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THERMAL DECOMPOSITION OF TRI-TERT-BUTYLMETHANE[1)]

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Tri-tert-butylmethane[2)] $\underline{1}$ is the most crowded aliphatic hydrocarbon the structure of which has been investigated in great detail. According to an electron diffraction study[3)] 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 calculations[4-6)] 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 $\underline{1}$ by DeTar and Tenpas[11)] using the Engler-Schleyer force field[6)] and a set of improved base values[11)]. A strain enthalpy E_{Sp}=39.8 kcal/mol was deduced therefrom using Schleyers "single conformation" increments[6)].

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 $\Delta G^{\ddagger}(300^{\circ}C)$ of their homolytic decomposition[12)].

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

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

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

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

When a 0.05 m solution of $\underline{1}$ in mesitylene or tetraline was heated in a sealed ampule under N_2 for 2 hours to 300°C $\underline{1}$ was completely decomposed and the main product determined by GC in > 70% yield was 2.2.4.4-tetramethyl pentane 2[14].

$$\underset{1}{[(CH_3)_3C]_3CH} \xrightarrow{k_1} (CH_3)_3C\text{-}\dot{C}H\text{-}C(CH_3)_3 \xrightarrow{+[H]} \underset{2}{(CH_3)_3C\text{-}CH_2\text{-}C(CH_3)_3} + (CH_3)_3C\cdot$$

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 hydrocarbons[15]. 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]	$\tau_{1/2}$ [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

$$T(\tau_{1/2}=1h)^{13)} = 237.5^{\circ}C; \quad \Delta G^{\ddagger}(300^{\circ}C) = 38.0\pm0.1\ \text{kcal/mol}^{16)};$$

$$\Delta H^{\ddagger} = 47.3\pm0.9\ \text{kcal/mol and } \Delta S^{\ddagger} = 16.2\pm1.9\ \text{e.u.}$$

were calculated.

Because 1 has three equivalent bonds to be cleaved, a statistical correction was introduced[18] to make these data comparable with those of other hydrocarbons[12]. Accordingly

$$T(\tau_{1/2}=1h)= 243^{o}C;\ \Delta G^{\ddagger}(300^{o})= 38.6\pm0.1\ \mathrm{kcal/mol};$$

$$\Delta H^{\ddagger}= 47.3\pm0.9\ \mathrm{kcal/mol\ and}\ \Delta S^{\ddagger}= 15.1\pm1.9\ \mathrm{e.u.}$$

The agreement between these experimental results and those predicted above is remarkable and almost approaching the standard deviation of the correlation used for the prediction[12].

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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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