to 1.13. The ΔΔstrain values also correlate with solvolysis rate constants of *tert*-alkyl tosylates, with a slope ($\Delta\Delta$strain$/\Delta G^{\ddagger}(70\ °C)$) of 0.36; tentative values for the strain energies of other bridgehead radicals are proposed and compared with the predictions of a radical force field.

It is generally agreed that tertiary alkyl radicals accept nonplanarity more easily than tertiary alkyl cations.[1] According to the latest calculations and interpretation of ESR spectra,[2] even the *tert*-butyl radical is slightly nonplanar. The result of this difference between radicals and carbocations is that solvolysis rates of bridgehead alkyl derivatives[3] range over many powers of 10, from 1-adamantyl (1) to 1-norbornyl (10^{-10}), for example, while the relative rates of reactions with rate-determining formation of the corresponding radicals differ much less (Ad/Nor = $10^{0.6}$–10^4).[4] However, the several studies re-

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Table I. Overall Rate Constants for the Thermolysis of Tertiary Alcohols $R^1R^2R^3COH$

compd	R^1	R^2	R^3	k, s^{-1} (T, °C)	k, s^{-1} (T, °C)	k, s^{-1} (T, °C)	k, s^{-1} (T, °C)
1[a]	*t*-Bu	Oc	Oc	1.12×10^{-4} (155.0)	5.78×10^{-4} (169.7)	2.74×10^{-3} (184.9)	1.15×10^{-2} (200.1)
2[a]	*t*-Bu	Oc	Nor	5.91×10^{-5} (200.1)	2.66×10^{-4} (215.1)	1.19×10^{-3} (230.0)	4.43×10^{-3} (245.1)
2[b]	*t*-Bu	Oc	Nor	5.43×10^{-5} (199.8)	2.71×10^{-4} (215.1)	1.18×10^{-3} (230.0)	4.46×10^{-3} (245.5)
2[c]	*t*-Bu	Oc	Nor	5.70×10^{-5} (199.8)	2.84×10^{-4} (215.1)	1.23×10^{-3} (230.1)	4.50×10^{-3} (245.5)
3[b]	*t*-Bu	Nor	Nor	4.74×10^{-5} (245.7)	2.35×10^{-4} (263.1)	1.23×10^{-3} (281.0)	4.93×10^{-3} (297.1)
4[c]	Ad	Ad	Ad	5.21×10^{-5} (134.8)	3.27×10^{-4} (150.1)	1.67×10^{-3} (165.0)	7.73×10^{-3} (180.1)
5[c]	Ad	Ad	Oc	5.44×10^{-5} (150.1)	3.29×10^{-4} (165.0)	1.58×10^{-3} (180.1)	7.62×10^{-3} (195.0)
6[a]	Ad	Ad	Nor	1.09×10^{-4} (215.1)	5.47×10^{-4} (230.0)	2.26×10^{-3} (245.1)	9.21×10^{-3} (260.3)
6[c]	Ad	Ad	Nor	1.20×10^{-4} (215.1)	6.19×10^{-4} (230.2)	2.45×10^{-3} (245.5)	8.40×10^{-3} (260.0)
7[c]	Ad	Oc	Oc	6.14×10^{-5} (164.9)	3.58×10^{-4} (181.0)	1.71×10^{-3} (195.7)	7.10×10^{-3} (210.9)
8[b]	Ad	Oc	Nor	4.29×10^{-5} (220.0)	1.97×10^{-4} (234.6)	7.69×10^{-4} (249.1)	3.25×10^{-3} (265.0)
9[b]	Ad	Nor	Nor	2.39×10^{-5} (267.7)	1.28×10^{-4} (287.1)	4.60×10^{-4} (302.0)	2.49×10^{-3} (322.6)
10[c]	Oc	Oc	Oc	5.88×10^{-5} (184.5)	3.16×10^{-4} (199.9)	1.48×10^{-3} (215.3)	6.93×10^{-3} (231.8)
10[a]	Oc	Oc	Oc	5.70×10^{-5} (184.9)	3.04×10^{-4} (200.1)	1.43×10^{-3} (215.1)	6.77×10^{-3} (230.0)
11[b,d]	Oc	Oc	Nor	6.47×10^{-5} (242.5)	2.85×10^{-4} (259.9)	1.51×10^{-3} (276.9)	3.36×10^{-3} (286.8)
12[b]	Oc	Nor	Nor	2.03×10^{-5} (287.1)	1.10×10^{-4} (307.2)	1.30×10^{-3} (337.7)	2.23×10^{-3} (345.3)
13[e]	Nor	Nor	Nor	9.7×10^{-5} (377.1)	2.8×10^{-4} (400.0)		

[a] In dodecane, ±3–5%. [b] In mesitylene, ±3–5%. [c] In toluene, method II, ±5–10%. [d] Additional data: 1.28×10^{-4} (250.3); 5.88×10^{-4} (267.2). [e] In prehnitene containing 0.1 M 2,6-di-*tert*-butylphenol.

ported to date reveal a marked lack of consistency about the effects of strain in bridgehead radicals as compared to the *tert*-butyl radical. There are several reasons for these discrepancies, the most important of which is that the rate of a reaction via a radical intermediate only partially reflects the nature of the radical itself. Reactions with transition states more or less close to the radical will, therefore, give different answers to the question of the steric demands of the trivalent carbon. Moreover, bridgehead reactivity in homolytic reactions may be controlled by polar effects,[5] and these effects may follow the same order as the supposed steric effects due to nonplanarity.[6] A further cause of error lies in the fact that the mechanism of a reaction, such as the thermolyses of peresters[6–8] or azoalkanes,[4,9,10] which have often been studied in this context, may depend on the radical being generated. Finally, there is the problem of leaving-group steric effects. It seems to have been widely assumed that the only important steric effect was that related to the nonplanarity of the trivalent carbon. However, it is known that in some systems reaction rates are also affected by steric interactions between the *tert*-alkyl moiety, giving rise to the radical, and the rest of the molecule.[11] Ignorance of this "front-strain" effect[12] can only lead to an erroneous idea of the magnitude of the former.

In order to achieve a more realistic assessment of the importance of bridgehead strain in radicals, it is therefore necessary to consider four aspects of the problem: (a) Is the mechanism the same throughout the reaction series? (b) Where is the transition state relative to the radical? (c) Are the rates dependent on polar effects? (d) How can front-strain be allowed for?

Recently this subject has been approached in two closely-related studies. Rüchardt, by comparing the rates of C_q–C_q (q = quaternary) bond fission in hexamethylethane and 1,1′-biadamantane, was able to conclude that there is no appreciable strain in 1-Ad radicals (i.e., not much greater than that in adamantane itself),[13] while Lomas and Dubois estimated, from the thermolysis products of *tert*-butyldi-1-adamantylmethanol, that the strain-energy difference between 1-Ad· and *t*-Bu· was 3–4 kcal mol^{-1} greater than that between the hydrocarbons.[14] The common feature of these two studies is the use of molecular mechanics[15] (empirical force field calculations) to estimate the strain energies of the reactants and intermediates, thereby answering question d.

The aim of the present work is to refine and extend this second approach to the comparison of *t*-Bu, 1-adamantyl (Ad), 1-bicyclo[2.2.2]octyl (Oc), and 1-norbornyl (Nor) radicals. To this end, we have attempted to determine the thermolysis kinetics of alcohols containing all possible combinations of these groups and have investigated the products in a number of representative cases. Ring-substituent effects on *o*-tolyldi-*tert*-butylmethanol thermolysis are so small (ρ^+ is ca. 0.1 at 240 °C)[16] that polar effects on alcohol thermolysis can be neglected, thus providing a satisfactory answer to question c.

Results

The synthesis of all the alcohols investigated has been described elsewhere.[17] Details of the calculated geometries and strain energies are also given in this reference, along with data on the related secondary alcohols and ketones. The overall thermolysis rates were measured by GLC; when significant amounts of different alkyl radicals are formed from a common alcohol precursor, partial rate constants are obtained by determining the relative amounts of oxygen-containing products arising from each pathway. No attempt was made to monitor the hydrocarbon products. The partial rate constants led to the activation parameters for the formation of *tert*-butyl and the three bridgehead radicals. By correlating the activation energy, $\Delta G^{\ddagger}$, against the strain-energy change associated with the reaction, as described previously,[14] the difference in the strain energies of a radical and the corresponding hydrocarbon is estimated. In the last section of this paper

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Table II. Overall Yields in the Thermolysis of Tertiary Alcohols in Toluene[a]

compd	*T*, °C	% ketone(s)	% sec alcohol(s)	% SA	% total	% Bz_2 found	% Bz_2 calcd
3	185	30.1 (66)	50.3 (23)	11.9 (4)	92.3 (93)		
4	165	60.5 (87)	26.3 (8)	9.8 (3)	96.6 (98)	29.5	28.0
5	180	53.2 (89)	35.6 (6)	6.2 (1)	95.0 (95)	33.1	38.1
6[b]	245	38.8 (72)	52.0 (23)		98.2 (99)	57.4	60.3
7	196	49.1 (83)	41.2 (12)	11.5 (3)	101.8 (98)	37.0	40.3
10	215	41.7 (81)	45.5 (15)	6.0 (1)	93.2 (97)	48.7	48.9

[a] Approximate values for nondegassed samples are given in parentheses. [b] Ring-opened products: 7.4 (4)%.

our results are compared with other estimates and with recent calculations.

Thermolysis Rates. Our previous work[14] was carried out in dodecane as solvent, although this is a poor hydrogen atom donor. In the present study, toluene and mesitylene were also used, and in some cases, kinetics were performed on degassed samples under vacuum. Control experiments (alcohols **2**, **6**, and **10**) indicated that neither degassing nor change of solvent had any significant effect (no variation of $\Delta G^{\ddagger}$ (T °C) greater than 0.1 kcal mol^{-1}) upon the rate constants (Table I). The data in this paper are therefore compatible with those reported previously.

Attempts to study the kinetics of alcohol **13** were unsuccessful. Neither by sealing under vacuum nor by adding substantial amounts of inhibitors (2,6-di-*tert*-butylphenol was the most promising of those tried) was it possible to obtain a smooth first-order plot. In the presence of inhibitor, initial rate constants (ca. 50% reaction) were measured at two temperatures. They indicated a negative activation entropy (about −20 cal mol^{-1} K^{-1}) whereas all other values are strongly positive. The anomalous behavior of **13** suggests that it is reacting via a different mechanism, probably one involving induced decomposition, while the other alcohols appear to constitute a homogeneous reaction series.

Reaction Products. (ii) Overall Yields. For six of the alcohols studied here total yields were determined by inclusion of a hydrocarbon standard, reaction to ten half-lives at a suitable temperature, and GLC analysis of the products (Table II). In all cases it was possible to account for more than 92% of the alcohol consumed, whether the solutions were degassed or not. Generally, in agreement with previous studies,[14,18] the major products are the secondary alcohol and the ketone resulting from the intermediate dialkylhydroxymethyl radical by hydrogen atom addition or abstraction (reactions 3–5, 8, and 9, Scheme I). Since these experiments were performed in a hydrogen-donor solvent, toluene, benzyl radicals are also produced. These couple to give dibenzyl (reaction 7) but also react with the hydroxymethyl radical to give stable alcohols (SA) (reaction 6). Coupling reactions other than these have been omitted from Scheme I since there was no evidence for their occurrence. When a norbornyl group is present in the intermediate radical, anomalous products, identified as ring-opened ketones (reaction 10) constitute a significant fraction of the total.

Scheme I

$$R^1R^2R^3COH \rightarrow R^1R^2C{\cdot}OH + [R^3]{\cdot} \qquad (1)$$

$$[R^3]{\cdot} + SH \rightarrow R^3H + S{\cdot} \qquad (2)$$

$$R^1R^2C{\cdot}OH + SH \rightarrow R^1R^2CHOH + S{\cdot} \qquad (3)$$

$$R^1R^2C{\cdot}OH + S{\cdot} \rightarrow R^1R^2C{=}O + SH \qquad (4)$$

$$R^1R^2C{\cdot}OH + [R^3]{\cdot} \rightarrow R^1R^2C{=}O + R^3H \qquad (5)$$

$$R^1R^2C{\cdot}OH + S{\cdot} \rightarrow R^1R^2SCOH\ (SA) \qquad (6)$$

$$S{\cdot} + S{\cdot} \rightarrow S_2 \qquad (7)$$

$$2\ R^1R^2C{\cdot}OH \rightarrow R^1R^2C{=}O + R^1R^2CHOH \qquad (8)$$

$$R^1R^2C{\cdot}OH + [R^3]{\cdot} \rightarrow R^1R^2CHOH + R^3(-H) \qquad (9)$$

$$R^1R^2C{\cdot}OH \rightarrow R^1Y{\cdot}C{=}O\ (R^2 = Nor) \qquad (10i)$$

$$R^1Y{\cdot}C{=}O + SH \rightarrow R^1(YH)C{=}O + S{\cdot} \qquad (10ii)$$

The outstanding effect of degassing is to considerably reduce the ketone yield, while the ratio of secondary alcohol to solvent-incorporated alcohol is virtually unaffected. This demonstrates that a mechanism involving molecular oxygen is responsible for at least part of the ketone when air is present, whereas the processes leading to the other products require only organic radicals and solvent molecules, as indicated in reactions 2–10.

Although the relative rates of these reactions cannot be evaluated, it is possible in some cases, and provided that the solutions are degassed, to obtain a relationship between the yields of oxygen-containing products and that of S_2 (dibenzyl). For example, if only reactions 2–7 (representing *a*–*f* percent, respectively) follow the homolysis step, we have the following equalities:

$$a + d = 100$$

$$b + c + d + e = 100$$

$$b = \%\ \mathrm{CHOH}\ (\text{secondary alcohol})$$

$$c + d = \%\ \mathrm{C{=}O}\ (\text{ketone})$$

$$e = \%\ \mathrm{SA}$$

$$f = \%\ S_2 = 0.5(a + b - c - e) = 0.5(100 + \%\ \mathrm{CHOH} - \%\ \mathrm{C{=}O} - \%\ \mathrm{SA})$$

It is easy to extend this treatment to include the formation of ring-opened ketones (reaction 10), but if reaction 9 is included no solution is possible without hydrocarbon analysis. When R^3 is a bridgehead group and reaction 9 can therefore be excluded, fairly good agreement is found between the experimental value of the dibenzyl yield and that calculated from the other yields. Unfortunately, this analysis tells us neither that *all* the reactions occur nor that *only* these reactions occur; for example, reaction 8 could be accommodated and either reaction 2 or 5 could be omitted with no perceptible change to the product balance sheet. Nevertheless, these results and the fact that one can study the kinetics of alcohol thermolysis by observing the rate of formation of dibenzyl (see Experimental Section) confirm that the reactions involving the benzyl radical obey a strict stoichiometry and that no chain reactions occur.

Reaction Products. (ii) Intramolecular Competition. When there is a *tert*-butyl group in a tertiary alcohol, thermolysis results almost exclusively in rupture of the *t*-Bu to carbon bond ([R^3]· = *t*-Bu·). When both Ad and Oc substituents are present, but not *t*-Bu, there is intramolecular competition between homolysis of the Ad–C and Oc–C bonds. This results in two different sets of oxy-

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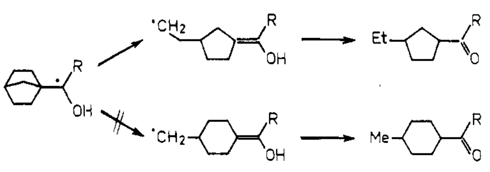
Table III. Relative Yields (±2%) of Products Derived from Nor$_2$C•OH in the Thermolysis of Alcohol 12 in Degassed Toluene

T, °C	% ring-opened ketone	% ketone	% sec alcohol	ketone/alcohol
286	20.3	49.8	29.9	1.67
305	31.8	40.1	28.2	1.42
325	45.8	32.8	21.3	1.54
345	54.2	28.4	17.4	1.64

gen-containing compounds (ketone, secondary alcohol, and solvent-incorporated product). By GLC analysis of these products the partial rate constants for the two fission modes can be evaluated.

Whereas for alcohols **5**, **7**, and **8** competition between Ad–C and Oc–C bond breaking is evident, it is less easy to be sure of eventual Nor–C bond breaking in **9**, **11**, and **12**. First results for alcohol **12** in the presence of atmospheric oxygen were irreproducible and irregular, but when samples were carefully degassed before thermolysis, somewhat lower yields of products from Nor–C cleavage, varying with temperature as expected, were obtained reproducibly. Since this finding suggests that a mechanism involving molecular oxygen can affect the apparent yield of Nor·, alcohol **8** was reexamined[19] in degassed toluene. It was found that Nor· formation was negligible, being less than 0.1% even at the highest kinetic temperature. Under the same conditions neither **9** nor **11** showed significant Nor–C fission.

Reaction Products. (iii) Anomalous Ketones. In addition to the above-mentioned products, in all cases where the Nor$_2$C·OH radical is generated by loss of *t*-Bu (alcohol **3**), Ad (**9**), Oc (**12**), or Nor (**13**), anomalous products are formed. Coupled GLC/MS revealed two components, isomeric with Nor$_2$CHOH, in equal amounts. Studies on the analogous products derived from OcNorC·OH and AdNorC·OH demonstrated that the norbornyl group no longer exists as such. IR and ^{13}C NMR spectra of the two-component mixture isolated from the thermolysis of **12** enabled us to identify the products as ring-opened ketones. Apart from signals that can be attributed to the norbornyl group,[20] by comparison with di-1-norbornyl ketone, the ^{13}C NMR spectrum consists of pairs of equally intense lines separated by 0.1–1.2 ppm (the line at δ 29.4 stands alone but the norbornyl C3,5 signal at δ 30.1 is significantly enhanced, indicating that the missing signal is coincident with the latter). Off-resonance experiments and comparison with chemical shift data[21] are consistent with the ketones being the cis and trans isomers of 1-(3-ethylcyclopentyl)-1-norbornylketone and with the assignments given in the Experimental Section. A plausible mechanism for the formation of these compounds would be ring opening to enol, followed by ketonization and proton abstraction from the solvent.[22] It is interesting to note that the corresponding cyclohexyl derivatives are *not* formed:



The results in Table III show that the importance of this side reaction increases with increasing temperature, which means that its activation entropy is less negative (or, less likely, more positive) than that of the normal reaction leading to ketone and secondary alcohol. This is consistent with the idea that ring opening is a unimolecular reaction competing with bimolecular reactions.

Discussion

The Relationship between Thermolysis Rates and Strain-Energy Changes. Radical reactions to which molecular mechanics calculations were first applied include hydrogen abstraction from polycyclic alkanes (radical-like transition-state model)[23] and the thermolysis of azoalkanes and peresters (carbonium ion-like transition-state model).[3,6] More recently, the rates of C–C bond fission in a wide range of compounds have been related to the strain enthalpies of the reactants only (no transition-state model),[24,25] but this approach can easily be improved, at least in the case of alkanes,[26,27] by taking into account the strain energies of the intermediates. In what follows we shall restrict our attention to systems where tertiary alkyl radicals are produced by C–C bond homolysis.

Kinetic data on the thermolysis of saturated alkanes of the C$_q$–C$_q$ type

$$R^1R^2R^3C\text{–}(t\text{-Bu}) \rightarrow R^1R^2R^3C\cdot + Me_3C\cdot$$

have been interpreted[27] by correlating $\Delta G^{\ddagger}$(300 °C) against D_{sp}^*, where

$$D_{sp}^* = H_{sp}(R^1R^2R^3C\text{–}(t\text{-Bu})) - H_{sp}(R^1R^2R^3CH)$$

The radical intermediates are thus presented by the corresponding alkanes, and since H_{sp}(Me$_3$CH) is zero, this term is dropped. It should be noted in passing that H_{sp}, the strain enthalpy, is the difference between the MM2-calculated enthalpy of formation[28] and the sum of the appropriate "single conformation" increments;[29] it differs slightly from the "strain energy" defined by Allinger.[28]

When R^1 and R^2 are alkyl and R^3 is H, $\Delta G^{\ddagger} = 64.8 - 0.82D_{sp}^*$, while for tetraalkylmethanes, where R^1, R^2, and R^3 are all alkyl, $\Delta G^{\ddagger} = 65.7 - 0.91D_{sp}^*$. For the latter set, to which can be added symmetrical hexaalkylethanes

$$R^1R^2R^3C\text{–}CR^1R^2R^3 \rightarrow 2R^1R^2R^3C\cdot$$

for which

$$D_{sp}^* = H_{sp}(R^1R^2R^3C\text{–}CR^1R^2R^3) - 2H_{sp}(R^1R^2R^3CH)$$

There is also a correlation with $\Delta H^{\ddagger}$: $\Delta H^{\ddagger} = 73.0 - 0.81D_{sp}^*$. The difference in the slopes of the $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ correlations is attributed to the temperature dependence of the $\Delta H^{\ddagger}$ values, which are measured at a variety of temperatures.

It has been argued that since radical recombinations (at least, those of *t*-Bu· and of Et$_3$C·) are not enthalpically but

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Table IV. Thermodynamic Parameters and Calculated Strain-Energy Changes (kcal mol^{-1}; $\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}) for the Formation of *tert*-Butyl Radical in the Thermolysis of Tertiary Alcohols *t*-BuR^1R^2COH, in Dodecane

compd	R^1	R^2	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$ (200 °C)	$\Delta strain_{calcd}$
[a]	*t*-Bu	*t*-Bu	43.2 ± 0.5	17.1 ± 1.4	35.05 ± 0.03	34.54
[a]	*t*-Bu	*t*-Am	40.2 ± 0.6	13.7 ± 1.4	33.65 ± 0.05	35.33[d]
[a]	*t*-Bu	Ad	40.1 ± 0.2	15.1 ± 0.5	32.99 ± 0.02	35.93[d]
[a]	*t*-Bu	Oc	41.3 ± 0.2	15.9 ± 0.5	33.83 ± 0.01	34.82
[a]	*t*-Bu	Nor	47.0 ± 0.2	18.1 ± 0.5	38.48 ± 0.01	30.47
[a]	Ad	Ad	37.4 ± 0.2	14.2 ± 0.5	30.68 ± 0.02	37.19
[a]	Ad	Oc	39.5 ± 0.2	16.8 ± 0.8	31.56 ± 0.08	36.08
[a]	Ad	Nor	45.0 ± 0.2	18.0 ± 0.5	36.52 ± 0.01	31.55[d]
1	Oc	Oc	40.5 ± 0.2	17.2 ± 0.5	32.33 ± 0.01	35.51
2	Oc	Nor	46.0 ± 0.5	18.4 ± 1.1	37.31 ± 0.03	30.48
2[b]	Oc	Nor	45.8 ± 0.8	18.0 ± 1.5	37.28 ± 0.04	30.48
2[c]	Oc	Nor	46.2 ± 0.7	18.7 ± 1.3	37.33 ± 0.04	30.48
3	Nor	Nor	52.2 ± 0.6	21.0 ± 1.1	42.21 ± 0.08	26.42

[a] Reference 14. [b] In toluene. [c] In mesitylene. [d] Revised value.

Table V. Thermodynamic Parameters and Calculated and Experimental Strain-Energy Changes (kcal mol^{-1}; $\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}) for the Formation of Bridgehead Radicals in the Thermolysis of Tertiary Alcohols

compd	solvent	R^3	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$ (200 °C)	$\Delta strain_{calcd}$	$\Delta strain_{expt}$	$\Delta\Delta strain$
4	toluene	Ad	39.7 ± 0.2	16.4 ± 0.5	31.95 ± 0.02	38.14	36.44	1.70
5	toluene	Ad	42.1 ± 0.5	19.3 ± 1.1	33.00 ± 0.04	37.39	35.41	1.98
6	dodecane[a]	Ad	49.7 ± 0.6	22.8 ± 1.1	38.91 ± 0.04	32.22	29.61	2.61
7	toluene	Ad	42.4 ± 0.4	17.7 ± 0.9	34.03 ± 0.02	36.89	34.40	2.49
8	mesitylene	Ad	49.3 ± 0.3	20.2 ± 0.7	39.77 ± 0.03	31.52	28.76	2.76
9	mesitylene	Ad	53.1 ± 0.7	17.3 ± 1.2	44.96 ± 0.11	26.71	23.66	3.05
5	toluene	Oc	44.2 ± 0.6	20.2 ± 1.4	34.63 ± 0.04	36.96	33.81	3.15
7	toluene	Oc	44.0 ± 0.3	17.5 ± 0.7	35.71 ± 0.01	36.90	32.75	4.15
8	mesitylene	Oc	51.1 ± 0.3	20.2 ± 0.6	41.51 ± 0.03	31.26	27.05	4.21
10	toluene[b]	Oc	45.4 ± 0.2	18.2 ± 0.5	36.75 ± 0.01	36.28	31.73	4.45
11	mesitylene	Oc	50.7 ± 1.1	18.0 ± 2.0	42.19 ± 0.13	30.78	26.39	4.39
12	mesitylene	Oc	54.7 ± 0.5	16.3 ± 0.8	46.98 ± 0.10	25.49	21.68	3.81
8		Nor			(49.0)[c]	27.33	(19.7)[c]	(7.6)[c]
11		Nor			(50.1)[c]	26.58	(18.6)[c]	(8.0)[c]
12	mesitylene	Nor	61.9 ± 0.7	16.8 ± 1.2	53.94 ± 0.14	22.55	14.84	7.71
13		Nor			(57.8)[c]	19.54	(11.3)[c]	(8.2)[c]

[a] In toluene: 47.8 ± 1.2, 19.1 ± 2.3, 38.73 ± 0.09 kcal mol^{-1}. [b] In dodecane: 47.4 ± 0.6, 22.5 ± 1.2, 36.79 ± 0.02 kcal mol^{-1}. [c] Extrapolated value (see Appendix).

entropically controlled,[30,31] plots of $\Delta H^{\ddagger}$ against D_{sp}^* (or better D_{sp}, where $D_{sp} = H_{sp}(\text{alkane}) - \sum H_{sp}(\text{radicals})$) should have unit slope.[27,32a] By manipulating the $\Delta H^{\ddagger}$ correlation it can be shown that $\Delta C_p^{\ddagger}$, the change in the standard molar heat capacity, must therefore be negative. Tsang's work on the gas-phase thermolysis of hexamethylethane[34] seems to support this hypothesis. However, for substituted di-*tert*-butylmethanes an excellent correlation exists with a slope *greater* than unity:[32b] $\Delta H^{\ddagger} = 81.1 - 1.11 D_{sp}^*$. Hellmann suggests that the quality of this correlation is attributable to the two *tert*-butyl groups, which will similarly affect the temperature dependence of the molar heats, C_p and $C_p^{\ddagger}$, throughout the series, but offers no explanation of the increased gradient.

Aside from these thermodynamic considerations, it should be noted that the choice of the force field can also affect the slope of any correlation against strain-energy changes. For a homogeneous set of compounds, $(t\text{-Bu})_2RCH$, the $\Delta G^{\ddagger}$(200 °C)/Δstrain gradients range from 0.90 to 1.08, depending on the force field used.[14] Furthermore, insofar as the imperfections in molecular mechanics calculations may be selective, i.e., may affect certain structural types more than others, small differences in the correlation parameters cannot be taken as significant.

It results from this discussion that it is difficult to give a precise interpretation to the parameters of $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ correlations against strain-energy changes. Nevertheless, they remain an invaluable tool for the understanding of steric effects upon reactivity. In this work, in agreement with generally accepted practice, activation energies will be used rather than enthalpies, since the former are more reliable, both statistically and because the "compensation effect" reduces the errors that can be introduced by performing measurements at different temperatures.[33]

The Relationship between Thermolysis Rates and Strain-Energy Changes. (ii) Tertiary Alcohols. In a previous paper[14] on the thermolysis of tertiary alcohols we considered various ways of interpreting the rates in terms of strain-energy changes and compared three force fields (MM1, MM2, and EAS). Only Allinger's MM2 force field[28,35] is parametrized for alcohols and thus allows a realistic description of the reaction. Activation energies for *t*-Bu· formation

$$(t\text{-Bu})R^1R^2COH \rightarrow R^1R^2C\cdot OH + t\text{-Bu}\cdot$$

are correlated with the difference in the strain energies (SE) of the tertiary and secondary alcohols

$$\Delta\text{strain} = \text{SE}((t\text{-Bu})R^1R^2COH) - \text{SE}(R^1R^2CHOH)$$

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(30) (a) Parkes, D. A.; Quinn, C. P. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1952. (b) Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2463. (c) Kaiser, J. H. Diplomarbeit, Universität Freiburg, 1980.

(31) The situation is quite different in the dimerization of bulky *secondary* alkyl radicals.[26]

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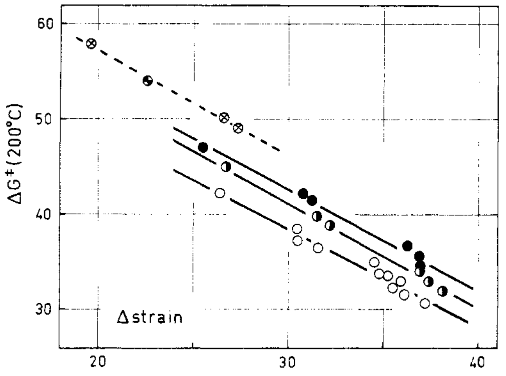

Figure 1. Correlation of activation energies for the formation of *tert*-butyl and bridgehead radicals against MM2-calculated strain-energy changes (all values in kcal mol^{-1}): (○) *t*-Bu; (◑) Ad; (●) Oc; (⊛) Nor (experimental); (⊗) Nor (extrapolated; see Appendix).

Again the term for Me_3CH is zero. Calculations based on Schleyer's EAS force field[36] indicate that the carbocation ($R^1R^2C^+H$) and dialkylmethane ($R^1R^2CH_2$) strain energies are very similar in this series. Consequently, there can be little error in treating a radical as either of these. By analogy, the strain energy of the secondary alcohol should be a good approximation to that of the corresponding dialkylhydroxymethyl radical. Therefore, the near-unity value (−1.08) of the slope of the $\Delta G^{\ddagger}/\Delta$strain correlation is consistent with a very late transition state for bond breaking, i.e., close to the radicals themselves.[14] This means that, although kinetic data are intrinsically related to transition states, in the present case quantitative information about the intermediate species can be extracted from the rate data.

The Evaluation of Bridgehead Radical Strain from Alcohol Thermolysis Rates. In Tables IV and V are presented thermodynamic parameters and calculated strain-energy changes for radical formation: Table IV pertains to *t*-Bu· and Table V to the three bridgehead radicals.

In this work we have studied three new dialkyl-*tert*-butylmethanols, alcohols **1–3**, and have revised some of the strain-energy data for three other compounds. With these additions and revisions (Table IV) the $\Delta G^{\ddagger}/\Delta$strain correlation (Figure 1) becomes

$$\Delta G^{\ddagger}(200\ {}^{\circ}\mathrm{C}) = 69.1\ (\pm 2.2) - (1.02\ (\pm 0.06))\Delta\mathrm{strain} \quad (r = 0.983)$$

There are now two ways of handling the data for compounds that give rise to radicals other than *tert*-butyl (Table V): by correlation or point by point. Both start by the calculation of Δstrain according to the naive assumption that the strain energy of a bridgehead radical is the same as that of the corresponding alkane

$$\Delta\mathrm{strain}_{\mathrm{calcd}} = \mathrm{SE}(R^1R^2R^3COH) - \mathrm{SE}(R^1R^2CHOH) - \mathrm{SE}(R^3H)$$

When $\Delta G^{\ddagger}$(200 °C) is plotted against Δstrain for the 1-adamantyl lies 1-bicyclo[2.2.2]octyl radicals, two straight lines almost parallel to the first one are obtained. The only data for the formation of the 1-norbornyl radical lies above the extension of the other lines (Figure 1).

$$\mathrm{Ad:}\ \Delta G^{\ddagger}(200\ {}^{\circ}\mathrm{C}) = 75.0\ (\pm 0.9) - (1.12\ (\pm 0.03))\Delta\mathrm{strain} \quad (r = 0.999)$$

$$\mathrm{Oc:}\ \Delta G^{\ddagger}(200\ {}^{\circ}\mathrm{C}) = 73.5\ (\pm 1.8) - (1.03\ (\pm 0.05))\Delta\mathrm{strain} \quad (r = 0.995)$$

The relative positions of the three lines are clear from the graph but, because of the slight differences in the slopes, it is not possible to give the separation between them exactly.[37] However, we can calculate the horizontal displacement of each Ad, Oc, and Nor point relative to the *t*-Bu line; this displacement will be designated as ΔΔstrain: If $\Delta\mathrm{strain}_{\mathrm{expt}} = (69.1 - \Delta G^{\ddagger})/1.02$, then $\Delta\Delta\mathrm{strain} = \Delta\mathrm{strain}_{\mathrm{calcd}} - \Delta\mathrm{strain}_{\mathrm{expt}}$. Taking the six ΔΔstrain estimates for Ad and for Oc (Table V) one obtains average values of 2.4 ± 0.5 and 4.0 ± 0.5 kcal mol^{-1}, respectively. For Nor the only measurable data leads to a value of 7.7±0.6 kcal mol^{-1} (see Experimental Section).

Alcohols **5**, **7**, and **8** are particularly interesting in that both Ad and Oc radicals are formed from common precursors. This means that the strain energy of the alcohol does not enter into the calculation of the difference in the front-strain steric effects upon the two pathways. Moreover, since the partial rate constants are measured at the same temperatures the problem of the temperature dependence of the thermodynamic parameters, particularly $\Delta H^{\ddagger}$, does not arise. Assuming then, in accordance with Rüchardt's hypothesis,[27] that a change in Δstrain is reflected by an equal change in $\Delta H^{\ddagger}$, we can correct the $\Delta H^{\ddagger}$ differences (2.09, 1.62, and 1.73 kcal mol^{-1} for alcohols **5**, **7**, and **8**, respectively) for the Δstrain differences (−0.43, 0.01, and −0.26 kcal mol^{-1}) to obtain values of 1.66, 1.63, and 1.47 kcal mol^{-1}, which represent ΔΔstrain(Oc) − ΔΔstrain(Ad). The good agreement between these values and the ΔΔstrain difference found above (4.0 − 2.4 = 1.6 kcal mol^{-1}) strongly supports our more general approach. Their constancy indicates that the temperature dependence of $\Delta H^{\ddagger}$ for Ad· and Oc· formation must be roughly the same throughout the range of measurement temperatures, which goes from 150–195 °C to 220–265 °C, i.e., about half the total span used for the kinetic measurements on alcohols **1–12**.[38] The activation entropies for the formation of these radicals are virtually the same (Table V), again in agreement with the conclusion, based on the Exner test, that the entire $\Delta G^{\ddagger}$ set behaves isoentropically (see Experimental Section).

The interpretation of these ΔΔstrain values seems obvious: The value of $\Delta\mathrm{strain}_{\mathrm{calcd}}$ is based on the assumption that the intermediate radicals can be described as a secondary alcohol and an alkane. The adoption of the secondary alcohol as a surrogate for $R^1R^2C{\cdot}OH$ has been justified above. Moreover, since this assumption is built into the reference line, no large error in the correlation can be attributed to this approximation. There remains only the assumption that the bi- and tricyclic bridgehead radicals can be represented by the corresponding alkanes. It is clear then that the difference between the calculated and experimental Δstrain values is simply the difference between the real and assumed value of the strain energy of the bridgehead radical or, in other words, the strain-energy change involved in going from the hydrocarbon to the radical: $R^3H \rightarrow [R^3]\cdot$. Since the strain energy of the *t*-Bu radical has been equated with that of Me_3CH, i.e., zero,

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(36) (a) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. (b) Iverson, D. J.; Mislow, K. *QCPE* **1981**, *13*, 410.

(37) It is even more hazardous to compare the $\Delta G^{\ddagger}$ intercepts, although they are simply related to the C–C bond-dissociation energies and therefore potentially interesting data.

(38) No more general comparison of $\Delta H^{\ddagger}$ values can be made, since the gradients of the $\Delta H^{\ddagger}/\Delta$strain correlations vary widely (*t*-Bu, −1.28 ± 0.07; Ad, −1.17 ± 0.13; Oc, −0.95 ± 0.08). Notwithstanding the Exner test, the *t*-Bu set taken alone appears to obey an isokinetic relationship; for this reason the difference between the $\Delta H^{\ddagger}$ and the $\Delta G^{\ddagger}$ correlations is particularly large.

Table VI. Relative Activation Energies for Reactions via *tert*-Butyl and Bridgehead *tert*-Alkyl Radical Intermediates

			$\Delta\Delta G^{\ddagger}$, kcal mol^{-1}						
	reaction	T, °C	t-Bu	Ad	Oc	Nor	gradient[a]	corr coeff	ref
A	iodide abstraction from RI by Ph·	60	0.0	0.33	0.45	1.22	0.157	0.986	39
B	chlorination of RH by nitrogen cation radicals	15		0.0	−0.11	1.61	0.332	0.937	40
C	Bu_3SnH reduction of RCl	80		0.0	0.48	2.23	0.430	0.996	41
D	Bu_3SnH reduction of RBr	80		0.0	0.19	2.17	0.431	0.976	41
E	thermolysis of t-BuN=NR	300	0.0	3.56	4.40	6.10	0.476[b]	0.999	42
F	photolysis of PhCOR	22	0.0	0.64	1.04	3.41	0.543[b]	0.986	43
G	perester thermolysis	80	0.0	−0.26	1.30	4.38	0.868[b]	0.999	6
H	perester thermolysis	65	0.0	0.60[c]	2.01	5.26	0.879[b]	0.999	44
I	perester thermolysis	80	0.0	−0.24	1.62	4.61	0.896[b]	0.996	45
J	aldehyde decarboxylation	135	0.0	−0.74	−0.17	4.05	0.945[b]	0.982	46
K	halide abstraction by $[Co(CN)_5]^{3-}$	25	0.0	3.50	4.22	8.96[d]	1.132	0.992	47

[a] Correlation of $\Delta\Delta G^{\ddagger}$ against ΔΔstrain. [b] Not t-Bu. [c] Mean Value. [d] Minimum value.

the reference reaction (for which ΔΔstrain = 0) is $Me_3CH \rightarrow t\text{-Bu}\cdot$.

In the light of these results it is apparent that the 1-adamantyl radical is distinctly more strained that the *tert*-butyl radical (2.4 kcal mol^{-1}) though, for reasons which may be related to inherent defects in the force field or to the temperature dependence of the activation energies, point values range from 1.7 to 3.0 kcal mol^{-1}. The bicyclo[2.2.2]octyl radical is even more strained, while the one value for 1-norbornyl shows it to be a highly strained radical, due no doubt to the unusually small bond angles at the trivalent carbon. This radical is doubly difficult to produce because the steric driving force (the front-strain effect) for its formation is much weaker than in the case of the bulkier radicals.

Comparison with Other Estimates of Bridgehead Radical Strain. A wide variety of reactions involving bridgehead radical intermediates have been investigated.[6,10,23,39-48] While they generally, but not always,[40] agree on the rate order, Ad > Oc > Nor, there are marked differences in relative rates, particularly of *tert*-butyl and 1-adamantyl derivatives. In Table VI are listed data for the more complete of these studies; $\Delta\Delta G^{\ddagger}$ values have been calculated from the relative rates, no corrections being made for supposed polar or any other effects. Usually there is a rough, or even good, correlation with our ΔΔstrain values, frequently improved by removing the anomalous *tert*-butyl data. The slopes vary enormously, but in the absence of reliable information about the position of the transition state and about steric and polar effects in these reactions, there is no way of interpreting the variations. It should be emphasized that these correlations are purely empirical and that they do not indicate that in a given reaction the same structural factors are operative as in the reference reaction, alcohol thermolysis. Nevertheless, those reactions that correlate best with our data (sets A and K) could conceiveably be used as a simple means for exploring the extension of the present study to other bridgehead *tert*-alkyl groups.

Table VII. Comparison of ΔΔstrain Values, from Thermolysis or Estimated from Solvolysis Data, with ΔBDE Values Calculated by Molecular Mechanics (All Values in kcal mol^{-1})

group	$\Delta\Delta G^{\ddagger}$(70 °C) [tosylate solvolysis]	ΔΔstrain	ΔBDE[a]
1-norbornyl	37.5[b]	7.7	5.1
1-bicyclo[2.2.2]octyl	26.5[b]	4.0	1.8
1-adamantyl	20.8[c]	2.4	1.7
1-bicyclo[3.3.1]nonyl	19.4[b]	1.4[f]	0.7
tert-butyl	16.4[d]	(0.0)	(0.0)
1-homoadamantyl	19.8[e]	1.6[f]	−0.8
1-bicyclo[3.2.2]nonyl	20.4[b]	1.8[f]	−1.1
3-homoadamantyl	17.1[b]	0.6[f]	−3.5
1-bicyclo[3.3.2]decyl	15.4[b]	−0.1[f]	−5.5

[a] BDE = bond dissociation energy. [b] Extrapolated (ref 49). [c] Reference 3. [d] t-Bu/Ad = 6 × 10^2 (ref 50). [e] 1-homoad/Ad = 4.6 (ref 50). [f] Estimated from solvolysis data.

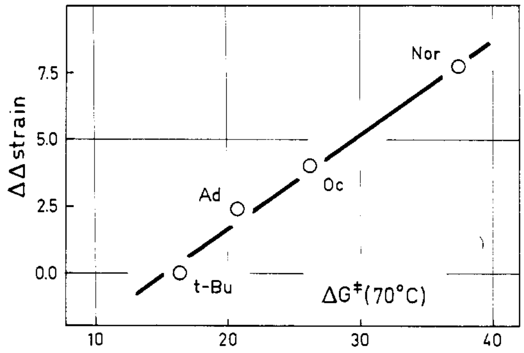

Figure 2. Correlation of strain energies for radical formation against activation energies for tosylate solvolysis in 80% aqueous ethanol at 70 °C (all values in kcal mol^{-1}).

Some of the first MM treatments of thermolysis rates employed a carbocation model for the transition state,[3,6] justified by the correlation of thermolysis with solvolysis rates.[1a,6,7,10,11] The ΔΔstrain values that we have just determined correlate well with tosylate solvolysis rates in 80% aqueous ethanol (extrapolated where necessary; see Table VII). Translated into a ΔΔstrain/$\Delta G^{\ddagger}$ relationship (Figure 2), this correlation has a slope of about 0.36, which confirms that any requirement for planarity or near pla-

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(51) We do not wish to comment upon the controversy about nucleophilic assistance in the solvolysis of *tert*-butyl halides[50,52] but acknowledge that a solvent other than 80% aqueous ethanol would not necessarily give a correlation which includes *tert*-butyl.

(52) (a) Abraham, M. H.; Taft, R. W.; Kamlet, M. J. *J. Org. Chem.* **1981**, *46*, 3053. (b) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741.

Table VIII. Mass Spectral Data on Solvent-Incorporated Products $PhCH_2R^1R^2COH$, 14–19 (*m/e* for fragments, M = parent)

compd	R^1	R^2	$PhCH_2$	R^1	R^2	R^1CO	R^2CO	M – (R^1)	M – (R^2)	M – ($PhCH_2$)	M – (OH)	M – (H)	M
14[a]	Ad	Ad	91	135	135	163	163	255	255	299	373		
15[b]	Ad	Oc	91	135	109	163	137	229	255	273	347[c]	363[c]	
16[b]	Ad	Nor	91	135	95	163	123	215		259	333[c]	349[c]	
17[b]	Oc	Oc	91	109	109	137	137	229	229	247	321[c]	337[c]	
18[b]	Oc	Nor	91	109	95	137	123	215		233			
19[a]	Nor	Nor	91	95	95	123	123	215	215				310

[a] JEOL. [b] Finnigan. [c] Chemical ionization.

narity about the trivalent carbon is much less severe than in the carbocation.

$$\Delta\Delta\text{strain} = (0.36\ (\pm 0.03))\Delta G^{\ddagger}(70\ ^\circ\text{C}) - 5.6\ (\pm 0.7) \quad (r = 0.994)$$

In the same way that Schleyer's force field was parametrized for carbocations in an attempt to correlate solvolysis rates with strain-energy changes,[53] MM2 has been extended so as to handle alkyl radicals.[54] At the present stage in the development of this radical force field it gives ΔBDE values (the difference between H_{sp} for the radical, R·, and the hydrocarbon, RH) of 5.1, 1.8, and 1.7 kcal mol^{-1} for Nor, Oc, and Ad, respectively (*t*-Bu = 0.0, by definition). These values are in tolerable agreement with our experimental results. An interesting aspect of these calculations is that both 1- and 3-homoadamantyl radicals, as well as those derived from the bicyclic [3.2.2] and [3.3.2] systems, are predicted to be *less* strained than the corresponding hydrocarbons (Table VII). Extrapolation of the solvolysis correlation, however, suggests that, apart from the last-mentioned, these systems will show small positive ΔΔstrain values.[55] This discrepancy invites further study of the thermolysis reaction. In view of their bulk it may be difficult to introduce the last four groups of this table into tri-*tert*-alkylmethanols, and if the radicals follow Beckhaus's predictions, in certain cases only alkyldi-1-norbornylmethanols will be accessible to synthesis and kinetic investigation. If feasible, more work along these lines would provide useful information regarding radical strain energies and their representation within the framework of molecular mechanics.

Conclusion

Study of the kinetics and the products of the thermolysis of congested tertiary alcohols containing, in particular, bridgehead tertiary alkyl groups makes it possible, by way of molecular mechanics calculations, to estimate the strain-energy change associated with the formation of a radical from the corresponding hydrocarbon. For 1-adamantyl and 1-bicyclo[2.2.2]octyl radicals, self-consistent (±0.5 kcal mol^{-1}) values are obtained from six different compounds, but because of the intrinsic difficulty of generating the 1-norbornyl radical, only one estimate of its strain energy is accessible. These data correlate quite well with tosylate solvolysis rates; this enables us to predict the strain energies of radicals not yet investigated by this approach.

Study of the products of the thermolysis reaction reveals a complex pattern of interrelated reactions involving the radicals arising from the initial C–C bond homolysis, the solvent, and atmospheric oxygen. Except perhaps in the case of Nor_3COH, whose kinetics are anomalous, there was no indication that any chain reaction occurs.

Experimental Section

General Methods. Mass spectra were obtained on JEOL JMS 200 and Finnigan MAT 44S spectrometers, IR spectra on a Perkin-Elmer 225 grating spectrometer, ^{13}C NMR spectra on a Bruker WP 200 FT spectrometer, and GLC analyses on a Girdel 330 with Delsi Enica 10 integrator/recorder.

Reaction Products. Ketones and secondary alcohols were identified by GLC comparison with authentic samples,[14,17] the latter being obtained by $LiAlH_4$ reduction of the former. The identification of the solvent-incorporated products, 14–19, is based on GLC/MS analysis only (Table VIII).

(i) Overall Yields. Yields of dibenzyl, ketones, secondary alcohols, and solvent-incorporated products from the 10 half-lives reaction of alcohols in toluene, sealed in the presence of air or under vacuum after several freeze–pump–thaw cycles, were determined by calibration against internal saturated hydrocarbon standards. The precision of the calibration procedure, which affects all the components, is ±2%. Additionally, slight differences between degassed samples induce variations of 1–2% on individual components. The differences between nondegassed samples are much greater, the standard deviations on the ketone and secondary alcohol yields sometimes attaining 8%; these latter are therefore purely indicative.

(ii) Fragmentation Paths. For alcohols 5, 7, 8 and 12 infinity samples in degassed toluene were analyzed by GLC, the detector response being calibrated by means of mixtures of ketones at about the same relative and absolute concentrations as in the sample. Results were as follows. Alcohol 5 (temperature in °C; percent products arising from Oc–C fission): 150.1, 6.3 ± 0.1; 165.0, 7.0 ± 0.2; 180.1, 7.4 ± 0.2; 195.0, 7.9 ± 0.3. Alcohol 7 (temperature, % Oc–C fission): 164.9, 22.3 ± 0.5; 181.0, 24.2 ± 0.6; 195.7, 24.5 ± 0.1; 210.9, 25.7 ± 0.3. Alcohol 8 (temperature, % Oc–C fission): 220.0, 14.5 ± 0.3; 234.6, 15.1 ± 0.3; 249.1, 15.8 ± 0.2; 265.0, 16.4 ± 0.1. Alcohol 12 (temperature, % Nor–C fission): 287.1, 0.38 ± 0.07; 307.2, 0.54 ± 0.05; 337.7, 0.68 ± 0.04; 345.3, 0.71 ± 0.02. No other alcohol gave more than 0.1% of products via a competing fragmentation path.

(iii) Anomalous Ketones. Capillary GLC revealed two poorly separated approximately equal components preceding ketone and secondary alcohol in all cases where $Nor_2C{\cdot}OH$ was formed (alcohols 3, 9, 12 (Table III), or 13). Smaller analogous components were detected in the thermolysis of 6 (Table II) and 11. The two components arising from $Nor_2C{\cdot}OH$ were indistinguishable by MS and had significant peaks at *m/e* 95, 123, 151, and 220. The products from 6 had *m/e* 135, 163, 191, and 260; those from 11 had *m/e* 109, 137, 165, and 234. Alcohol 12 (0.8 g) dissolved in toluene (15 mL) and sealed under argon in glass ampules was heated 5–10 min at 380 °C. Chromatography (Al_2O_3 in petroleum ether) of the oil remaining after solvent evaporation yielded a fraction (75 mg, 15% yield) running just ahead of di-1-norbornylketone. GLC showed it to be the two-component mixture free from significant amounts of other products: IR (film) 1690 cm^{-1}; ^{13}C NMR ($CDCl_3/Me_4Si$) δ 12.9, 13.0 (CH_3), 28.2, 28.6 (CH_2Me), 29.4, 30.1 (C4), 32.0, 33.2 (C5), 36.0, 37.2 (C2), 41.8, 43.0 (C3), 46.5, 47.6 (C1) [of the 1-(3-ethylcyclopentyl) group], 30.1, 32.6, 37.4, 41.6, 59.9 [of the 1-norbornyl group], 217.0 (C=O). For comparison, the ^{13}C NMR data of di-1-norbornyl ketone are as follows: δ 30.0 (C3,5), 33.4 (C2,6), 36.4 (C4), 41.6 (C7), 60.3 (C1), 217.3 (C=O).

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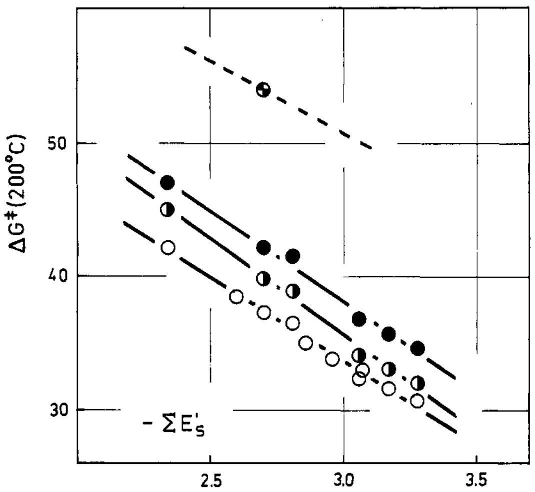

Figure 3. Relationship between the activation energies, for the formation of *tert*-butyl and bridgehead radicals, and the sum of the steric parameters of the remaining substituents (R^1 and R^2 in $R^1R^2R^3COH$): (○) *t*-Bu; (◑) Ad; (●) Oc; (◉) Nor.

Kinetic Measurements. Method I. Generally rate constants were determined in dodecane or mesitylene, whichever was the most convenient, as previously described.[14]

Method II. Because of the very low solubility of some of the alcohols and their tendency to decompose under even the mildest GLC conditions, a new method was devised. Alcohols **2**, **4–7**, and **10** (ca. 5×10^{-3} M) were dissolved in toluene with *n*-hexadecane (ca. 2×10^{-3} M) as internal standard. Samples were sealed in glass ampules under vacuum (10^{-2}–10^{-3} torr) after three freeze–pump–thaw cycles and then treated as usual. Rate constants were calculated from the rate of dibenzyl formation, determined by GLC. The standard deviation on four infinity samples, generally about 2%, limits the precision of the rate constant to about ±6% (without considering any eventual dispersion of the points), equivalent however to an error of only 0.05 kcal mol^{-1} in $\Delta G^{\ddagger}$(200 °C).

Activation Parameters. The results in Table IV and V show $\Delta H^{\ddagger}$ to range from 37.4 to 61.9 kcal mol^{-1}, while $\Delta S^{\ddagger}$ varies from only 13 to 23 cal mol^{-1} K^{-1}, this latter term making therefore a relatively small contribution to the observed 23 kcal mol^{-1} activation-energy range. Nevertheless, the variations in $\Delta S^{\ddagger}$ raise the possibility that comparisons of $\Delta G^{\ddagger}$ values will be temperature dependent. When the Exner test[57] is applied to $\Delta G^{\ddagger}$ values at 100, 200, and 300 °C (calculated by unweighted least-squares correlation of the experimental $\Delta G^{\ddagger}(T\ ^{\circ}C)$ values obtained from the Eyring equation) good correlations are found, indicating that any $\Delta G^{\ddagger}$ set taken as a whole behaves almost isoentropically,

$$\Delta G^{\ddagger}(100\ ^{\circ}C) = (1.01\ (\pm 0.01))\Delta G^{\ddagger}(200\ ^{\circ}C) + 1.42\ (\pm 0.29) \quad (r = 0.999)$$

$$\Delta G^{\ddagger}(300\ ^{\circ}C) = (0.99\ (\pm 0.01))\Delta G^{\ddagger}(200\ ^{\circ}C) - 1.42\ (\pm 0.29) \quad (r = 0.999)$$

Although relative $\Delta G^{\ddagger}$ values are therefore approximately temperature independent, 200 °C was taken as reference temperature in order to minimize extrapolation errors.

It should be noted that the standard deviations on the $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ values indicate only the scatter of the data points about the regression lines and ignore the errors in the data themselves. Normally this is unimportant,[58] but in the particular case of alcohol **12** the precision of the partial rate constants for the formation of Nor· falls as T °C decreases; assumption of the worst plausible error configuration raises the uncertainty on $\Delta G^{\ddagger}$ from 0.14 to 0.6 kcal mol^{-1}.

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Appendix

Taft–Ingold Treatment of Tertiary Alcohol Thermolysis Rates. The strain energies of the tertiary and secondary alcohols can be approximately expressed as linear combinations of contributions from the substituents (*t*-Bu, Ad, Oc, and Nor) to the carbon bearing the OH group:[17]

$$SE = a + bn_{Ad} + cn_{Oc} + dn_{Nor}$$

Since the differences between the coefficients b, c, and d for the two series correlate roughly with E_s' (Taft–Ingold steric constants modified by MacPhee, Panaye, and Dubois)[56] any data that correlate with Δstrain will also correlate with E_s', as was found previously for (*t*-Bu)–C cleavage.[14]

If the effects of substituents are assumed to be additive, the activation energies of thermolysis can be correlated with E_s' by taking the sum of the constants of the two groups which remain (R^1 and R^2) after the bond to the third group (R^3) has been broken. The results fall into three lines (Figure 3) corresponding to the departure of *t*-Bu, Ad, and Oc:

$$\text{Ad:}\quad \Delta G^{\ddagger} = 78.5\ (\pm 1.9) - (14.3\ (\pm 0.7))E_s' \quad (r = 0.996)$$

$$\text{Oc:}\quad \Delta G^{\ddagger} = 78.9\ (\pm 1.9) - (13.6\ (\pm 0.7))E_s' \quad (r = 0.995)$$

$$t\text{-Bu}^{a}\text{:}\quad \Delta G^{\ddagger} = 71.6\ (\pm 1.7) - (12.6\ (\pm 0.6))E_s' \quad (r = 0.996)$$

$$t\text{-Bu}^{b}\text{:}\quad \Delta G^{\ddagger} = 71.1\ (\pm 1.4) - (12.5\ (\pm 0.5))E_s' \quad (r = 0.995)$$

Set *t*-Bu^{a} contains the six pairs of substituents common to the Ad and Oc sets also; set *t*-Bu^{b} contains ten pairs of R^1 and R^2 but not the data for *tert*-amyldi-*tert*-butylmethanol which deviates markedly.[14] The correlations of $\Delta G^{\ddagger}$ against are as good as those against Δstrain and have slopes corresponding to high δ values ranging from −5.8 to −6.6. The stacking of the lines closely resembles that of the strain-energy correlations and, presumably, reflects both the difficulty of forming a given radical and its steric interaction with the residue, R^1R^2COH. The more strained the radical, the higher will the corresponding line be on the $\Delta G^{\ddagger}$ scale; conversely, the greater the interaction between the residue and the incipient radical, the lower will the line be. In agreement with the second part of this reasoning, the lines are not parallel. In fact, if we restrict our correlation of *tert*-butyl to set *t*-Bu^{a}, the slopes also vary linearly with the E_s' of the leaving group. We can therefore calculate the coefficient for the hypothetical Nor set (10.6) and, using the data for compound **12**, extrapolate values of $\Delta G^{\ddagger}$ for compounds **8**, **11**, and **13**. These are given in parentheses in Table V and are plotted against Δstrain in Figure 1 (- - -).

$$\text{Nor:}\quad \Delta G^{\ddagger}(200\ ^{\circ}C) = 79.0\ (\pm 1.4) - (1.10\ (\pm 0.06))\Delta\text{strain} \quad (r = 0.997)$$

Of course, these data give no additional information about the strain energy of the norbornyl radical, but they do tend to confirm the coherence of the molecular mechanics and the Taft–Ingold approaches to the treatment of steric effects in this system.