Kinetics and Mechanism of the Pyrolysis of Cyclohexa-1,3-diene

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The pyrolysis of cyclohexa-1,3-diene (C_6H_8) has been studied between 512·3 and 672·5 K at pressures between 10 and 500 Torr. The products are benzene (B), cyclohexene (C), a compound with formula $C_{12}H_{18}$(E), hydrogen, and traces of C_2 compounds. The formations of benzene, cyclohexene, and $C_{12}H_{18}$ are all of the second order and their rates are unaffected by the surface-to-volume ratio of the reaction vessel or by the presence of added propene. The rate constants (in l mol^{-1} s^{-1}) are given by equations (i)—(iii). The rate of formation of H_2 is *ca.* $\frac{1}{7}$ that of B.

$$\log_{10} k_B = -(35{,}500 \pm 100)/4{\cdot}576T + (10{\cdot}13 \pm 0{\cdot}04) \quad \text{(i)}$$

$$\log_{10} k_C = -(36{,}400 \pm 1100)/4{\cdot}576T + (10{\cdot}25 \pm 0{\cdot}40) \quad \text{(ii)}$$

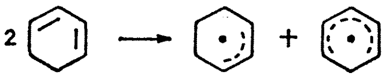
$$\log_{10} k_E = -(35{,}600 \pm 1800)/4{\cdot}576T + (9{\cdot}52 \pm 0{\cdot}67) \quad \text{(iii)}$$

The results are explained by a non-chain, radical mechanism where the initiation step is the bimolecular disproportionation (iv) to cyclohex-2-enyl and cyclohexadienyl radicals. The estimated value of the rate constant k_a is

(iv)

$\log_{10} k_a = -(35{,}500 \pm 1000)/4{\cdot}576T + (10{\cdot}04 \pm 0{\cdot}40)$ l mol^{-1} s^{-1}.

THE pyrolysis of cyclohexa-1,3-diene has been studied between 635 and 694 K by Benson and Shaw.[1] They observed complex kinetics and suggested that the initiation step is the bimolecular disproportionation (1) to cyclohex-2-enyl and cyclohexadienyl radicals.



(1)

During our study of the thermal dimerization of cyclohexadiene between 471 and 672 K[2] it appeared that the pyrolysis was already measurable at 512 K. This paper describes the rather simple kinetics of this reaction in the range 512—672 K and supports the occurrence of the exceptional type of initiation[3] [step (1)].

EXPERIMENTAL

The materials, apparatus, and technique have been described.[2]

Products condensable at −78 °C were analysed by gas chromatography as reported;[2] a product (E) with a retention time of 118 min was shown to be $C_{12}H_{18}$ by mass spectrometry. The total pressure of the products non-condensable at −78 °C (mainly H_2 and a trace of C_2 compounds as verified by mass spectrometry) was measured in the reaction cell. In all experiments the percentage of reaction was ⩽15%.

RESULTS

In the range 512—672 K, cyclohexadiene decomposes to yield benzene (B), cyclohexene (C), a compound with formula $C_{12}H_{18}$(E), hydrogen, and traces of C_2 compounds. These products and the dimers of cyclohexadiene (see ref. 2) account for at least 98% of the cyclohexadiene which has reacted.

Figures 1—3 show all the experimental results for the formation of benzene, cyclohexene, and $C_{12}H_{18}$, respectively.

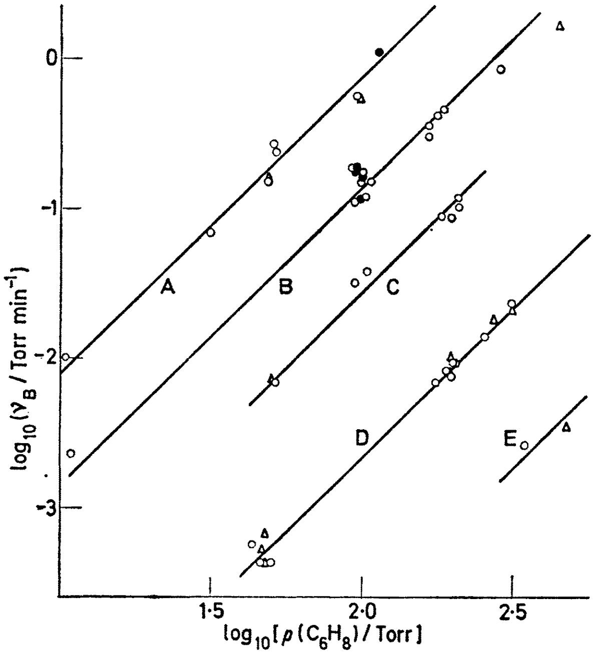


FIGURE 1 Dependence of the rate of formation of benzene (v_B) on the pressure of cyclohexadiene; ○ and △, surface-to-volume ratio 1·2 and 9·0 cm^{-1}, respectively (absence of propene); ● surface-to-volume ratio 1·2 cm^{-1} (presence of propene); $p(C_6H_8) = [p(C_6H_8)_0 + p(C_6H_8)_t]/2$ is the mean pressure of cyclohexadiene during the reaction time t: $p(C_6H_8)_t$ was always kept $\geqslant 0{\cdot}85p(C_6H_8)_0$; straight lines of slope 2; temperatures: A, 672·5 K; B, 638·5 K; C, 603·3 K; D, 552·4 K; E, 512·3 K

The reaction rates can all be represented by equation (2)

$$v_X = d[X]/dt = k_X[\text{Chd}]^2 \qquad (2)$$

where X = benzene, cyclohexene, and $C_{12}H_{18}$. The rates

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[1] S. W. Benson and R. Shaw, *J. Amer. Chem. Soc.*, 1967, **89**, 5351.

[2] G. R. De Maré, G. Huybrechts, M. Toth, and P. Goldfinger, *Trans. Faraday Soc.*, 1971, **67**, 1397.

[3] S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968, p. 132.

are unaffected when the surface-to-volume ratio S/V of the reaction vessel is changed from 1·2 to 9·0 cm^{-1} or when propene (20—420 Torr) is added.*

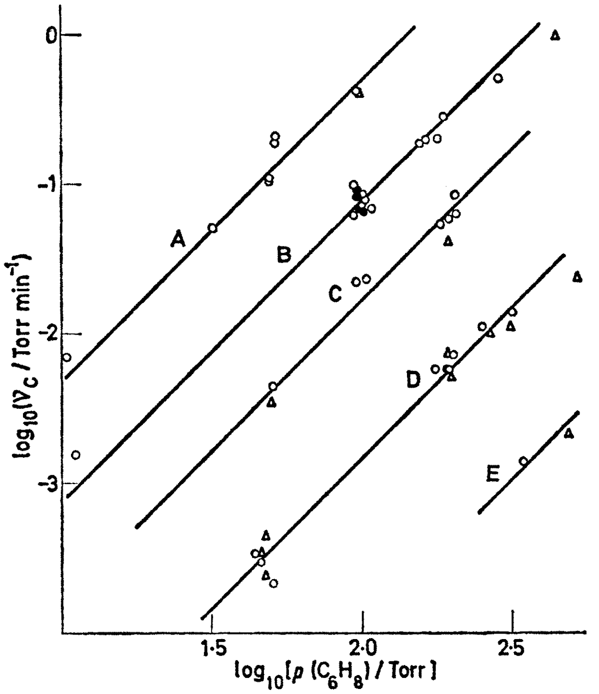

FIGURE 2 Dependence of the rate of formation of cyclohexene (v_C) on the pressure of cyclohexadiene; see caption of Figure 1

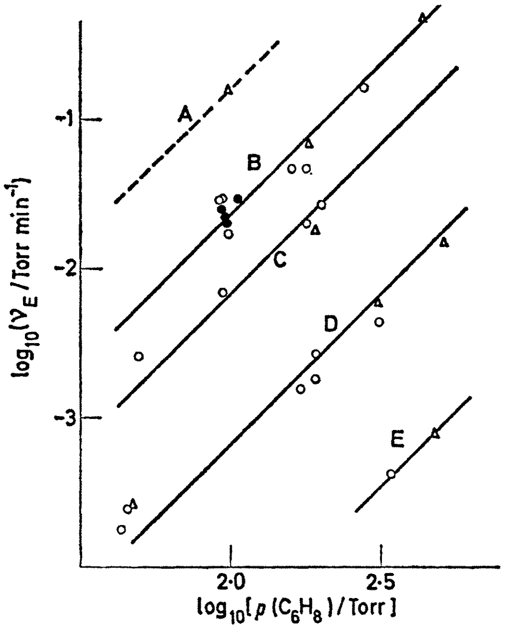

FIGURE 3 Dependence of the rate of formation of ($C_{12}H_{18}$) (v_E) on the pressure of cyclohexadiene; see caption of Figure 1

Arrhenius plots of the rate constants k_X (in l mol^{-1} s^{-1}) are shown in Figure 4. Least-mean-squares treatment of these values gives equations (3)—(5). The quantities of

$$\log_{10} k_B = -(35{,}500 \pm 100)/4{\cdot}576T + (10{\cdot}13 \pm 0{\cdot}04) \quad (3)$$

$$\log_{10} k_C = -(36{,}400 \pm 1100)/4{\cdot}576T + (10{\cdot}25 \pm 0{\cdot}40) \quad (4)$$

$$\log_{10} k_E = -(35{,}600 \pm 1800)/4{\cdot}576T + (9{\cdot}52 \pm 0{\cdot}67) \quad (5)$$

H_2 and of the C_2 compounds formed (*ca.* 1/7 and 1/70 that of B, respectively) are too small to permit an accurate determination of the rate equations. The rate of formation of H_2 can however be represented approximately by equation (2) with $k_X = k_{H_2} = 0{\cdot}15k_B$, where k_B is given by equation (3).

DISCUSSION

Although the rates of formation of benzene, cyclohexene, $C_{12}H_{18}$, and hydrogen are all of the second order in cyclohexadiene, have similar temperature-dependences, and are not influenced by added propene, there is little doubt that the reactions are complex and of radical nature. Indeed the ratios $[H_2]:[B]$ and $[C]:[B]$ are 0·15 and 0·62 respectively and the formation of $C_{12}H_{18}$ † as a primary product indicates the participation of C_6H_9 radicals. Support for the hypothesis that the reactions are homogeneous is found in that no 'seasoning' of the reaction cell was needed to obtain reproducible results and that the results do not depend on S/V of the reaction vessel. We therefore suggest

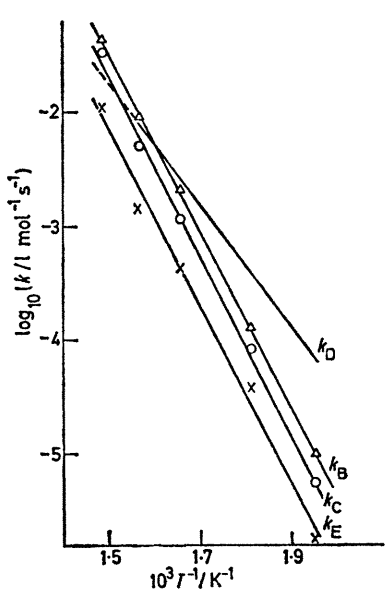

FIGURE 4 Arrhenius plots of the rate constants. The rate constant k_D for the second-order dimerization of cyclohexadiene [see ref. (2)] is given for comparison

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* For experiments in the presence of propene, one observes the formation of *endo*- and *exo*-5-methylbicyclo[2,2,2]oct-2-ene.[4]

† $C_{12}H_{18}$ is probably 2,2′-bicyclohexenyl, an important product of the radiolysis of cyclohexadiene and cyclohexene.[5,6]

[4] G. Debande and G. Huybrechts, in preparation

[5] B. R. Wakeford and G. R. Freeman, *J. Phys. Chem.*, 1964, **68**, 2635.

[6] B. R. Wakeford and G. R. Freeman, *J. Phys. Chem.*, 1964, **68**, 2992.

the non-chain, radical mechanism shown in reactions (6)—(11), where C_6H_7 is the cyclohexadienyl radical

$$C_6H_8 + C_6H_8 \xrightarrow{a} C_6H_7 + C_6H_9 \qquad k_a \qquad (6)$$

$$C_6H_7 \xrightarrow{b} C_6H_6 + H \qquad k_b \qquad (7)$$

$$H + C_6H_8 \xrightarrow{c} C_6H_9 \qquad k_c \qquad (8)$$

$$H + C_6H_8 \xrightarrow{d} C_6H_7 + H_2 \qquad k_d \qquad (9)$$

$$C_6H_9 + C_6H_9 \xrightarrow{e} C_6H_{10} + C_6H_8 \qquad k_e \qquad (10)$$

$$C_6H_9 + C_6H_9 \xrightarrow{f} C_{12}H_{18} \qquad k_f \qquad (11)$$

and C_6H_9 the cyclohex-2-enyl radical. Reaction (a) is the bimolecular disproportionation suggested by Benson and Shaw.[1]

Application of the steady-state treatment to the suggested mechanism, yields equations (12)—(15).

$$v_B = d[B]/dt = k_a(1 + k_d/k_c)[C_6H_8]^2 \qquad (12)$$

$$v_C = d[C]/dt = (k_ak_e/(k_e + k_f)\}[C_6H_8]^2 \qquad (13)$$

$$v_E = d[E]/dt = (k_ak_f/(k_e + k_f)\}[C_6H_8]^2 \qquad (14)$$

$$v_{H_2} = d[H_2]/dt = (k_ak_d/k_c)[C_6H_8]^2 \qquad (15)$$

These equations are of the same form as the experimental equations. Comparing the latter with equations (12)—(15), one obtains $k_B = k_a(1 + k_d/k_c)$, $k_C = k_ak_e/(k_e + k_f)$, $k_E = k_ak_f/(k_e + k_f)$, and $k_{H_2} = 0{\cdot}15k_B = k_ak_d/k_c$. As can be seen from equations (3)—(5), the temperature-dependences of the rate constants k_B, k_C, and k_E are the same within the given limits of standard error. We therefore suggest the values shown in equations (16)—(19). The limits of error are ±1 kcal

$$\log_{10} k_a(1 + k_d/k_c) = 35{,}500/4{\cdot}576T + 10{\cdot}13 \qquad (16)$$

$$\log_{10}k_ak_e/(k_e + k_f) = -35{,}500/4{\cdot}576T + 9{\cdot}92 \qquad (17)$$

$$\log_{10} k_ak_f/(k_e + k_f) = -35{,}500/4{\cdot}576T + 9{\cdot}48 \qquad (18)$$

$$\log_{10} k_ak_d/k_c = -35{,}500/4{\cdot}576T + 9{\cdot}31 \qquad (19)$$

mol^{-1} for the activation energies and ±0·4 logarithmic units for the pre-exponential factors. Combining equations (16), (19) (17), and (18), one obtains $\log_{10}k_a = -35{,}500/4{\cdot}576T + 10{\cdot}02$ and $\log_{10}k_a = -35{,}500/4{\cdot}576T + 10{\cdot}05$, respectively. These values are in close agreement so that we suggest equation (20).

$$\log_{10}k_a/\text{l mol}^{-1}\,\text{s}^{-1} = -(35{,}500 \pm 1000)/4{\cdot}576T + (10{\cdot}04 \pm 0{\cdot}40) \qquad (20)$$

If the reverse of reaction (a) has no activation energy, using the activation energy given in equation (20), $\Delta H^\circ_{f,298}(H) = 52{\cdot}1$,[7] $\Delta H^\circ_{f,298}(C_6H_8) = 25{\cdot}9$,[8] and $\Delta H^\circ_{f,298}(C_6H_{10}) = -1{\cdot}3$ kcal mol^{-1},[9] one calculates $D(C_6H_7\text{–}H) + D(C_6H_9\text{–}H) = 167 \pm 1$ kcal mol^{-1}. Comparing this sum of C–H bond energies with $2D(\text{cyclo-}C_6H_{11}\text{–}H) = 189 \pm 2$ kcal mol^{-1},* one obtains a value of 22 ± 3 kcal mol^{-1} for the sum of the stabilisation energies in the C_6H_7 and the C_6H_9 radicals. This value is comparable with a value of 25·2 ± 2 kcal mol^{-1} for twice the allyl stabilisation energy.[11] According to Benson [12] the stabilisation energy in the C_6H_7 radical could be *ca.* 9 kcal mol^{-1} greater than the allyl one. This would imply that the reverse of reaction (a) would have an activation energy of *ca.* 9 kcal mol^{-1}, as has been suggested.[1] Combining equations (19) and (20), one obtains $k_d/k_c = 0{\cdot}19$ which is comparable with a suggested value of 0·25.[1] From equations (17) and (18) one calculates $k_e/k_f = 2{\cdot}8$, indicating that the disproportionation of the C_6H_9 radicals is faster than their combination.

The kinetics observed here for the pyrolysis of cyclohexa-1,3-diene yields better evidence for the occurrence of initiation step (a) than that reported by Benson and Shaw [1] for which an accurate assessment of the reaction order was not possible ($0{\cdot}5 \leqslant n \leqslant 1{\cdot}5$).†

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* Estimated using $\Delta H^\circ_{f,298}$ (cyclo-$C_6H_{11}\cdot$) = 13 kcal mol^{-1}.[10]

† This could result from the fact that wall effects were important under their experimental conditions.

[7] JANAF Interim Thermodynamic Tables, Thermal Laboratory, Dow Chemical Company, Midland, Michigan, 1960—65.

[8] D. R. Stull, E. F. Westrum, jun., and G. C. Sinke, 'The Chemical Thermodynamics of Organic Compounds,' Wiley, New York, 1969, p. 674.

[9] Ref. 8, p. 347.

[10] Ref. 3, p. 204.

[11] Ref. 3, p. 86.

[12] S. W. Benson, personal communication: a value of *ca.* 22 kcal mol^{-1} for the stabilization energy in the $C_6H_7\cdot$ radical would be preferred to a value of 25 kcal mol^{-1} (D. G. L. James and R. D. Suart, *Trans. Faraday Soc.*, 1968, **64**, 2752).