

THERMAL DECOMPOSITION OF TRI-TERT-BUTYLMETHANE¹⁾

Christoph Rüdhardt* and Siegfried Weiner

Chemisches Laboratorium der Universität Freiburg,

D-7800 Freiburg i.Br., Albertstr. 21, West-Germany

Tri-tert-butylmethane²⁾ 1 is the most crowded aliphatic hydrocarbon the structure of which has been investigated in great detail. According to an electron diffraction study³⁾ it has abnormal bond lengths (CH 1,111 Å, C-C 1,611 Å) and bond angles (CCC 116°, HCC 101.6°) at the central carbon atom. The agreement of the results of force field calculations⁴⁻⁶⁾ with these experimental data is astoundingly good taking into account the fact, that the force fields used^{4,6-10)} were not parametrized for such highly strained hydrocarbons. An enthalpy of formation of -53.69 kcal/mol was calculated for 1 by DeTar and Tenpas¹¹⁾ using the Engler-Schleyer force field⁶⁾ and a set of improved base values¹¹⁾. A strain enthalpy $E_{Sp}=39.8$ kcal/mol was deduced therefrom using Schleyers "single conformation" increments⁶⁾.

For a large group of strained aliphatic hydrocarbons we have recently recognized the existence of a linear relationship between their strain enthalpy E_{Sp} as calculated by the Engler-Schleyer force field^{6,11)} and the free enthalpy of activation $\Delta G^\ddagger(300^\circ\text{C})$ of their homolytic decomposition¹²⁾:

$$\Delta G^\ddagger(300^\circ\text{C}) = -0.60[+0.03]E_{Sp} + 65.6[+2.0]\text{kcal/mol}$$

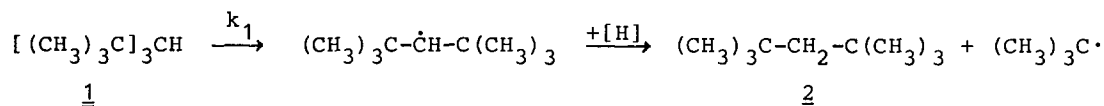
which allowed us to predict for 1 from the calculated E_{Sp} mentioned above:

$$\Delta G^\ddagger(300^\circ\text{C}) = 41.7 \pm 2.2 \text{ kcal/mol and } T(t_{1/2}=1\text{h})^{13)} = 274 \pm 15^\circ\text{C}.$$

In order to test this prediction we have investigated now the thermal decomposition of 1, which was prepared by the procedure of Lee^{2a)}.

When a 0.05 m solution of 1 in mesitylene or tetraline was heated in a sealed ampule under N_2 for 2 hours to 300°C 1 was completely decomposed

and the main product determined by GC in > 70% yield was 2.2.4.4-tetramethyl pentane 2¹⁴).



This is evidence for rather clean decomposition of 1 in tert-butyl- and di-tert-butylmethyl radicals^{2b}). The kinetics of the thermolysis of 1 (0.05 m in mesitylene) was followed over a temperature range of 55.5°C measuring the decrease in concentration of 1 by GC as previously described for the decomposition of other strained hydrocarbons¹⁵). The results are recorded in the table.

Table. Thermolysis of Tri-tert-butylmethane 1 in mesitylene

T [°C]	10 ⁴ k ₁ [s ⁻¹]	Δk ^{a)} [%]	n ^{b)}	r ^{c)}	τ _{1/2} [min]
257.3 _{±.4}	12.7	4.3	7	0.995	9
254.8 _{±.4}	8.71	3.4	8	0.997	13
239.5 _{±.4}	2.33	2.6	8	0.998	50
225.5 _{±.2}	0.691	2.5	6	0.999	167
201.8 _{±.2}	0.0538	1.7	8	0.999	2147

a) standard deviation σ b) n=number of points

c) r=correlation coefficient

From these data

$$T(\tau_{1/2}=1\text{h})^{13)} = 237.5^\circ\text{C}; \Delta G^\ddagger(300^\circ\text{C}) = 38.0 \pm 0.1 \text{ kcal/mol}^{16)};$$

$$\Delta H^\ddagger = 47.3 \pm 0.9 \text{ kcal/mol and } \Delta S^\ddagger = 16.2 \pm 1.9 \text{ e.u.}$$

were calculated.

Because 1 has three equivalent bonds to be cleaved, a statistical correction was introduced¹⁸⁾ to make these data comparable with those of other

hydrocarbons¹²⁾. Accordingly

$$T(\tau_{1/2}=1\text{h}) = 243^{\circ}\text{C}; \Delta G^{\ddagger}(300^{\circ}) = 38.6 \pm 0.1 \text{ kcal/mol};$$

$$\Delta H^{\ddagger} = 47.3 \pm 0.9 \text{ kcal/mol and } \Delta S^{\ddagger} = 15.1 \pm 1.9 \text{ e.u.}$$

The agreement between these experimental results and those predicted above is remarkable and almost approaching the standard deviation of the correlation used for the prediction¹²⁾.

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- 13) Temperature at which the half time of thermal decomposition is 1h.
- 14) A sample of 2 was available; as internal standard for GC n-octane was used.
- 15) See e.g. H.-D.Beckhaus, G.Hellmann, C.Rüchardt, B.Kitschke, H.J.Lindne and G.Fritz, Chem.Ber. 111, 3764 (1978)
- 16) $r=0.994$; deviation 0.2 kcal/mol (confidence level 95%)¹⁷⁾
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- 18) The Eyring equation used for this correction was
$$\ln k_1/T = \ln k_B/h + \ln 3 - \Delta G^\ddagger/RT$$

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