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ALCOHOL THERMOLYSIS : INTRAMOLECULAR COMPETITION AS A PROBE FOR COMPARING RADICAL STRAIN ENERGIES

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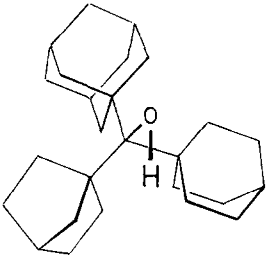
Summary : The relationship between $\Delta G^{\ddagger}$ for thermolysis of tertiary alcohols and strain energy change has been extended to compare the strain energy changes associated with the formation of bi- and tricyclic alkyl radicals from the corresponding alkanes.

Radical reactivity at bridgehead positions has long been used as a probe for investigating the geometrical requirements of the trivalent carbon[1] but, due to differences in mechanism and in the position of the transition state, and the confusion of straightforward steric effects upon rates with those involving the trivalent carbon specifically, a fairly incoherent picture of radical "stabilities" has emerged.[2]

Attempts have been made to ally conventional thermolysis studies with molecular mechanics calculation,[3-5] in order to compare the strain energies of radicals with those of the corresponding alkanes, which they resemble. Thermolysis rates of 1,1'-biadamantane and 2,2,3,3-tetramethylhexane[4] suggest that the strain energies of 1-adamantyl (Ad) and tert-butyl (B) are very similar, while studies on tertiary alcohol thermolysis[5] at rather lower temperatures indicate that the strain energy difference between $Ad^{\bullet}$ and $B^{\bullet}$ could be as much as 3-4 kcal.mol^{-1} (using Schleyer's force field[6]) greater than that between the hydrocarbons AdH and BH.

We now report results on the thermolysis of adamant-1-ylbicyclo[2.2.2]oct-1-ylnorborn-1-ylcarbinol, 1, (Ad Oc Nor COH) which relate the strain energies of all three possible radicals to that of the tert-butyl radical.

Alcohol 1, m.p. 221-223°C (decomp.) was synthesised by the one-pot Barbier-type organolithium condensation[7] of 1-bromoadamantane with bicyclo[2.2.2]oct-1-ylnorborn-1-ylketone in ether. Its decomposition kinetics in mesitylene were studied in the 220-265°C range by GLC on Carbowax 20 M.



1

$$R^1R^2R^3COH \rightarrow R^{3\cdot} + R^1R^2C^{\cdot}OH \rightarrow R^3H + R^1R^2C{=}O$$

$$ArCH_3 + R^{3\cdot} \rightarrow ArCH_2^{\cdot} + R^3H$$

$$ArCH_3 + R^1R^2C^{\cdot}OH \rightarrow ArCH_2^{\cdot} + R^1R^2CHOH$$

$$2\ ArCH_2^{\cdot} \rightarrow ArCH_2CH_2Ar$$

TABLE 1 : Rate constants and relative yields[8] for the decomposition of alcohol 1 in mesitylene

Temp. (°C)	10^4k_{total} (s^{-1})	Relative yields (%) Ad$^{\cdot}$	Oc$^{\cdot}$	Nor$^{\cdot}$
220.0	0.429	85.3 ± 0.2	14.5 ± 0.2	0.17 ± 0.03
234.6	1.97	84.6 ± 0.3	15.1 ± 0.2	0.26 ± 0.02
249.1	7.69	83.9 ± 0.1	15.7 ± 0.1	0.39 ± 0.02
265.0	32.5	83.2 ± 0.2	16.3 ± 0.2	0.45 ± 0.08
$\Delta H^{\ddagger}$ (kcal.mol^{-1})		49.3 ± 0.3	51.0 ± 0.3	61.2 ± 1.8
$\Delta S^{\ddagger}$ (cal.mol^{-1}K^{-1})		20.2 ± 0.7	20.1 ± 0.6	32.1 ± 3.4
$\Delta G^{\ddagger}$ (kcal.mol^{-1})(200°C)		39.8	41.5	46.1

Rate constants for the formation of each radical, and the related activation energies, enthalpies and entropies (Table 1) were calculated from the overall rate constants and the combined alcohol and ketone yields, measured under near-kinetic conditions by GLC on SE30.

These data can be interpreted in terms of strain energy changes based on Allinger's MM2 force field[9]. We previously showed[5] that the thermolysis of R^1R^2BCOH can be described by :

$$R^1R^2BCOH \rightarrow R^1R^2CHOH$$

and that the activation energy at 200°C is given by the equation[10] :

$$\Delta G^{\ddagger} = -1.09\ \Delta strain + 71.6 \qquad \text{(equation 1)}$$

where Δstrain is the difference between the strain energies of the tertiary and secondary alcohols. This approach can be extended to the formation of other radicals by making the naive assumption that the strain energy of the radical $R^{3\cdot}$ is that of the corresponding alkane, R^3H, and calculating the appropriate Δstrain values :

$$R^1R^2R^3COH \rightarrow R^1R^2CHOH \quad + \quad R^3H$$

These are to be compared with the "experimental" Δstrain values derived from the $\Delta G^{\ddagger}$ for the formation of the three bridgehead radicals by applying eqn. 1. The difference, ΔΔstrain (Table 2), is always positive and increases in the order : Ad < Oc < Nor.[11]

TABLE 2 : MM2 strain energies for tertiary and secondary alcohols and alkanes

			Strain energy (kcal.mol^{-1})			Δstrain	Δstrain	ΔΔstrain
R^1	R^2	R^3	$R^1R^2R^3COH$	R^1R^2CHOH	R^3H	(calc.)	(expt.)	($R^3H \rightarrow R^\cdot$)
Oc	Nor	Ad	81.4	39.4	10.4	31.5	29.3	2.2
Ad	Nor	Oc	81.4	35.8	14.3	31.2	27.7	3.5
Ad	Oc	Nor	81.4	35.6	18.5	27.3	23.5	3.8

We have argued elsewhere[5] that the strain energy difference between R^1R^2CHOH and $R^1R^2C^\cdot OH$ is negligible; consequently, ΔΔstrain must be the error incurred in assuming that the strain energy of $R^{3\cdot}$ is that of R^3H. Since the strain energy of BH is zero and that of $B^\cdot$ can be taken as zero also, ΔΔstrain is then the energy increase involved in the formation of $R^{3\cdot}$ from R^3H, relative to $\Delta strain_{BH \rightarrow B^\cdot} = 0$.

The three bridgehead radicals, 1-adamantyl included, are therefore all more strained than the tert-butyl radical, but the spread of energies is rather less than previous studies suggest.[1] As regards 1-adamantyl and tert-butyl, our result makes the strain energy for the formation of $Ad^\cdot$ from AdH 2.2 kcal.mol^{-1} higher than that for $B^\cdot$ from BH.[12] This value is in good agreement with the computational prediction[13] of 1.4 kcal.mol^{-1} and with the experimental value ("nearly the same") reported by Rüchardt et al..[4]

The very small yield of the 1-norbornyl radical makes the corresponding data subject to somewhat greater uncertainty than those for $Ad^\cdot$ and $Oc^\cdot$. Nevertheless, the remarkable similarity of the ΔΔstrain values for $Nor^\cdot$ and $Oc^\cdot$ suggests that the slow rate of formation of the 1-norbornyl radical both in this study and elsewhere is attributable more to the small steric drive for this reaction, indicated by Δstrain (calc.), than by any intrinsic "instability" due to strain about the trivalent carbon. Because both Ad and Oc are more sterically demanding than Nor, it is energetically preferable to eject one of these from the system rather than the latter.

The advantage of the present approach, based on intramolecular competition, as opposed to reactions where only one alkyl radical is formed or consumed, is that the conventional steric effect upon reactivity can be calculated explicitly.

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8. Relative yields obtained by normalising absolute yields of 70-75% and assuming that losses occur unselectively.
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10. This equation applies to thermolysis in dodecane ; there is no significant difference between rates of 1 in dodecane and mesitylene but it was more convenient to use the latter for product studies.
11. Apart from eventual errors arising in the measurement of $\Delta G^{\ddagger}$ it should be noted that the standard deviation on eqn. 1 is ± 0.6 $kcal.mol^{-1}$. This constitutes a conservative estimate of the probable uncertainty on Δstrain (expt.) and, therefore, upon ΔΔstrain.
12. Applying the procedure of the present note to our datum on Ad_2BCOH (5% AdH at 200°C) gives a concordant value of 2.3 $kcal.mol^{-1}$ (MM2 force field).
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