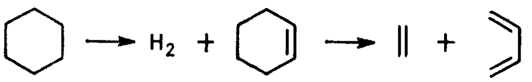
The Pyrolysis of Cyclic Hydrocarbons. Part 1. 1,4-Dimethylcyclohexane

By **Harold M. Gillespie, Brian G. Gowenlock,** and **Christopher A. F. Johnson,*** Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS

1,4-Dimethylcyclohexane has been pyrolysed in a continuous-flow stirred reactor at 767—835 K and pressures up to 9 Torr (1 200 Pa). The formation of the complex mixture of products is interpreted on the basis of a free-radical chain process, with chains of moderate length (<30). Arrhenius parameters for production of a number of products have been determined, and these are consistent with the proposed mechanism. Considerable radical isomerisation occurs, as shown by the large yields of, for example, butenes, which cannot be produced by direct decomposition of 1,4-dimethylcyclohexyl radicals. The pyrolysis is self-inhibiting, even at low conversion, and secondary reaction of cycloalkene products results in the formation of aromatics.

THE cracking of cycloalkanes, which are of widespread occurrence in some petroleum feedstocks, is of considerable importance in the production of butadiene and other intermediates in the petroleum industry. Although a number of studies of cycloalkane pyrolysis have been reported much data in the literature is concerned with empirical optimisation of yield of some specific product of the thermal cracking at high conversion. Product distributions and certain general features are documented, but kinetic data are lacking, and little is known about these processes at low conversion. With an increasing need for reliable modelling of hydrocarbon pyrolyses, an investigation of the thermal decomposition of cycloalkanes, particularly the mechanism during the initial stages of the reaction, seemed appropriate. We exclude from consideration cyclopropanes and cyclobutanes which decompose by molecular processes[1,2] and are in no way typical of higher cycloalkanes.



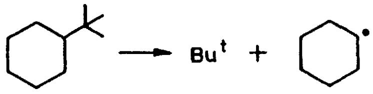
(1)

Considerable emphasis upon molecular processes such as (1), proposed in early studies,[3] has persisted throughout the literature. Cyclopentane itself gives hydrogen, ethene, and propene, with smaller amounts of C_1 through C_6 products.[4,5] Propene is the main alkene product from methylcyclopentane,[5,6] although at high conversion C_1 and C_2 products dominate.[6] McNesby and Gordon[7] in the pyrolysis of [$^2H_2$]cyclopentane and cyclopentane–[$^2H_6$]acetone mixtures, as part of a photochemical study, found ethene and propene in nearly equal amounts, a significant fraction of the propene having a free-radical precursor. Cyclohexane pyrolysis gives hydrogen, ethene, and butadiene, with smaller amounts of C_1 through C_7 products, including aromatics.[4,6] Ethene often exceeds butadiene by as much as three times.[8,9] [Compare reaction (1) above.] Pyrolysis of methylcyclohexane[10,11] yields a complex mixture of gaseous and liquid products. The yields of cyclohexenes pass through maxima at *ca.* 40% conversion while aromatics increase sharply at higher conversion. Schultze and Wassermann[12] report the following overall first-order rate constants determined from pressure measurements in static systems:

Cyclohexane: $\log(k/\mathrm{s}^{-1}) = 13.8 - 268\ \mathrm{kJ\ mol^{-1}}/2.3\,RT$
Methylcyclohexane: $\log(k/\mathrm{s}^{-1}) = 12.6 - 242\ \mathrm{kJ\ mol^{-1}}/2.3\,RT$
while Tanji[10] obtained for methylcyclohexane
$\log(k/\mathrm{s}^{-1}) = 12.16 - 230\ \mathrm{kJ\ mol^{-1}}/2.3\,RT$

The thermal stability of a number of hydrocarbons, including fourteen substituted cyclohexanes has been studied[13] in a high-pressure isoteniscope. The rate of decomposition is increased by increasing the number of ring substituents or the length of the side-chain, but is decreased with increasing branching of the side-chain (of constant carbon number). This latter conclusion is surprising when compared with acyclic alkane decomposition. Ritchie and Nixon[14] found the overall rate of decomposition to decrease in the order ethylcyclohexane > diethylcyclohexane > dimethylcyclohexane > methylcyclohexane, although conversions were taken to over 50%.

Tsang[15] has decomposed t-butylcyclohexane in a shock tube. This is mechanistically simpler than conventional pyrolysis and must be in large part a study of the decomposition and isomerization of the cyclohexyl radical formed in the initial step (2). The Arrhenius parameters obtained for (2) are



(2)

$$\log(k/\mathrm{s}^{-1}) = 16.3 - 310\ \mathrm{kJ\ mol^{-1}}/2.3\,RT$$

In general, none of the conventional pyrolyses reported refers to the initial stages of reaction at, say, less than 1% conversion, while complicating effects of carbonaceous surfaces and traces of oxygen are present in many of these studies. The wide range of products, the accelerating effect of radical-producing additives,[10] and some of the values of overall activation energy (around 240 kJ $\mathrm{mol^{-1}}$) suggest that the pyrolyses of both substituted and unsubstituted cycloalkanes involve radical chains.

We have undertaken a series of kinetic studies on the gas-phase decomposition of various cycloalkanes at low conversion using a continuous-flow stirred-reactor. We report here the pyrolysis of 1,4-dimethylcyclohexane.

EXPERIMENTAL

Stirred-flow reactors were originally used for liquid-phase studies but more recently a variety of designs have been used in gas-kinetic studies.[16-18] The continuous-flow stirred reactor (CFSR) offers certain advantages over the tubular-flow reactor more commonly used. In tubular reactors a time-independent state is attained, but this varies along the direction of flow, and sometimes radially as well. The CFSR combines the advantage of uniform composition found in static reactors with the time invariance of flow reactors. Furthermore, the stirring ensures a uniform temperature. Provided certain precautions are taken, the measured composition of the outflowing gases from the CFSR gives the steady-state composition at any point within the reactor. The flow-rate must be constant, with small outlet volume and rapid cooling, so that negligible after-reaction occurs. The mixing time must be short compared to the mean residence time in the reactor. A number of workers have studied reactions with well established rate constants in CFSRs to test the validity of the assumptions made. In particular Mulcahy and Williams [16] determined the rate constant for di-t-butyl peroxide pyrolysis in a reactor of the type used in this work and found good agreement with literature data. In this laboratory [19] cyclopentene pyrolysis has been used as a test reaction, yielding good agreement with the literature.[20]

The spherical CFSRs were constructed in silica to a design of Mulcahy and Williams.[16] In this reactor, substrate vapour enters through a small perforated sphere near the centre, giving mixing by forced convection while products flow out tangentially. Three vessels were used: two were of *ca.* 310 cm^3 volume and S/V ratio about 0.72 cm^{-1}, while the third reactor was packed evenly with ' Vitreosil type A ' silica wool, increasing the S/V ratio to *ca.* 1 000 cm^{-1}. (The surface area was estimated by adsorption of CO_2 at 195 K using the BET isotherm.) The reactor temperature was maintained to better than $\pm 1/2$ K for the duration of an experiment. The pressure and flow rate of substrate were controlled by (i) thermostatting the substrate vessel, (ii) adjustment of needle valve between substrate vessel and reactor, and (iii) using one of a number of interchangeable capillaries of varying length and bore inserted between reactor and analytical section. The pressure immediately after the reactor was measured by a transducer and flow rate of substrate was determined by weight loss. All taps in the flow and analytical sections of the system were grease free, and the apparatus was evacuated to better than 10^{-5} Torr (1.3×10^{-3} Pa) by means of a two-stage mercury diffusion pump and rotary oil pump.

The analytical section consisted of a series of flow-through traps, which could be isolated in pairs and opened to small take-off traps. Typical trapping temperatures were 250, 177, 77, and 77 K. This section also contained a small vessel of n-nonane, used as gas chromatographic internal standard. The product fractions were condensed at 77 K in the narrow take-off traps and flame sealed for subsequent g.l.c. analysis. After the product traps a single-stage mercury diffusion pump took uncondensed gases into a gas-burette and Töpler pump. At the end of a run the total amount of uncondensed gas was measured, and the Töpler pump used to remove one or more samples of the gas in small sealed-off sample tubes by the technique previously described.[21]

Hydrocarbon analyses were carried out by gas chromatography with flame ionisation detection, while hydrogen was analysed using a Katharometer. The following columns were employed. (i) 150 ft × 0.01 in i.d.s.s. open tubular column, wall coated with squalane. (ii) 50 ft × 0.02 in i.d.s.s. squalane-support coated open tubular (SCOT) column. (iii) 12 ft × 1/8 in o.d.s.s. column containing 18.5% of bis-2-ethylhexyl sebacate on AW Chromosorb P (100—120 mesh) in series with 12 ft × 1/8 in o.d.s.s. column containing 5.5% $AgNO_3$ + 4.5% triethylene glycol on AW Chromosorb P (100—120 mesh). (iv) 4 ft × 1/4 in o.d. copper column containing molecular sieve 5A (60—80 mesh). (v) 6 ft × 1/4 in o.d. copper column containing 10% dimethylsulpholan on Chromosorb P (60—80 mesh). Products were analysed in three fractions: (a) uncondensed gas, (b) C_2—C_5 products, and (c) liquid products. The trapping system did not give complete separation of these fractions, C_2 hydrocarbons were found in (a) and C_4/C_5 products were also found in (c). Fraction (a) was analysed for hydrogen content on column (iv), hydrocarbon content being determined on column (iii). Most fraction (b) analyses used column (iii) at room temperature, which gave complete separation of all C_1—C_4 products. Liquid products [fraction (c)] were analysed mainly on column (ii). Column (i) gave higher resolution, but sample size capacity was limited and minor products could not be measured. Identities of products were confirmed by retention time comparison with authentic samples, injecting product samples enriched with very small amounts of pure component, and by determination of temperature coefficient of the retention index, which is specific for groups of hydrocarbons.

Gaseous and liquid hydrocarbons for g.c. calibration were obtained from commercial sources. We are grateful to B.P. Chemicals International Ltd. for the gift of some hydrocarbons. n-Nonane was Fluka grade puriss, 99.73% by weight after several distillations. 1,4-Dimethylcyclohexane (Fluka puriss) was subjected to trap-to-trap distillation until a ' blank ' sample was better than 99.9% by weight by g.l.c. Due to the difference in vapour pressure of the two isomers, the composition varied slightly over the duration of the experiments, but remained within *ca.* 1% of a mixture consisting of 52% *trans* and 48% *cis*. (A limited number of experiments have been carried out with the pure *trans*-form, we could detect no difference in rate of product distribution between this and the *trans*/*cis* mixture.)

RESULTS

Pyrolyses were carried out at temperatures of 767—835 K, pressures of 2—9 Torr (260—1 200 Pa), mean residence times of 0.25—37 s, and extents of decomposition of 0.01—5.5%. The raw experimental data are too extensive for inclusion in full. We list the products (μ mol/mol reactant) determined in a run at 793 K, 4.03 Torr, 1.59 s contact time, and 0.11% decomposition. The main products are hydrogen (600), methane (540), ethane (51), ethene (149), propene (209), isobutene (176), buta-1,3-diene (150), isoprene (95), 4-methylcyclohexene (316), and 1,4-dimethylcyclohexene (243). Other products identified included propane (3.8), isobutane (4.2), but-1-ene (67), *trans*-but-2-ene (35), *cis*-but-2-ene (20), *trans*-penta-1,3-

diene (27), *cis*-penta-1,3-diene (13), 1-methylcyclohexene (18), toluene (2), pentenes, mainly 2-methylbut-1-ene (28), total C_6 (130), other C_7 (24). In higher conversion pyrolyses small amounts of xylenes and other C_8/C_9 products were detected.

From the chromatographic data and reaction conditions product yields, rates of formation, percentage decomposition, and rate constants were calculated. A meaningful carbon balance cannot be obtained at low conversion: even if the unchanged feed is determined to g.c. with an error of 1%, this cannot be used to compare substrate decomposed with total products formed when the total decomposition is much less than 1%. The total H : C ratio in the products was always close to 2.0, the H : C ratio of the feed.

Rate constants for formation of some of the products were derived for assumed orders of 1.0 or 1.5 (see Discussion section). The Arrhenius parameters obtained are listed in the Table. The error limits of these parameters include contributions due to variation in rate constant with contact time caused by onset of self-inhibition (see below) and to the existence of an apparent induction period at very short contact times, especially at the lower pyrolysis temperature. Figure 1 demonstrates this effect for the formation of 4-methylcyclohexene at 793 and 831 K. The reason for this behaviour is uncertain. A purely physical cause, *e.g.* mixing or streaming, seems unlikely due to the temperature dependence. An alternative explanation may be in the reaction kinetics, which are considered later.

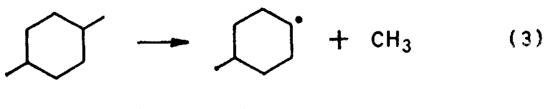
Derived Arrhenius parameters

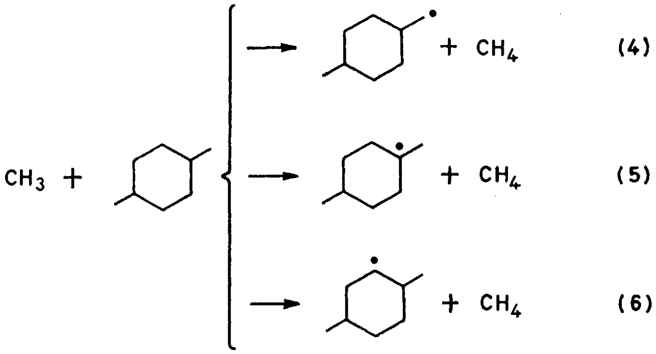
1st order	$\log_{10}A$/S^{-1}	E/kJ mol^{-1}
Ethane	13.8 ± 2.6	280.3 ± 40.2
1.5 order	$\log_{10}A$/ l$^{1/2}$ mol$^{-1/2}$ s^{-1}	E/kJ mol^{-1}
$H_2 + CH_4$	17.4 ± 1.1	281.6 ± 20.1
4-Methylcyclohexene	10.4 ± 1.2	183.3 ± 18.8
1-Methylcyclohexene	12.4 ± 0.9	231.8 ± 14.2
1,4-Dimethylcyclohexene	12.4 ± 1.7	218.8 ± 25.6
Isoprene	13.2 ± 3.0	233.5 ± 46.0
Propane	12.0 ± 2.0	239.3 ± 37.7
Ethene	15.6 ± 1.9	267.4 ± 29.7
Propene	16.7 ± 2.5	281.2 ± 37.7
Isobutane	16.9 ± 3.7	308.8 ± 56.1
Total C_6	13.0 ± 1.8	227.6 ± 27.2

The data obtained in the packed reactor show the most important effect of greatly increased *S*/*V* ratio to be a reduction in the rate of decomposition by a factor of about two, while the product distribution is little altered. There was some irreproducibility for the first few runs in this reactor and ' carbon conditioning ' of the wool packing may have been occurring. The fractional yield of toluene and other aromatics was increased in the packed reactor due presumably to some surface-catalysed dehydrogenation.

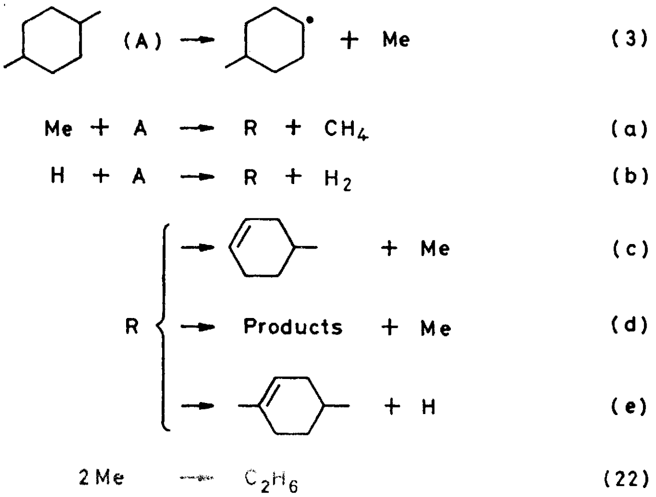
DISCUSSION

The pyrolyses of acyclic alkanes occur by free-radical chain processes. The wide range of products, effect of surface, and activation energies obtained in the present studies suggest similar chain processes are involved and there is no *a priori* reason for supposing molecular reactions to occur. As a basis for discussion we assume that initiation occurs by fission of a methyl radical from the ring (3), and the radical chains are propagated as shown in (4)—(23) below. There will be analogous reactions (4′), (5′), and (6′) involving abstraction by H atoms, and there may also be abstraction by other alkyl or alkenyl radicals. At 800 K the substituted cyclohexyl radicals will decompose, leading to a range of olefinic products and smaller radicals. Some possible reactions have been omitted from this scheme because the products were not detected or were produced in only trace amounts. The scheme predicts the formation of the following products: hydrogen, methane, ethane, ethene, propene, buta-1,3-diene, isoprene, hexadienes, 1,4-dimethylcyclohexene, 4-methylcyclohexene, and perhaps small amounts of radical abstraction and combination products. Some products found are not explained by this scheme, notably isobutene, but-1-ene, and but-2-ene. This aspect of the reaction is discussed below.





Even for the simplified mechanism (3)—(23), steady-state analysis gives complex expressions for the rate of formation of products not reducible to the form rate = $k[C_8H_{16}]^n$. It is perhaps instructive to consider an even simpler scheme in which average values for abstraction and radical decomposition rate constants are used.



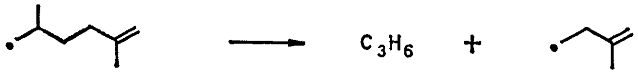

(7)

(8)

(9)

(10)

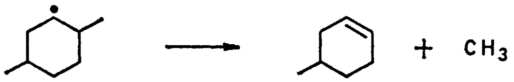

(11)



(12)

(13)

(14)

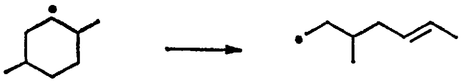


(15)

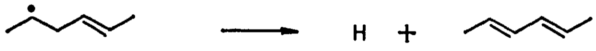

(16)

(17)

(18)


(19)

(20)

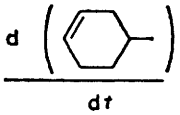


(21)

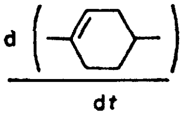
$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad (22)$$

$$H \longrightarrow \tfrac{1}{2}\,H_2 \text{ (surface)} \qquad (23)$$

When (22) is assumed to be the only termination step, the following expressions may be derived:



$$= \frac{k_a k_c}{(k_c + k_d)} \left[\frac{k_3}{2k_{22}}\right]^{1/2} [A]^{3/2}$$



$$= \frac{k_a k_e}{k_c + k_d} \left[\frac{k_3}{2k_{22}}\right]^{1/2} [A]^{3/2}$$

$$\frac{d(CH_4 + H_2)}{dt} = \frac{k_a(k_c + k_d + k_e}{k_c + k_d} \left[\frac{k_3}{2k_{22}}\right]^{1/2} [A]^{3/2}$$

$$\frac{d(C_2H_6)}{dt} = \tfrac{1}{2} k_3 [A]$$

Setting $E_{22} = 0$, $E_3 \simeq 345$ kJ mol^{-1} and $E_a \simeq 50$ kJ mol^{-1} [22] the activation energies for product formation would be *ca.* 220 kJ mol^{-1}. When 3/2 order kinetics are assumed, the activation energies for formation of a number of products lie within the range 180—240 kJ mol^{-1}, values consistent with a chain mechanism with chains of moderate length. Similarly pre-exponential factors of 10^{12}—10^{13} l$^{1/2}$ mol$^{-1/2}$ s^{-1} are not inconsistent with the above mechanism.

A first-order treatment of the data for ethane production leads to an activation energy lower than expected, while data for methane and hydrogen production gives a high value. Both these trends would be expected if (23) contributes to termination, reactions forming H atoms usually having activation energies higher than those producing methyl.[23] As soon as (23) is taken into account, the kinetic analysis becomes complex even for this symbolic scheme.

$$H \xrightarrow{\text{wall}} \tfrac{1}{2}H_2 \qquad (23)$$

In the mechanism proposed the chain carriers are methyl and H atom. By assuming that $(CH_4 + H_2)$ gives a measure of total propagation and ethane is a measure of termination we obtain for the kinetic chain length an upper limit of *ca.* 30 (averaged over all runs). In reality some hydrogen will be produced in (23) although the fraction may be small as the gas-phase reactions of the H atom are *ca.* 100 times faster at 800 K than those of the methyl radical. Even if as much as 10% of the hydrogen arises from (23) the chain length will only fall by *ca.* two. Using literature rate data for hydrogen abstraction by methyl, estimated half-life times for methyl radicals at 4 Torr reactant pressure are 9×10^{-3}—4×10^{-2} s at 760—830 K. Each propagation cycle may include three unimolecular radical decompositions with half-life times at 800 K > 10^{-3} s. It is, therefore, conceivable that the kinetic chain lifetime may be comparable with the shorter contact times used at the lower end of the temperature range, causing some truncation of the chains. This would be seen as a drop in reaction rate at short contact times at the lower temperatures (*cf.* Figures 1 and 2).

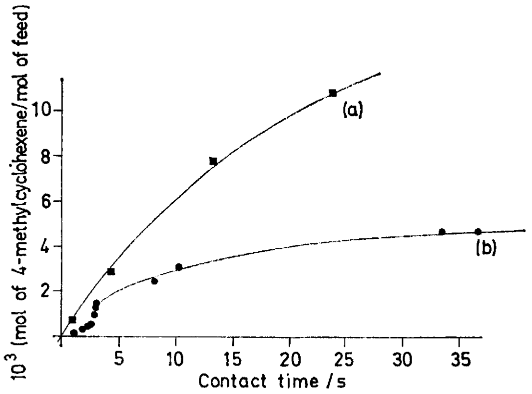


FIGURE 1 Progress curves for production of 4-methylcyclohexene: ● pyrolysis at 793 K and ■ pyrolysis at 831 K

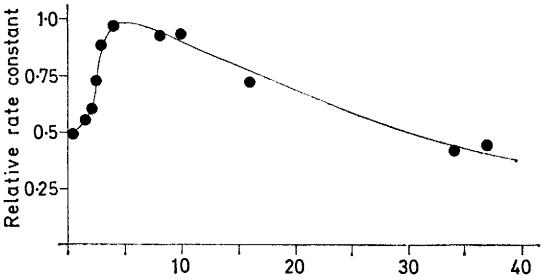
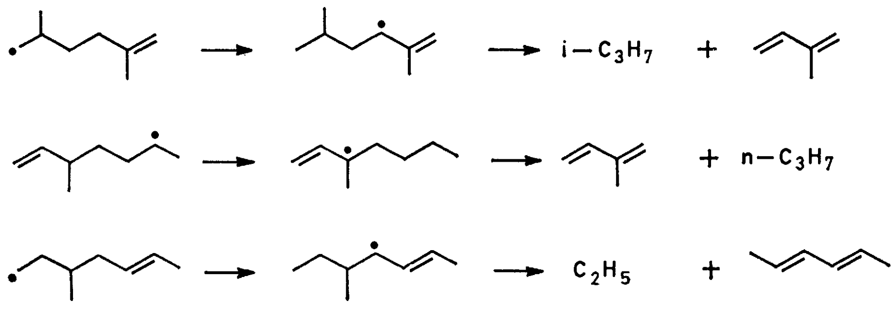


FIGURE 2 Variation of calculated rate constants with increasing contact time. Data for each of hydrogen, methane, ethene, propene and 4-methylcyclohexene are normalised at $k_{max.} = 1.0$, and then averaged at each contact time to give each point

Radical Isomerisation.—The scheme proposed [(3)—(23)] cannot account for some important products, notably butenes, without the occurrence of radical

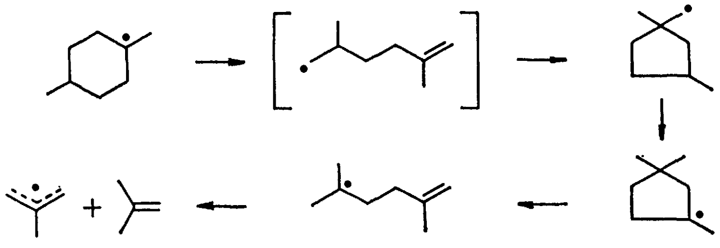


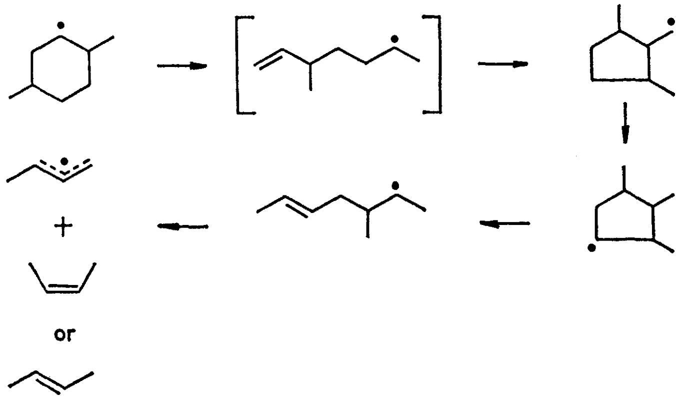
(24)

(25)

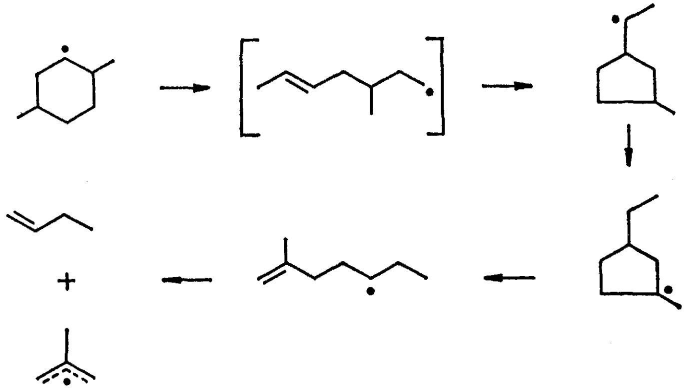
(26)

isomerisation. 1,5- and 1,4-H atom shifts in acyclic C_8 radicals may be considered. We assume those processes in which an allylic H atom is abstracted will be the more probable, and (24)—(26) are typical examples. The introduction of ethyl and propyl radicals into the system, albeit at low levels, will result in small quantities of propane, isobutane, and n-butane, but isomerisations of this type will not lead to significant amounts of unsaturated C_4 products. The alternative possibility that 1,2-H atom shifts lead to butene formation would provide a simple explanation but in view of the compelling evidence against these shifts in other hydrocarbon systems, we must reject such reactions.


(27)



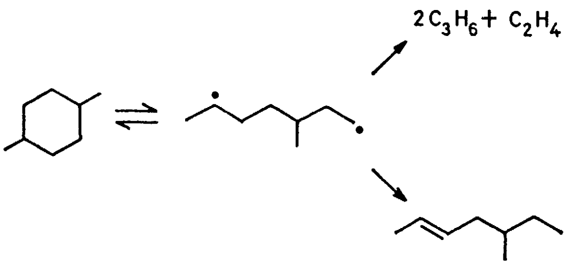
(28)



(29)

The possibility of isomerisation *via* radical derivatives of cyclopentane remains to be considered. The cyclopentylmethyl radical has been observed[24,25] as a major product of the cyclohexyl radical in thermal systems, while the addition of H atoms to cyclohexene leads to methylcyclopentane in significant yields.[26] In these cases the isomerisation has been assumed to occur *via* a tight transition state, although a ring open-ring close sequence cannot be excluded. Methyl- and methylenecyclopentane have also been reported[27] in the photolysis of acetone–cyclohexane mixtures, and this type of isomerisation has been invoked to explain propene production from the cyclohexyl radical.[15] Processes (27)—(29) are among those likely in the present system. With the inclusion of (27)—(29) in the scheme the production of unsaturated C_4 compounds is explained without proposing unusual or speculative elementary reactions.

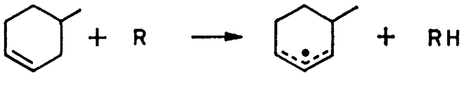
Biradical Mechanism.—We have assumed that cleavage of the methyl group from the ring is the only initiation reaction which needs to be considered. Formation of a biradical by C–C bond fission in the ring may well occur but is unlikely to propagate chains at any appreciable rate. If the radical chains are not long, this pathway could contribute a few percent to the overall decomposition. Since no unique products are formed by breakdown of the biradical there is no means of determining the importance of this pathway. The isomerisation product 5-methylhept-2-ene was not identified, but, from g.c. evidence, could be of only very minor importance if formed. The propene and ethene produced by breakdown of the biradical are, of course, indistinguishable from propene and ethene produced by radical processes. The calculated activation energies for production of propene and ethene are significantly higher than for other presumed propagation products, and this may be indirect evidence for the occurrence of a small amount of biradical participation in the overall decomposition. We postpone further consideration of this aspect of the reaction mechanism to a later publication.



(30)

Self-inhibition.—The pyrolysis is clearly self-inhibited, as can be seen in the fall-off of rate of product formation with increasing reaction (Figure 2). Two types of inhibition reaction are likely, *viz.* addition of H or CH_3 to unsaturated species, and abstraction of H atoms β to the double bond to form allylic radicals. The second type of reaction is responsible for the pronounced self-inhibition in neopentane pyrolysis.[28] Since we find isobutene as an important product, similar inhibition presumably occurs [reaction (31)]. Halstead *et al.*[28] consider the butenyl radicals to disappear by combination processes. In our work the self-combination product 2,5-dimethylhexa-1,5-diene was not positively identified, but appreciable amounts of 2-methylbut-1-ene were found (from combination with methyl). The yield of this product cannot be taken as a measure of self-inhibition, since the same butenyl radical is a product of steps (27) and (29) above, although we note its greater importance at higher conversion. Self-inhibition due to propene should be unimportant, since n-butane pyrolysis is essentially free from this complication despite the propene formed.[29] But-1-ene might participate to some extent, but it is produced in smaller amounts than isobutene. The other possible inhibitors are the cyclohexenes, indeed cyclohexene itself has been used as an inhibitor on numerous occasions.[30] Reactions such as (32) will almost certainly occur. During the course of this work, we have obtained some data on the pyrolysis of 4-methylcyclohexene, the decomposition being partly unimolecular, partly radical chain. Thus 4-methylcyclohexene will cause self-inhibition only to the extent that the radical-chain pyrolysis of 4-methylcyclohexene is slower than that of 1,4-dimethylcyclohexane; our data suggest that it is slower.[31]

(31)



(32)

The possibilities for H atom (or CH_3) addition are numerous. Some reactions which should be particularly favoured by both a high rate constant and high alkene or diene concentration are (33)—(37)

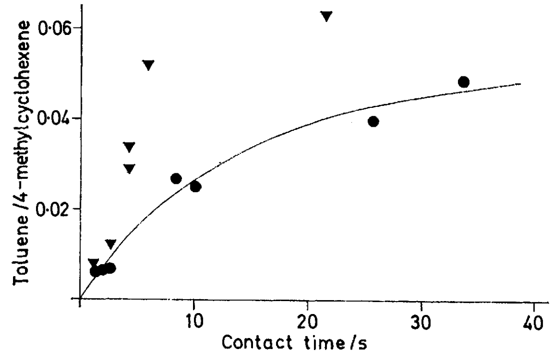
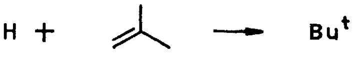
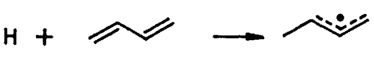


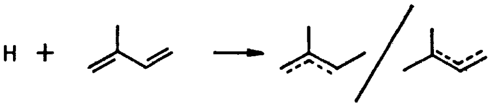
FIGURE 3 Variation of toluene/4-methylcyclohexene with contact time during pyrolysis at 793 K and 4 Torr: ● unpacked reactor and ▼ packed reactor



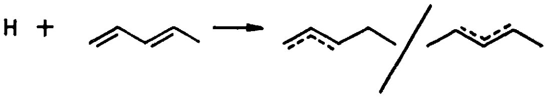
(33)



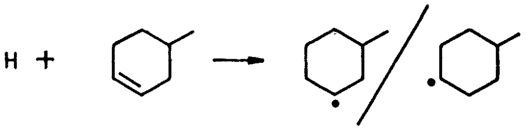
(34)



(35)



(36)

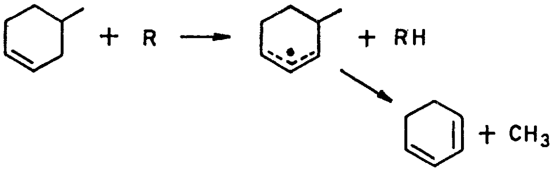


(37)

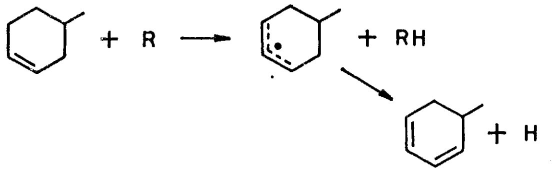
Aromatic Formation.—Even at low conversion some toluene is formed, and we suggest this arises from secondary decomposition of the substituted cyclohexenes. Figure 3 shows the rise in the yield of toluene relative to that of 4-methylcyclohexene with increasing contact time, the shape of this curve suggesting that toluene production is entirely secondary in nature. An estimated rate constant for the overall process (38) at 793 K is close to the rate constant determined for the

(38)

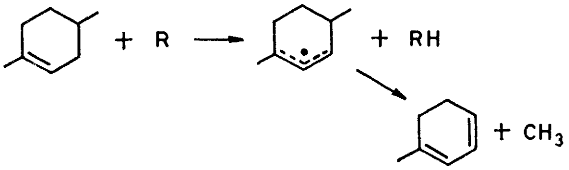
same process in the pyrolysis of 4-methylcyclohexene.[31] Other unsaturated products detected are cyclohexadienes, benzene, and xylene. All these may result from radical attack on the cyclohexenes, reactions (39)—



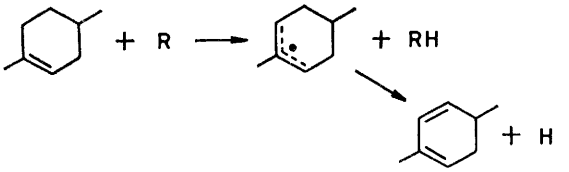
(39)



(40)



(41)



(42)

(42). Aromatics would be produced either by further radical attack on the dienes, or by the direct molecular elimination of hydrogen.[32] These dehydrogenation processes may be in part surface catalysed, as evidenced by the increase in aromatics in the packed reactor (*cf.* Figure 3).

The authors thank The British Petroleum Company for the award of a studentship (to H. M. G.) and an equipment grant, and Mr. K. R. Wagstaff of B.P. Chemicals International Limited, Grangemouth, for much helpful advice and discussion.

[8/871 *Received*, 11*th May*, 1978]

REFERENCES

[1] K. J. Laidler and L. F. Loucks, in ' Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1971.

[2] H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, 1961, **83**, 3935.

[3] D. T. Jones, *J. Chem. Soc.*, 1915, **107**, 1582.

[4] F. E. Frey, *Ind. and Eng. Chem.*, 1934, **26**, 198.

[5] B. A. Kazanskii and A. F. Plote, *Ber.*, 1934, **67**, 1023.

[6] J. Coull, L. Berg, G. L. Sumner, and C. W. Montgomery, *Ind. and Eng. Chem.*, 1945, **37**, 352.

[7] J. R. McNesby and A. S. Gordon, *J. Amer. Chem. Soc.*, 1957, **79**, 852, 4593.

[8] S. D. Mekhtiev, A. F. Aliev, Yu. G. Kambarov, and V. V. Sharov, *Azerb. Khim. Zhur.*, 1959, 3.

[9] S. D. Mekhtiev, Yu. G. Kambarov, F. A. Iseeva, and T. A. Pashaev, *Azerb. Neft. Khoz.*, 1967, **46**, 34.

[10] H. Tanji, M. Uchiyama, and H. Tokuhisa, *Kogyo Kagaku Zasshi*, 1966, **69**, 1154.

[11] S. D. Mekhtiev, Yu. G. Kambarov, and A. F. Aliev, *Doklady Akad. Nauk Azerb.*, 1959, **15**, 125.

[12] G. R. Schultze and G. Wassermann, *Z. Electrochem.*, 1941, **47**, 774.

[13] M. A. Fabuss, A. S. Borsanyi, B. M. Fabuss, and J. O. Smith, *J. Chem. Eng. Data*, 1963, **8**, 64.

[14] A. W. Ritchie and A. C. Nixon, *Amer. Chem. Soc., Div. Fuel Chem., Reprints*, 1966, **10**, C–100.

[15] Wing Tsang, *J. Phys. Chem.*, 1972, **76**, 143.

[16] M. F. R. Mulcahy and D. J. Williams, *Austral. J. Chem.*, 1961, **14**, 534.

[17] J. M. Sullivan, A. E. Axworthy, and T. J. Houser, *J. Phys. Chem.*, 1970, **74**, 2611.

[18] J. de Graaf and H. Kwart, *J. Phys. Chem.*, 1963, **67**, 1458.

[19] C. A. F. Johnson, P. John, and A. J. Al-Kanani, unpublished results.

[20] D. A. Knecht, *J. Amer. Chem. Soc.*, 1973, **95**, 7933.

[21] A. U. Chaudhry and B. G. Gowenlock, *J. Organometallic Chem.*, 1969, **16**, 221.

[22] S. W. Benson, ' Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters,' Wiley, New York, 1968.

[23] H. M. Frey and R. Walsh, *Chem. Rev.*, 1969, **69**, 103.

[24] A. S. Gordon, *Pure Appl. Chem.*, 1962, **5**, 441.

[25] R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Amer. Chem. Soc.*, 1963, **85**, 3483.

[26] S. E. Stein and B. S. Rabinovitch, *J. Phys. Chem.*, 1975, **79**, 191.

[27] A. S. Gordon and S. R. Smith, *J. Phys. Chem.*, 1962, **66**, 521.

[28] M. P. Halstead, R. S. Konar, D. A. Leathard, R. M. Marshall, and J. H. Purnell, *Proc. Roy. Soc.*, 1969, **A310**, 525.

[29] D. A. Leathard and J. H. Purnell, *Ann. Rev. Phys. Chem.*, 1970, **21**, 197.

[30] B. G. Gowenlock, *Progr. Reaction Kinetics*, 1966, **3**, 171.

[31] H. M. Gillespie, B. G. Gowenlock, and C. A. F. Johnson, unpublished data.

[32] S. W. Benson and R. Shaw, *Trans. Faraday Soc.*, 1967, **63**, 985.