

THE THERMOLYSIS OF 1,1'-BIADAMANTANE<sup>1)</sup>\*)

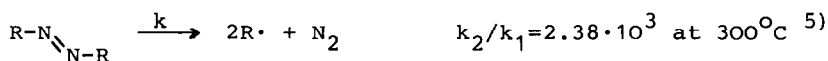
Hans-Dieter Beckhaus, Manuela A. Flamm and Christoph Ruchardt<sup>†)</sup>

Chemisches Laboratorium der Universität Freiburg, Albertstr. 21, D-7800 Freiburg i.Br. (Germany)

**Abstract** The activation parameters for the homolytic cleavage of the central CC-bond in 1,1'-biadamantane 5 and their comparison with corresponding data for 2,2,3,3-tetramethylbutane 6 together with the strain enthalpies of 5 and 6 are conclusive experimental evidence for the absence of appreciable strain in 1-adamantyl radicals 3. This supports predictions made on the basis of calculations using a recently developed force field for radicals.

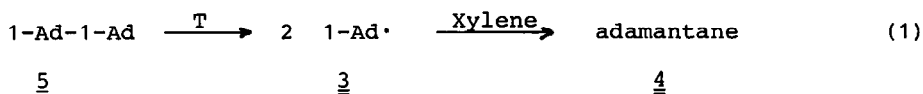
Investigations of the reactivities at bridgehead positions in dissociation reactions leading to trivalent carbon intermediates have been used for deciding on the question of the preferred geometry of such intermediates<sup>3-6)</sup>. The decreased reactivity in S<sub>N</sub>1-solvolysis reactions at bridgehead positions is the classic example and is in agreement with force field calculations<sup>4)</sup>, which show e.g. that the strain enthalpy increases by as much as 12.6 kcal·mol<sup>-1</sup> in going from adamantane to the 1-adamantyl carbenium ion<sup>4)</sup>. The large force constants for bending a planar carbenium center to pyramidal geometry are responsible for this increase<sup>3)</sup>.

The picture of the radical reactivity at bridgehead positions is much less uniform<sup>5,6)</sup>. Not only the thermodynamic stabilities of the radicals being generated, but frequently also polar effects and other steric shielding effects<sup>5)</sup> are responsible for reactivity patterns, depending e.g. on the position of the transition state on the reaction coordinate<sup>5,6)</sup>. The low rate of thermolysis of 1-azoadamantane 1 as compared with that of azoisobutane 2,



is believed<sup>5,7)</sup> to reflect substantial bridgehead strain in 1-adamantyl

radicals 3. EFF calculations, on the other hand, predict only 1.4 kcal·mol<sup>-1</sup> increase in strain on going from adamantane 4 (H<sub>sp</sub>=7.9 kcal·mol<sup>-1</sup>) to the 1-adamantyl radical 3 (H<sub>sp</sub>=9.3 kcal·mol<sup>-1</sup>)<sup>8)</sup>. This reflects the high flexibility of alkyl radicals in comparison to the corresponding carbenium ions or, <sup>8,3a)</sup> in other words, the comparatively small bending force constants in radicals. In order to test this prediction independently, we investigated the thermolysis of 1.1'-biadamantane 5<sup>9)</sup>



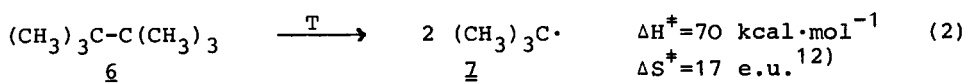
between 440 and 500°C in glass ampules under N<sub>2</sub> in the presence of xylene as radical trap<sup>10)</sup>. Adamantane 4 was formed under these conditions in a yield ≥ 1.2 mol per mol 5 (GC). Because 4 itself decomposes slowly under these conditions, this is a lower limit for eq. (1) being the main thermolysis process. The activation parameters in the table were calculated from a weighted least squares fit<sup>11)</sup> of the recorded k values.

Table. Kinetics of Thermal Decomposition of 5

T[°C]	n <sup>a)</sup>	10 <sup>5</sup> k ± σ <sup>b)</sup> [sec <sup>-1</sup> ]	ΔH <sup>‡</sup> ± σ <sup>b)</sup> [kcal·mol <sup>-1</sup> ]	ΔS <sup>‡</sup> ± σ [e.u.]
440.0	8	0.707 ± 0.062		
450.0	5	1.61 ± 0.18		
460.0	12	2.24 ± 0.19	68.8 ± 2.2	12.7 ± 2.9
475.0	5	6.88 ± 0.32		
500.0	11	31.9 ± 1.3		

a) number of points for determining k    b) standard deviation of the mean

A comparison of the kinetic data for the decomposition of 5 on the one hand and for the open chain analogue 2.2.3.3-tetramethylhexane 6 on the other



is revealing. Because the enthalpies of decomposition of 5 and 6 are almost identical and the strain enthalpies of 5 ( $H_{sp}=6.7 \text{ kcal}\cdot\text{mol}^{-1}$ )<sup>13)</sup> and 6 ( $H_{sp}=6.9 \text{ kcal}\cdot\text{mol}^{-1}$ )<sup>10)</sup> are almost the same, it is concluded that the strain enthalpy of the t-butyl radicals 7 is also nearly the same as that of 1-adamantyl radicals 3<sup>14)</sup>.

This experimental result supports the computational prediction of  $1.4 \text{ kcal}\cdot\text{mol}^{-1}$  difference in strain enthalpy between 3 and 4 mentioned above, and it illustrates the high flexibility of the bond angles at aliphatic carbon radical centers<sup>3a,8)</sup>. Although  $49^\circ$  out of plane bending is calculated for the radical center in 3, no appreciable additional strain was recognized experimentally. The difference in thermal stability between 5 and 6 is apparently mainly due to differences in  $\Delta S^\ddagger$ . The higher  $\Delta S^\ddagger$  value for reaction (2) than for (1) may reflect the higher flexibility of the t-butyl radical 7<sup>15)</sup> than of 1-adamantyl 3 at transition state. This is the first experimental evidence for the very flat out of plane bending potentials at the trivalent carbon in alkyl radicals<sup>3a,15,16)</sup>. Preliminary kinetic data of high precision for the decomposition of 1-azoadamantane point in the same direction<sup>17)</sup>.

Acknowledgements Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie and technical assistance by D.Man1 are gratefully acknowledged. Thanks are due to Dr.J.S.Lomas for communicating preliminary results.

#### References and Notes

\*) *Dedicated to Prof.P D.Bartlett for his 75th birthday.*

- 1) Paper XV of the series: Thermolabile Hydrocarbons (paper XIV see Ref.2) and paper V of the series: Application of Force Field Calculations (paper IV: H.-D.Beckhaus, Chem.Ber., submitted).
- 2) R.Winiker, H.-D.Beckhaus and C.Ruchardt, Chem.Ber. 113, 3456 (1980).
- 3) a) R.C.Fort and P.v.R.Schleyer, Advances in Alicyclic Chemistry (H.Hart and G.J.Karabatsos Ed.), Academic Press, New York, London, Vol.I, 283 (1966); b) R.C.Fort in Carbonium Ions (G.Olah and P.v.R.Schleyer Ed.), J.Wiley-Interscience, Vol.IV, 1783 (1973).
- 4) R.C.Bingham and P.v.R.Schleyer, J.Am.Chem.Soc. 93, 3189 (1974).

- 5) a) V.Golzke, F.Groeger, A.Oberlinner and C.Ruchardt, *Nouv.J.Chim.* 2, 169 (1978); b) B.Giese and H.Stellmach, *Chem.Ber.* 113, 3294 (1980); c) H.-D.Beckhaus, *Angew.Chem.* 90, 633 (1978); *Angew.Chem.Int.Ed.Engl.* 17, 594 (1978).
- 6) C.Ruchardt, V.Golzke and G.Range, *Chem.Ber.* 114, 2769 (1981).
- 7) Azoalkane decompositions are believed to pass through a late, radical-like transition state; therefore radical stability effects on rates are observed, see ref. 5) and P.S.Engel, *Chem.Rev.* 80, 99 (1980).
- 8) H.-D.Beckhaus, *Chem.Ber.*, in preparation; MM2 force field of Allinger [cf. N.L.Allinger, *J.Am.Chem.Soc.* 99, 8127 (1977)] with parametrisation for free radicals.
- 9) R.Reinhardt, *J.Org.Chem.* 27, 3258 (1962).
- 10) For a detailed review of homolytic CC cleavage reactions and the procedures used, see C.Ruchardt and H.-D.Beckhaus, *Angew.Chem.* 92, 417 (1980).
- 11) Programme of W.Barbe (PhD.-thesis 1981, U. of Freiburg) following the methods of R.J.Cvetanovic and D.L.Singleton, *Int.J.Chem.Kinetics* 9, 481 (1977).
- 12) J.A.Welker and W.Tsang, *Int.J.Chem.Kinetics* XI, 867 (1979); Eyring parameters calculated from Arrhenius parameters at 800 K.
- 13) Calculated using the MM2 force field<sup>8)</sup> N.L.Allinger and Y.H.Yuh, *QCPE* 395. The inherent strain of the adamantyl ring system was accounted for by subtraction of  $2 \times 7.9 \text{ kcal}\cdot\text{mol}^{-1}$ <sup>4)</sup>.
- 14) In addition the central CC-bond lengths in 6 (158 pm)<sup>10)</sup> and 5 (157.8 pm) are the same: R.A.Alden, J.Kraut and T.G.Traylor, *J.Am.Chem.Soc.* 90, 74 (1968).
- 15) A slightly bent geometry of 7 is the structure of lowest energy (by  $0.5 \text{ kcal}\cdot\text{mol}^{-1}$ ) for conformational reasons<sup>8)</sup>.  
O.Griller, K.U.Ingold, P.J.Krusic, H.Fischer, *J.Am.Chem.Soc.* 100, 6750 (1978), see also M.Yoshimine, J.Pacansky, *J.Chem.Phys.* 74, 5168 (1981); M.N.Paddon-Row, K.N.Houk, *J.Am.Chem.Soc.* 103, 5046 (1981).
- 16) J.S.Lomas and J.E.Dubois (unpublished results) came to the same conclusion from thermolysis data of di-1-adamantyl-t.butyl-methanol.
- 17) The activation parameters for thermolysis of 1<sup>18)</sup> are apparently seriously in error: M.Schmittel, C.Ruchardt, work in progress. We are now considering the possibility that trans-cis-isomerisation may be the first step in some thermal decompositions of trans-azoalkanes, e.g. 1.
- 18) M.Prochazka, O.Ryba and D.Lim, *Collect.Czechoslov.Chem.Comm.* 33, 3387 (1968).

(Received in Germany 5 February 1982)