The Pyrolysis of Cubane; an Example of a Thermally Induced Hot Molecule Reaction[1]

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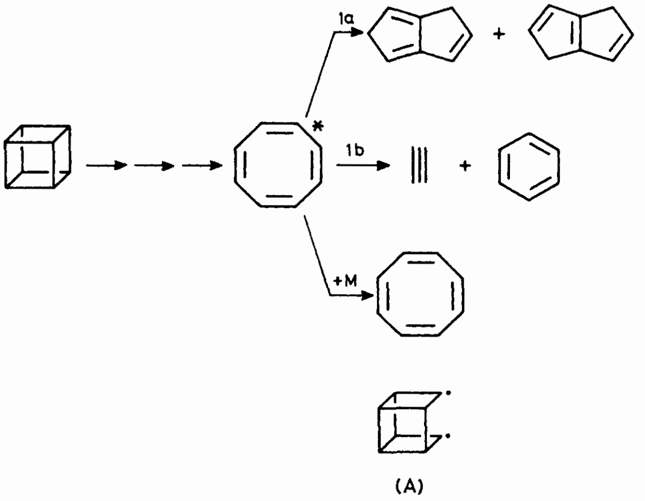
The pressure dependence of the product distribution of cubane pyrolysis supports a mechanism involving cyclo-octatetraene formed in a highly vibrationally excited state through the release of ring strain energy.

Amongst polycyclic hydrocarbons cubane (pentacyclo-[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane) holds a particular fascination both because of its symmetry and because of its highly strained structure. Cubane pyrolysis has not hitherto been the subject of a detailed kinetic study and, because of our general interest in C_8H_8 hydrocarbons,[1] we have turned our attention to its thermal stability and decomposition. We report here results which help to account for its surprising stability (no decomposition below 200 °C) but at the same time reveal the formation of highly vibrationally excited products arising from the release of strain during the decomposition.

Cubane was prepared by a literature method, with modifications to obtain better yields.[2] Pyrolyses were carried out by the static method, with g.l.c. analysis (OV101 silicone oil column). Pressurization was by cyclo-C_4F_8 (or N_2). The products were acetylene, benzene, cyclo-octatetraene (COT), styrene, and three dihydropentalenes (1,4-, 1,5-, and 1,2-



Scheme 1

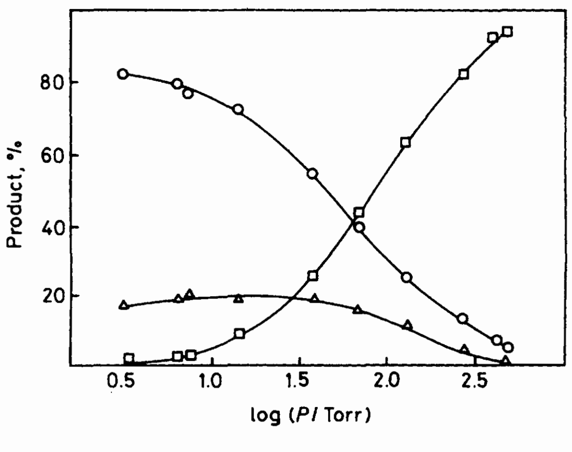


Figure 1. Dependence of product distribution on pressure (cyclo-C_4F_8 bath gas): ○, benzene; □, COT; △, 1,5-DHP + 1,4-DHP + styrene.

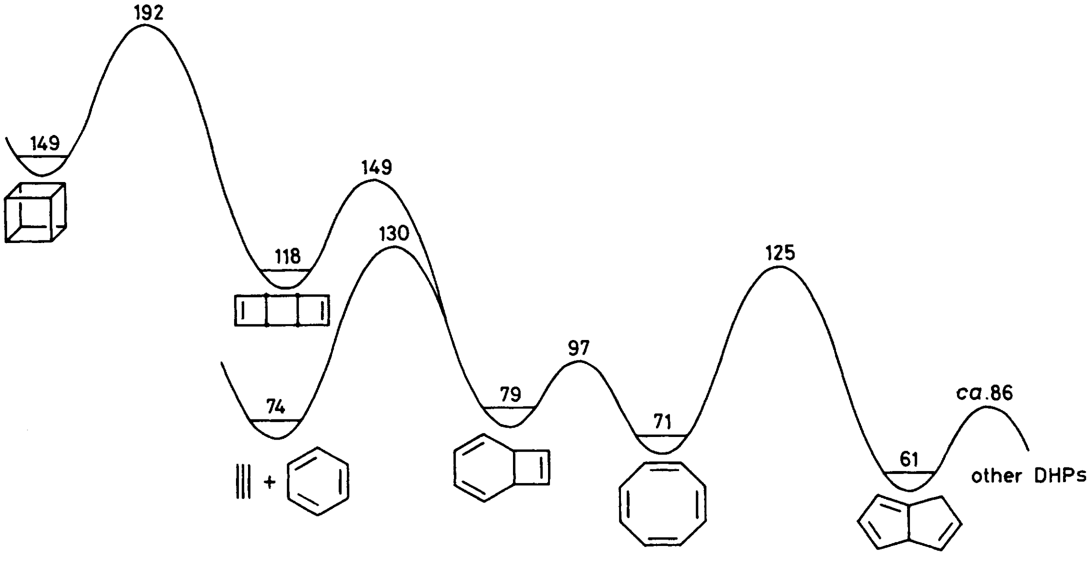


Figure 2. Simplified potential energy hypersurface for cubane rearrangement (ΔH_f° values in kcal mol^{-1}).

DHP).† Cubane pyrolysis was investigated as a function of time, temperature, and pressure. Provided the temperature and pressure were kept constant, product distributions were found to be invariant with time up to 80% conversion, indicating that all products are primary. At a constant pressure, the product distribution varied little with temperature. An Arrhenius plot of data obtained in the range 230—260 °C gave equation (1) (1 cal = 4.184 J).[3]

$$\log(k/\text{s}^{-1}) = (14.68 \pm 0.44) - (43.1 \pm 1.0 \text{ kcal mol}^{-1})/RT\ln 10 \quad (1)$$

In contrast to these observations the product distribution (30 min; 249.4 °C) showed a striking pressure dependence, as indicated in Figure 1. Benzene (and C_2H_2) predominate at high pressures whereas COT is the major product at low pressures. These findings strongly point to pressure quenching of vibrationally excited COT as the key process. The mechanism in Scheme 1 is suggested. Apart from COT itself, all the other observed products are known to be formed in the thermal decomposition of COT.[4] Furthermore they are all quenched with increasing pressure.

In order to gain further support for this mechanism Rice–Ramsperger–Kassel–Marcus (RRKM) calculations[5] were carried out to assess the decomposition rate of COT* relative to quenching under the experimental conditions. Details will be given in a full paper. The thermochemistry (see Figure 2) with allowance for thermal energy indicated a mean initial excitation energy of COT* of 129.5 kcal mol^{-1} (assuming no collision energy removed *en route* from cubane to COT*). The transition state assignments and critical energies were obtained by fitting to new Arrhenius parameters for pathways 1a and 1b, remeasured in an independent study.[6] The results of the calculation reproduced the correct order of magnitude for the average rate constants ($10^{8.5}$—$10^{9.5}$ s^{-1}) and the correct ratio of products (k_{1b}/k_{1a} ~3.5) even though in the *thermal* COT decomposition DHPs exceed benzene substantially.[6] The pressure dependence can be well matched when allowance is made for weak collisional deactivation. The average energy removed per collision $\langle\Delta E\rangle$ = 5000 cm^{-1} (c-C_4F_8).

The rearrangement of cubane undoubtedly initially forms a diradical by single C–C bond breaking, *viz.* structure (A). This (rate-determining) step, offers very little by way of strain release since the original molecular cage is largely intact. This explains why cubane, in spite of its high strain, has such considerable thermal stability. Once past the initial diradical, however, the molecule progressively unzips, through intermediates (see Figure 2) too unstable to be detected, until finally COT* is reached. The original strain energy has then been converted into vibrational energy in COT. This energy is high but COT possesses high enough barriers to be partially stabilised. Further reactions will only ensue if the pressure is low enough. The energetic course of the rearrangement can be seen from Figure 2.

The authors thank the European Photochemistry Association, the British Council, the Fonds der Chemischen Industrie, the Dr. Jost-Henkel-Stiftung, and the BASF AG for financial support.

Received, 15th April 1985; Com. 501

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† In addition to these products, small quantities of tricyclo-[3.3.0.0^{2,8}]octa-3,6-diene (semibullvalene, SBV) are also formed. COT and SBV are not resolved on *this* column, and interconvert thermally fairly rapidly (ref. 1). For practical purposes ([SBV]/[COT] = 0.05 ± 0.02) they are treated as a single product here.

References

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