

Thermal Behaviour of C₈H₈ Hydrocarbons

Gas-Phase Thermolysis of Cuneane, a New Example of a High-Strain Energy Release Process¹⁾

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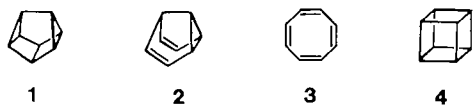
The kinetics of thermal decomposition of cuneane²⁾ (1) in the gas phase have been investigated in the temperature range 180–220°C. The reaction is a clean first-order homogeneous process leading to the formation of two C₈H₈ isomers, viz., semibullvalene³⁾ (2) and cyclooctatetraene (3). The rate constant varies with temperature according to the Arrhenius equation $\log(k/s^{-1}) = (13.82 \pm 0.09) - (37.7 \pm 0.2 \text{ kcal mol}^{-1})/RT \ln 10$. The Arrhenius parameters are consistent with a biradical mechanism leading to the formation of semibullvalene (2). The product proportions are pressure-dependent which strongly suggests that semibullvalene (2) is initially formed with high vibrational energy content (ca. 74 kcal mol⁻¹) and can react further to give cyclooctatetraene (3).

Das Thermolyseverhalten von C₈H₈-Kohlenwasserstoffen. – Gasphasen-Thermolyse von Cuneane, ein neues Beispiel für die Freisetzung hoher Spannungsenergie

Die Kinetik der Gasphasenthermolyse von Cuneane²⁾ (1) wurde im Temperaturbereich von 180–220°C untersucht. Es handelt sich um eine Reaktion erster Ordnung, die zu zwei C₈H₈-Isomeren führt, zu Semibullvalen (2) und Cyclooctatetraen (3). Die Geschwindigkeitskonstante ist abhängig von der Temperatur entsprechend der Arrhenius-Gleichung $\log(k/s^{-1}) = (13.82 \pm 0.09) - (37.7 \pm 0.2 \text{ kcal mol}^{-1})/RT \ln 10$. Die Arrheniusparameter stimmen mit einem biradikalischen Mechanismus überein, der zur Bildung von Semibullvalen (2) führt. Die Produktverteilung ist druckabhängig. Dies deutet darauf hin, daß das zuerst gebildete Semibullvalen (2) hoch schwingungsangeregt (ca. 74 kcal mol⁻¹) ist und zu Cyclooctatetraen (3) weiterreagiert.

The family of C₈H₈ hydrocarbons contains molecules of both remarkable reactivity and surprising stability. Semibullvalene (2), for instance, undergoes a rapid degenerate Cope rearrangement at –150°C⁴⁾, whilst cubane⁵⁾ (4), with a strain energy of ca. 164 kcal mol⁻¹, is stable up to 230°C. Cuneane (1), the subject of this study, resembles cubane (4), in being another pentacyclic molecule, but differs from it in having molecular “faces” consisting of two 3-membered, two 4-membered, and two 5-membered rings rather than six 4-membered rings as can be seen from the structures shown in Scheme 1.

Scheme 1



From the principle of additivity of ring strains^{6,7)} a strain energy of $\geq 120 \text{ kcal mol}^{-1}$ is expected for cuneane (1). Thus, cuneane (1) may be expected to decompose with substantial energy release. This aspect, as well as our general interest in these hydrocarbons^{1,8,9)}, led us to investigate the thermal decomposition of 1. There has been no previous study.

Results

(i) *Reaction Stoichiometry*: Preliminary pyrolyses revealed that the only products were semibullvalene (2) and cyclooctatetraene (3).

tetraene (3). No other C₈H₈ isomer was detected down to a level of < 1%; cubane (4), barrelene (bicyclo[2.2.2]octa-2,5,7-triene), and the dihydropentalene isomers can all be unequivocally eliminated. A small quantity of benzene as a product could have escaped detection because of the benzene impurity (see Experimental). In order to try to eliminate this and any other unscen side reaction, a mass balance check was made. A mixture of cuneane with toluene (91.4% 1, 8.6% toluene) was pyrolysed to 40% conversion, and the proportion of C₈H₈ hydrocarbons (91.3%) was identical within experimental error with expectation. Thus the benzene offered no serious impediment and was a non-interfering impurity. Rate data (see below) were independent of the percentage of benzene impurity. The reaction was studied as a function of time, pressure, and temperature.

(ii) *Time Dependence*: Runs were performed at each of five temperatures at constant initial pressures of $2.0 \pm 0.2 \text{ Torr}$ at times corresponding to between 9% and 83% conversion. An example of the analytical results is shown in Table 1.

Good first-order plots [$\ln(\%1)$ vs. time] were obtained from these data. The data in Table 1 gave a rate constant of $k = (4.063 \pm 0.035) \times 10^{-5} \text{ s}^{-1}$ ($r = 0.998$) by least-squares fitting. The product ratio 2/3 shows some scatter but no systematic trend with time, suggesting no secondary conversion of 2→3 (but see Discussion).

(iii) *Temperature Dependence* (including test of homogeneity): The first-order rate constants obtained from the time dependence are shown in Table 2.

Table 1. Product variation with time at 180.0°C

Time [min]	1	Total % 2	3	Ratio 2/3
60	85.09	3.64	11.27	0.323
180	63.78	6.76	29.46	0.229
300	47.84	9.84	42.32	0.233
420	36.15	8.93	54.92	0.163
540	26.40	12.51	61.09	0.205

Table 2. Rate constant variation with temperature

T [°C]	180.0	190.1	200.0	209.0	220.3
$10^4 k/s^{-1}$	0.406 ± 0.004	1.030 ± 0.007	2.44 ± 0.01	5.55 ± 0.04	12.37 ± 0.16

They are fitted by the following Arrhenius equation:

$$\log(k/s^{-1}) = (13.82 \pm 0.09) - (37.7 \pm 0.2 \text{ kcal mol}^{-1})/RT \ln 10$$

The errors correspond to one standard deviation. A run carried out in a properly conditioned vessel packed with pyrex tubes (see Experimental) gave a rate constant $k = (2.44 \pm 0.03) \times 10^{-4} \text{ s}^{-1}$ at 200.0°C in excellent agreement with the unpacked vessel result. This removes any possibility of a surface contribution to the rate and strongly supports a purely homogeneous reaction.

(iv) *Pressure Dependence*: A series of runs was performed at 200.0°C for a time of 45 min. Conversions were found to be constant ($52 \pm 1\%$ remained), but the proportions of the two products varied substantially. This was investigated by systematic variation of pressure between 6 and 600 Torr for two added gases. Nitrogen [an inefficient (weak) collision partner] and *cyclo*-C₄F₈ [a relatively efficient (strong) collision partner] were chosen for their likely different energy transfer characteristics. The results are shown in Figure 1.

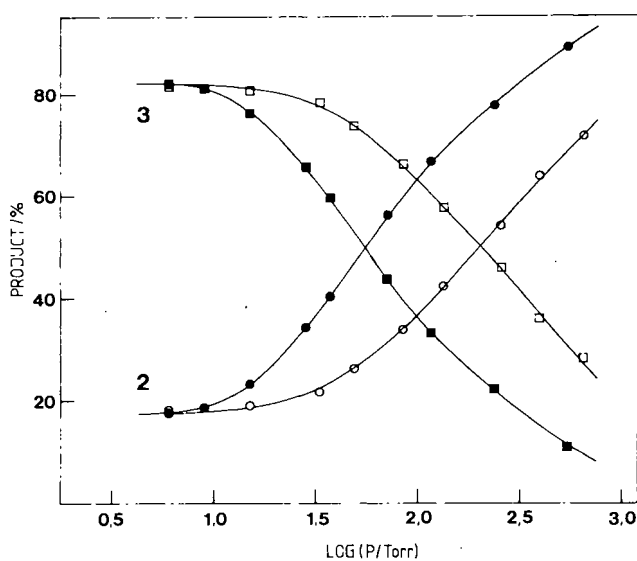


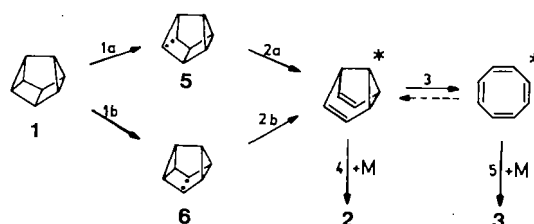
Figure 1. Product pressure dependence. Semibullvalene (2), ○ added N₂; ● added *cyclo*-C₄F₈. Cyclooctatetraene (3), □ added N₂; ■ added *cyclo*-C₄F₈.

It can be seen that (a) for both collider gases, cyclooctatetraene (3) is the major product at low pressures, but semibullvalene (2) is the major product at high pressures, and (b) at intermediate pressures the proportion of 2 is greater (and the proportion of 3 is less) in the presence of *cyclo*-C₄F₈ compared with N₂. It is also noteworthy that at low pressures, in the presence of both collider gases, the ratio 2/3 seems to reach an approximately constant limit of ca. 0.20. We are not able to reach a high-pressure limit, but the data are not inconsistent with a possible limit of 100% of 2 (and 0% of 3).

Discussion

(i) *The Rate Determining Step*: In order to discuss the results it is helpful to consider at the outset the mechanism proposed in Scheme 2.

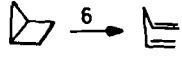
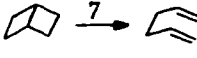
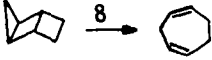
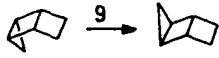
Scheme 2



The first step in the decomposition of 1 is envisaged as the breaking of a C—C bond leading either to biradical 5 (tetracyclo[3.3.0.0^{3,7}.0^{6,8}]octa-2,4-diyl) via step 1a or biradical 6 (tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octa-3,7-diyl) via step 1b. The second step is then the opening of an adjacent C—C bond either from biradical 5 or 6 to give 2 (energized form). These steps together are formally equivalent to a $\sigma_{2s} + \sigma_{2s} \rightarrow \pi_{2s} + \pi_{2s}$ symmetry-forbidden process. The formation of either biradical does not loosen up the structure significantly and therefore no significant entropy of activation is to be expected. This is consistent with the observed low *A* factor of $10^{13.82} \text{ s}^{-1}$. On the basis of strain energy release it is not easy to choose between 5 or 6 as the important intermediate. Formation of 5 requires formal release of the strain of one 3-membered and one 4-membered ring with formation of a 5-membered ring. This could involve a total strain energy release of ca. 48 (= 28 + 26 - 6) kcal mol⁻¹ (6,7). Formation of 6 requires formal release of the strain of two 4-membered rings with formation of one 6-membered ring (but in a strained boat conformation). This should involve a total strain energy release of ca. 48 (= 2 × 26 - 4) kcal mol⁻¹ (6,7). Thus the energies of formation of 5 and 6 are the same. Interestingly, if we take a C—C bond to have ca. 82 kcal mol⁻¹ (7,10), this implies a minimum activation energy of 34 kcal mol⁻¹. In practice, because of a small increment of extra strain (vide infra) the minimum energy of steps (1a) or (1b) may be slightly lower than this but in any case the figure of 34 kcal mol⁻¹ is reasonably consistent with the measured activation energy of 37.5 kcal mol⁻¹.

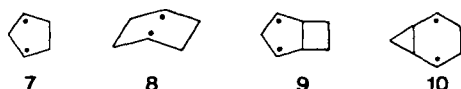
A clue to the likely pathway may be provided by consideration of the model polycyclic systems shown in Table 3.

Table 3. Comparison of Arrhenius parameters in some polycyclic systems, A [s⁻¹], E_a [kcal mol⁻¹]

Reaction	log A	E_a	Ref.
 6	14.4	52.3	12
 7	13.4	36.0	12
 8	13.7	33.2	13
 9	13.8	29.5	13

Reaction (6) proceeds via the cyclopenta-1,3-diyli biradical (7) and reaction (7) proceeds via the cyclohexa-1,4-diyli biradical (8).

Scheme 3

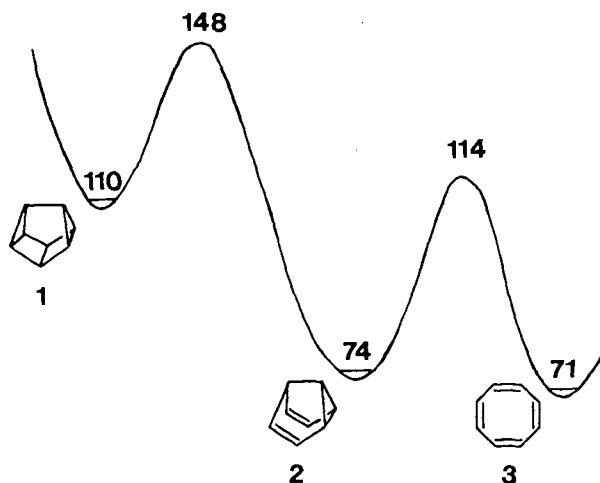


These intermediates have been much discussed¹⁴, and it is clear that the high activation energy for reaction (6) stems from the difficulty of ring opening of 7, not from any difficulty of formation, while reaction (7) is much faster because of the ease of ring opening of 8, arising from its greater flexibility (conversion to chair form). This is further confirmed in the work of Roth et al.¹³ who showed that although biradical 9 is implicated in the *syn*→*anti* tricyclo[3.2.0.0^{2,4}]heptane rearrangement [reaction (9)], it is biradical 10 which leads to dienes when generated photochemically from the azo precursor. This suggests that pathway b [steps (1b) and (2b)] via biradical 6 is the more likely route for 1→2 in this study. A word of caution should be sounded, however, that the ring opening of 8 and 10 is facilitated by the flexibility of the 6-membered ring. In 6 this will be restrained by the rigidity of the polycyclic system. A decision between 6 and 5 is therefore not clear-cut.

(ii) *The Formation of Vibrationally Excited Products*: The pressure dependence of the proportions of semibullvalene 2 and cyclooctatetraene 3 offers strong evidence of vibrational excitation in these two products as shown in Scheme 2. Initially formed 2 via step (2a) or (2b) contains ca. 74 kcal mol⁻¹ (see Figure 2) excess vibrational energy, well in excess of the barrier to isomerisation⁹ to 3 of 40 kcal mol⁻¹.

Thus at low pressures step (3) readily occurs, leading to an excess of cyclooctatetraene 3 [stabilized via step (5)], whereas at high pressures stabilization of vibrationally excited 2 via step (4) occurs leading to an excess of semibullvalene 2.

At very high pressures this should be essentially complete (i.e. 100%) formation of 2 but from the observed thermal isomerisation rate data⁹ a small amount (ca. 5%) of the

Figure 2. Simplified potential energy hypersurface for cuneane rearrangement (ΔH^\ddagger values in kcal mol⁻¹)

stabilized 2 will be converted into 3 under the reaction conditions. At intermediate pressures, stabilization by *cyclo*-C₄F₈ is more effective than by N₂ in accord with their anticipated properties as collision partners. The finding of a limiting proportion of 2 at low pressures in the presence of both colliders supports the idea that step (3) is reversible to a small extent and that a steady state is achieved between energized 2 and 3. The higher proportion of 2, viz. 17%, compared to the equilibrium proportion⁹ (ca. 1.8%) reflects the greater reversibility of reaction (3) under chemical activation conditions. If deactivation of the vibrationally excited molecules takes place via a multistep cascade process, then the observed ratio 2 to 3 represents the steady state situation at energies somewhat above the isomerisation barrier prior to the last (deactivating) collision. RRKM calculations have been carried out to simulate this process and these will be reported elsewhere¹⁵.

These isomerisations can be readily understood in terms of the potential energy surface shown in Figure 2. The enthalpies of formation of 2 and 3 are known⁹ and that of cuneane (1) is obtained with the aid of an additivity estimate^{6,7}. The enthalpy of formation of 1, 110 kcal mol⁻¹, is confirmed by molecular mechanics (MM2) calculation¹⁶, which we have carried out. This study shows that cuneane (1) resembles cubane (4) in its thermal behaviour. Both are molecules of high-strain energy but with surprising stability. Both, however, give rise to high-energy release upon decomposition which leads to vibrationally excited products, capable of further reaction unless collisionally stabilized¹⁷.

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Experimental

Apparatus for Kinetic Measurements: This was similar to that used in earlier publications¹⁸. The reaction vessel used for most experiments was spherical (volume ca. 250 cm³) with a surface area-to-volume ratio (S/V) of 0.7 cm⁻¹. A packed vessel of $S/V = 5.0$

cm⁻¹ was used for the surface activity test. Gaseous pressures were measured with a Baratron (MKS instruments) for pressures up to 10 Torr, or with a conventional Hg manometer.

Experimental Procedure: Prior to use, each reaction vessel was conditioned at reaction temperature with hexamethyldisilazane vapour for at least one hour. This was repeated three times for the packed vessel to suppress all surface activity. Runs were carried out by admitting a known pressure of cuneane (**1**) to the reaction vessel for a known time. Where added gases were used, they were admitted to the vessel quickly after the cuneane. This involved a time delay of ca. 90 s, for which a small analytical correction was made. After the desired time the reaction was quenched and analysed as described previously¹⁸.

Analysis: Chromatographic analyses of all product mixtures were carried out consecutively on two columns. This was necessary to obtain the complete compositions because of peak overlap. The first column was 3 m × 3 mm diameter silicone oil (OV101, 10% on Chromosorb W) operated at 35°C with nitrogen carrier gas (20 lbf in⁻²). Retention times were: benzene, 3.4 min; **2** + **3**, 19.2 min; **1**, 25.4 min. The second column was a 3 m × 3 mm diameter fluorosilicone oil (20% on Chromosorb W treated with hexamethyldisilazane and 1% ATPET). Retention times were: benzene, 10.3 min; **3**, 35.4 min; **1** + **2**, 44.2 min. It is worth noting that the second column is the only reliable one known to us⁹ capable of separating semibullvalene **2** and cyclooctatetraene **3**. Retention times were confirmed by comparison with authentic samples. It was assumed that all C₈H₈ isomers had the same response factors to the flame ionization detector. The gas sample loop was heated to > 40°C to avoid problems of condensation during injection. A check was made that no memory effects were present after injection.

Materials: Cuneane (**1**) was prepared according to the established procedure¹⁹. It was separated from benzene (solvent) by preparative GC (4 m SF.30 column) but not completely purified since, in practice, benzene was a non-interfering contaminant (no interference with analyses or rate measurements). Semibullvalene (**2**) was prepared as previously⁹ and cyclooctatetraene (**3**) was obtained from BASF AG. Nitrogen (British Oxygen) and Perfluorocyclobutane

(Pierce Chemicals) were both ≥ 99% pure and were degassed before use.

CAS Registry Number

1: 20656-23-9

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