The Kinetics of the Thermal Gas Phase Reactions of Methylspiro[2,2]-pentane at Low Pressure

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A study of the thermal unimolecular reactions of methylspiro[2,2]pentane has been carried out at three temperatures in the range 347·6 to 387·1 °C and at pressures between 3·8 and 0·004 Torr.† As the pressure is reduced decomposition products, allene, ethylene, propene, and buta-1,2-diene, are formed in increasing amounts at the expense of the isomerization products ethylidenecyclobutane, 2-methyl(methylene)cyclobutane, and 3-methyl-(methylene)cyclobutane. A similar increase in the proportion of 2-ethylbuta-1,3-diene and 2-methylpenta-1,4-diene relative to the methylenecyclobutanes is also observed. Calculations using the RRKM theory of unimolecular reactions are carried out in an attempt to confirm the detailed reaction mechanism.

EXPERIMENTAL

The apparatus used was a ' static ' Pyrex vacuum system similar to that described previously.[1] All runs were performed in a 680 cm^3 Pyrex reaction vessel ' aged ' by pyrolysis of 10 Torr light petroleum at 450 °C. After four days, reproducible results were always obtained. The portion of the vacuum line involved in handling pyrolysed material utilised mercury cut-off valves exclusively. The chromatograph inlet was linked to the sampling system on the vacuum line by Teflon diaphragm valves heated to approximately 70 °C. A desired pressure of methylspiropentane was expanded into the reaction vessel and after an equilibration period of 60 s the pressure in the vessel was read on one of two calibrated McLeod gauges. The reaction vessel was then isolated by a mercury cut-off valve. The unused reactant trapped in the McLeod gauges was retained for further use as reactant. The gas trapped in the gauge was analysed occasionally to ensure that it was free from contamination by products from the pyrolysis that may have diffused back from the reaction vessel during the equilibration period.

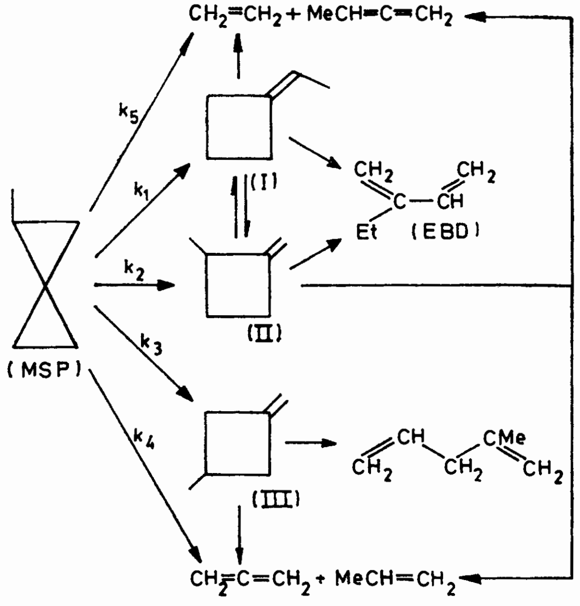
At the desired reaction time a sample was removed from the reaction vessel by sharing with an evacuated 1-l bulb. A Toepler pump was used to transfer the sample into the sample loop of the gas chromatograph, the number of Toepler cycles depending on the pressure of reactant and products in the vessel.

The sample was analysed as described previously [1] but a small portion was retained for further analysis on a 2 m × $\frac{1}{4}$ in o.d. stainless-steel column packed with 20% diisodecyl phthalate on Chromosorb P support, maintained at 40°. This provided a partial check on the main analysis and supplied accurate data on the formation of 2-ethylbuta-1,3-diene.[2]

Product identification and preparation of materials have been described previously.[1,2]

RESULTS

The investigation of the thermal isomerization of methylspiro[2,2]pentane (MSP) reported earlier [1] showed that the reaction had the features of a true unimolecular process. It was expected therefore that at sufficiently low pressures the first-order rate constant would diminish and become pressure dependent. Initial investigations at 368·4 °C showed this to be the case. Fall-off in the rate became observable below 2 Torr and the first-order rate constant had decreased to *ca.* 60% of its high pressure value at 0·02 Torr. The same products detected in the earlier work were found in this study and no additional products were discovered. Scheme 1 summarises the reaction scheme proposed previously.[1] Between 25 and 30 runs at each temperature (*i.e.* 347·6, 368·4, and 387·1 °C) were carried out at pressures ranging from 3·8 Torr down to 0·004 Torr. The first series of runs at each temperature were conducted at fixed pressures. Readings were taken at several reaction times at pressures close to 0·4, 0·1, and 0·02 Torr in order to study the variations of product distribution with time. Product distributions were studied up to 70% conversion in this way. Plots of log (% MSP) against time at each of the three pressure regions were linear. The remainder of the runs were carried out at varying pressures and generally not taken above 40% conversion, except for pressures below 0·02 Torr where higher conversions were necessary to produce sufficient amounts of products for good analysis. The high-pressure limiting value of the first-order rate constant (k_∞) was obtained by extrapolating a plot of $1/k_T$ against 1/pressure, where k_T is the overall first-order rate constant representing loss of methylspiropentane at a particular pressure, making use of the curve shape predicted from RRKM calculations described later in this paper. Using these values of k_∞ at the three



SCHEME 1

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† 1 Torr = 133 N m^{-2}.

[1] M. C. Flowers and A. R. Gibbons, *J. Chem. Soc.* (*B*), 1971, 612.

[2] M. C. Flowers and A. R. Gibbons, *J. Chem. Soc.* (*B*), 1971, 362.

temperatures, the Arrhenius expression was calculated by the method of least squares to be $k_\infty/\text{s}^{-1} = 10^{14{\cdot}88} \exp(-53{,}723/1{\cdot}987T)$. This compares very favourably with the expression obtained from the high-pressure study *i.e.* $k_\infty/\text{s}^{-1} = 10^{14{\cdot}88 \mp 0{\cdot}15} \exp(-53{,}816 \mp 420/1{\cdot}987T)$.

Table 1 illustrates the effect of pressure on the product distribution. Decomposition reactions and the formation of 2-methylpenta-1,4-diene (MPD) and 2-ethylbuta-1,3-diene (EBD) became increasingly important as the pressure was reduced. Using the results obtained from the time studies in the 0·02, 0·1, and 0·4 Torr pressure regions, graphs of percentage of individual products against percentage decomposition of methylspiropentane were plotted for each pressure region and temperature (product distribution plots). The results for each temperature were similar and a typical set is illustrated in Figures 1 and 2. Several features distinguish these results from the product distribution plots obtained in the high pressure study.

TABLE 1

Typical product distributions at several pressures

	Product yield at 40% reaction as a percentage of total products				
Pressure (Torr)	10	0·4	0·1	0·02	0·005
Product					
(I) + (II) + (III)	91	78	59	40	30
Olefin/allene	6	16	28	43	45
MPD	3	6	10	13	15
EBD	0·1	1	3	4	9

At 10 Torr 3-methyl(methylene)cyclobutane (III) made up *ca.* 33% of the total methylenecyclobutane products. The yield of methylenecyclobutanes decreased below 3 Torr but (III) showed a much more rapid decline than ethylidenecyclobutane (I) and 2-methyl(methylene)cyclobutane (II). At 0·02 Torr it constituted only *ca.* 16% of the total methylenecyclobutane products. The curvature in the product distribution plot for (III) decreased as the pressure was reduced and below 0·1 Torr the plot became linear. The behaviour of the MPD plot helps to explain this. At 0·4 Torr the curvature of the MPD plot is greatly reduced and no longer looks like the characteristic curve for a secondary product as it did at high pressure (*cf.* Figure 2, and Figure 2 of ref. 1). At 0·1 Torr the curvature of the MPD plot was very small and at 0·02 Torr it had disappeared completely indicating that it is now apparently a primary reaction product and that none is coming *via* (III).

EBD exhibited similar behaviour. Below 0·1 Torr its formation was mainly by a primary reaction and the small curvature at 0·4 Torr is indicative of minor secondary contributions from (I) and (II). The product distribution plots for (I) + (II) were straight lines at all pressures as their secondary decomposition was negligible.

The decomposition products gave linear product distribution plots at all pressures indicating no secondary decomposition processes were contributing to their formation. However these products also showed a change in their behaviour compared to that at high pressures. The ratio of (propene + allene) to (ethene + methylallene) decreased from its high-pressure value of approximately 1·6 to about half that value at 0·02 Torr. At 0·1 Torr their rates of formation were about the same.

It was from the evidence of the above plots that the individual rate constants for isomerization and decomposition were calculated at each pressure. This was carried out in the following manner.

The product distribution plots for decomposition products were linear at all pressures and hence k_d (*i.e.* k_4 or k_5) could be calculated from the relationship $\frac{1}{2}$(olefin + allene)/(total products) = k_d/k_T. Similarly $k_1 + k_2$ could be calculated

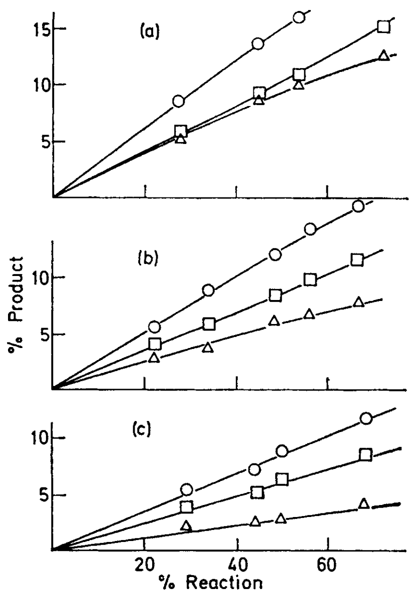


FIGURE 1 Product distribution plots for ethylidenecyclobutane, 2-methyl(methylene)cyclobutane, and 3-methyl(methylene)cyclobutane at 387·1 °C. □ = Ethylidenecyclobutane (I); ○ = 2-methyl(methylene)cyclobutane (II); △ = 3-methyl(methylene)cyclobutane. (a) 0·41—0·48 Torr; (b) 0·084—0·120 Torr; (c) 0·022—0·032 Torr

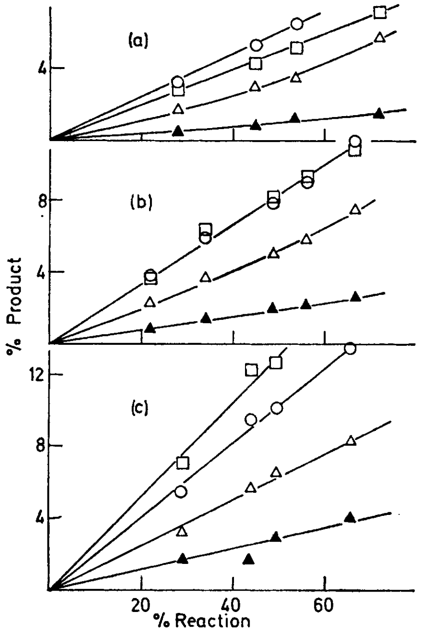


FIGURE 2 Product distribution plots for 2-methylpenta-1,4-diene, 2-ethylbuta-1,3-diene, allene, and buta-1,2-diene at 387·1 °C. △ = 2-Methylpenta-1,4-diene (MPD); ▲ = 2-ethylbuta-1,3-diene (EBD); □ = (buta-1,2-diene + ethene)/2; ○ = (allene + propene)/2. (a) 0·41—0·48 Torr; (b) 0·084—0·120 Torr; (c) 0·020—0·032 Torr

at each pressure from the equation [(I) + (II)]/(total products) = $(k_1 + k_2)/k_T$. Individual rate constants k_1 and k_2 were not calculated due to the rapid interconversion of (I) and (II).

At 0·02 and 0·1 Torr nearly all the MPD was formed from a primary reaction as the product distribution plot of (III) was linear. Hence, for all readings below 0·1 Torr the following equation was assumed: (III)/(total products) = k_3/k_T. The curvature in the plots at 0·1 and 0·4 Torr was due to secondary formation of MPD from (III). The amount of primary reaction was estimated at these two pressures by drawing tangents to the initial slopes of the curves in the MPD product distribution plots. In this way the amounts of secondary reaction of (III) at any percentage reaction at 0·1 and 0·4 Torr was estimated. A reasonable assumption was then made, based on evidence from high pressure work, that any MPD formed above 1 Torr was the result of a secondary reaction of (III). Secondary contributions to MPD were then calculated for all other pressures for which time studies were not undertaken, by interpolation of the secondary contributions calculated at 0·1, 0·4, and 10 Torr. The rates of formation of (III) for all the pressures were then calculated as follows:

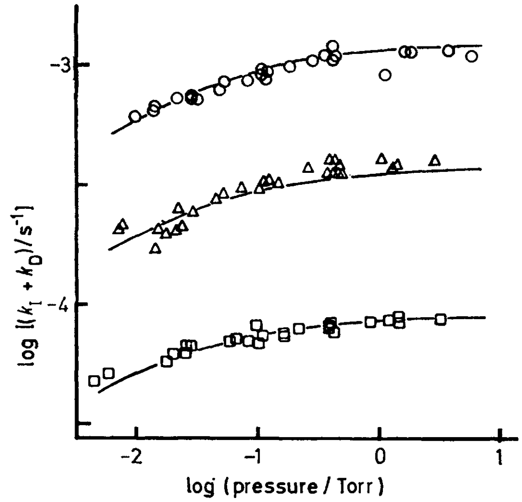


FIGURE 3 Fall-off curves for overall loss of methylspiropentane. Solid curves are computed fall-off curves shifted to higher pressures by 0·8 log units. ○ 660·3 K; △ 641·6 K; □ 620·9 K

[(III) + calculated secondary formation of MPD]/(total products) = k_3/k_T.

Similar, but much smaller, corrections were made for the secondary amounts of EBD formed from (I) and (II). The primary rates of formation of MPD and EBD were then calculated at all pressures using the complimentary relationship, *i.e.*

[MPD − secondary correction]/(total products) = k_{MPD}/k_T.

Using values of k_T the absolute rates of isomerization to methylenecyclobutanes (k_I), MPD and EBD, and of decomposition (k_d), were calculated for each of the three temperatures. Data obtained are plotted in Figures 3—7. Rate constants obtained from smooth curves through the experimental data at each temperature are listed in Table 2.

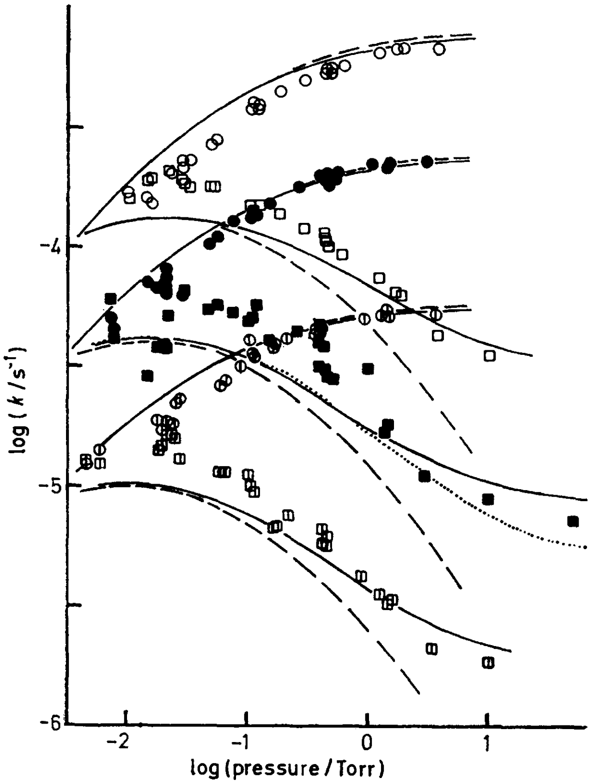


FIGURE 4 Experimental data and computed curves (shifted to higher pressures by 0·8 log units) for (I) + (II) and methylallene/ethylene yields. (I) + (II): ○ 660·3 K; ● 641·6 K; ⦶ 620·9 K. Methylallene/ethylene: □ 660·3 K; ■ 641·6 K; ⊞ 620·9 K. Solid curve, Scheme 4; dashed curve, scheme 5; dotted curve, Scheme 5 with direct decomposition to methylallene and ethylene

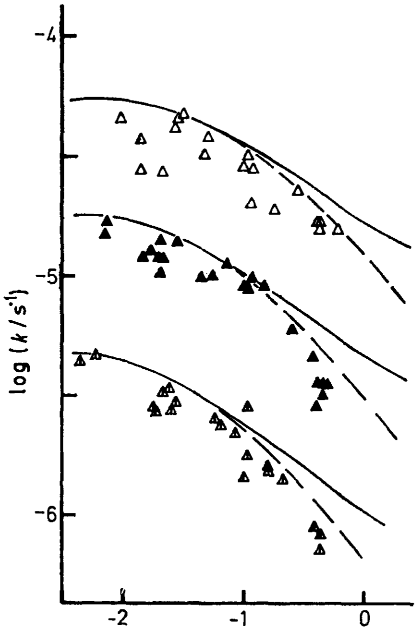


FIGURE 5 Experimental data and computed curves (shifted to higher pressures by 0·8 log units) for ethylbutadiene. △ 660·3 K; ▲ 641·6 K; ⧋ 620·9 K. Solid curve, Scheme 4; dashed curve, Scheme 5

TABLE 2

Reaction rate constants at various pressures

Pressure (Torr)	k_T/k_∞	$(k_1 + k_2) \times 10^5/s^{-1}$	$k_3 \times 10^5/s^{-1}$	k_d * $\times 10^5/s^{-1}$	$k_{MPD} \times 10^5/s^{-1}$	$k_{EBD} \times 10^5/s^{-1}$
347·6 °C $k_\infty = 8{\cdot}97 \times 10^{-5}\ s^{-1}$						
3·1	0·975	5·25	2·88	0·59	—	—
1·0	0·944	5·00	2·29	0·98	0·20	0·040
0·40	0·898	4·47	1·82	1·38	0·33	0·083
0·10	0·787	3·39	1·07	2·04	0·60	0·191
0·02	0·670	1·91	0·48	2·75	0·76	0·309
0·005	0·565	1·31	0·20	2·14	0·81	0·447
368·4 °C $k_\infty = 3{\cdot}98 \times 10^{-4}\ s^{-1}$						
3·1	0·982	23·4	12·9	2·88	—	—
1·0	0·938	21·9	10·0	5·01	—	—
0·40	0·891	19·5	7·76	6·92	1·82	0·49
0·10	0·766	13·5	4·07	9·75	2·82	0·93
0·02	0·612	7·08	1·32	11·2	3·31	1·32
0·007	0·520	4·68	0·56	11·0	3·02	1·62
387·1 °C $k_\infty = 1{\cdot}20 \times 10^{-3}\ s^{-1}$						
3·1	0·971	70·8	36·3	12·6	—	—
1·0	0·933	63·1	28·3	19·1	—	—
0·40	0·883	54·9	20·9	24·6	6·61	1·78
0·10	0·752	38·0	11·2	30·9	8·71	3·02
0·02	0·581	20·0	3·63	34·7	9·55	4·47
0·008	0·485	13·4	2·00	31·0	8·91	4·57

* Sum of all decomposition reactions.

DISCUSSION

A mechanism for the reactions of spiropentane has been proposed[1,4-6] in which both cyclopropane rings have been opened to give an allylically stabilised, chemically activated, biradical intermediate (R). Decomposition of this biradical gives rise to ethylene and allene whereas cyclization, and subsequent collisional deactivation, will produce methylenecyclobutane. In a previous paper[1] we suggested that as the methylspiropentane reaction appeared to be in the high pressure region at 10 Torr then the allenes and olefins produced in this instance must be the result of a reaction not involving the biradical (R). This reaction could be the result of a concerted mechanism (a symmetry allowed process requiring conrotatory motion of the two methylene groups on one cyclopropane ring with synchronous elongation of the radial carbon–carbon bonds of the other ring) or by decomposition of the biradical formed by opening only one cyclopropane ring (*i.e.*, the biradical responsible for the rapid interconversion of *cis*- and *trans*-1,2-dideuteriospiropentane[4]).

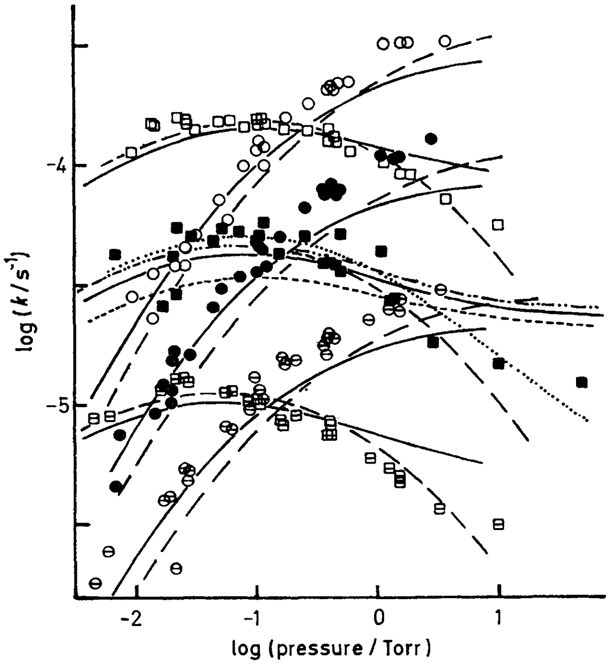
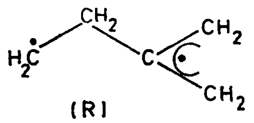
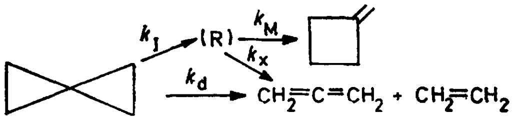


FIGURE 6 Experimental data and computed curves (shifted to higher pressures by 0·8 log units) for (III) and allene/propene. (III): ○ 660·3 K; ● 641·6 K; ⊖ 620·9 K. Allene/propene: □ 660·3 K; ■ 641·6 K; ⊟ 620·9 K. Arrhenius parameters used were as listed in Table 3 except where otherwise indicated. Solid curve, Scheme 4 with Arrhenius equation for MPD formation of $10^{13 \cdot 38} \exp(-51{,}600/1{\cdot}987T)\ s^{-1}$; – – – – Scheme 4; — ·· — ·· — Scheme 4 with biradical and concerted MPD formation; ——— Scheme 5; · · · · Scheme 5 with direct decomposition to allene and propylene



(R)

For simplicity we will consider in detail the case for spiropentane itself. Steady-state treatment for biradical



SCHEME 2

(R) gives $k_{decomp} = k_I k_x/(k_M + k_x) + k_d$. At the high pressure limit k_M is found experimentally to be much

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[3] P. J. Burkhardt. Ph.D. Thesis, University of Oregon, 1962.

[4] J. C. Gilbert, *Tetrahedron*, 1969, **25**, 1459.

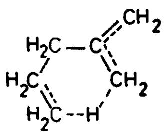
[5] W. von E. Doering and J. C. Gilbert, *Tetrahedron*, *Suppl.* **7**, 1966, 397.

[6] M. C. Flowers and A. R. Gibbons, preceding paper.

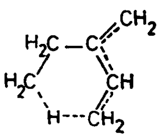
greater than k_x. Hence $k_{\text{decomp}} = k_I k_x/k_M + k_d$. If we assume no direct decomposition of spiropentane ($k_d = 0$) then the energy of activation for decomposition is given by the activation energy for the structural isomerization (55·5 kcal mol^{-1}) * weighted by the temperature dependence of k_x/k_M. A maximum value for this activation energy will result when (R) has a thermal energy distribution. In this case $E_{\text{decomp}} = E_I + E_x - E_M$ where E_x and E_M are the activation energies for decomposition and ring closing from (R), which are obtainable from the energy diagram in ref. 1. Hence the maximum value for the decomposition activation energy *via* a biradical pathway is *ca.* 69 kcal mol^{-1}. The corresponding parameters obtained in the methylspiropentane case yield a maximum of 66 kcal mol^{-1}. The actual value will be less because (R) is formed with a non-thermal energy distribution with a minimum energy of *ca.* 25 kcal mol^{-1}. The experimental Arrhenius parameters [$k_4/\text{s}^{-1} = 10^{15\cdot48} \exp(-59{,}600/1\cdot987T)$; $k_5/\text{s}^{-1} = 10^{15\cdot32} \exp(-59{,}800/1\cdot987T)$ [1]] could therefore represent exclusive formation of the decomposition products by a biradical mechanism.

Results at various pressures above 10 Torr showed a decrease in the rate of decomposition from 12 to 50 Torr of *ca.* 20%, but the rate of decrease appears to diminish above 2 Torr. The participation of a direct path would mean that at high pressure the rate of decomposition of methylspiropentane could only increase (if k_d were in the fall-off region) or remain the same (if it had reached the limiting high pressure value). The continuing decrease in the yield of decomposition products as the pressure is increased suggests that the majority, if not all, of these products at 10 Torr do result from the decomposition of the chemically activated biradical intermediate (R).

The formation of EBD and MPD may be readily explained as resulting from the energised biradical intermediates,[2] *via* six-membered cyclic transition states [T.S. (MPD) and T.S. (EBD)].



T.S.(MPD)



T.S.(EBD)

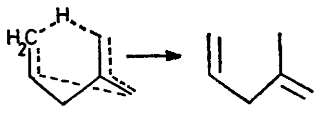
On the basis of these transition states, however, it is difficult to see why the rate of formation of MPD should be *ca.* 50 times faster than the rate of formation of EBD. Indeed as formation of MPD involves an internal hydrogen abstraction by an allylic radical (losing the allylic resonance energy) whereas EBD involves abstraction by a primary radical with subsequent conversion of an allylic radical into a substituted butadiene (losing the allylic resonance energy but gaining the butadiene delocalization energy) formation of EBD might be expected to be energetically favoured. Detailed consideration of the statistical factors for the biradical mechanism provides a partial explanation for the rate constant differences. Only two of the four possible modes of ring opening of (I) can lead to a biradical capable of adopting the right configuration for rearrangement to EBD, *i.e.* that biradical in which the two substituents attached to the allyl radical are *cis* to each other. This assumes, not unreasonably, that the rate of geometric isomerization of this allylic biradical is slow compared to the rate of cyclization. The statistical factor for rearrangement of the biradical to EBD is six (the transition state is optically active with the transferring hydrogen atom not in the plane defined by the allylic system). Similarly only one out of the four modes of ring opening of (II) will lead to the biradical precursor of EBD. Hence the overall statistical factor for conversion of the mixture of (I) and (II) produced in the methylspiropentane system ($k_1/k_2 = 0\cdot4$) will be $\{\frac{6}{4} + \frac{6}{2} . 0\cdot4\}/1\cdot4 = 1\cdot9$. All biradicals formed from the ring opening of (III) can readily adopt the configuration required for the hydrogen-transfer reaction and this leads to a statistical factor of 12 for the formation of MPD (again the transition state is optically active with the transferring hydrogen atom not in the plane of the allylic system). The biradical mechanism for reactions of (I), (II), and (III) is summarised by the following Scheme:

$$\text{(I), (II), or (III)} \underset{k_c}{\overset{k_{-c}}{\rightleftharpoons}} \text{(R)} \xrightarrow{\Sigma k_x} \text{Products (X)}$$

SCHEME 3

The overall rate constant (k) for formation of product X is then given by the equation $k = k_{-c}k_x/(k_c + \Sigma k_x)$ and if, as is believed to be the case, $k_c \gg \Sigma k_x$ then, $k \simeq k_{-c}k_x/k_c$. Statistical factors of 4 for ring opening and closing were adopted and hence overall statistical factors for formation of products are equal to the statistical factors for the subsequent rearrangement of the biradicals. The difference in statistical factors for the formation of MPD and EBD thus can account for more than a factor of 6 in the difference in the rates of these reactions.

An additional possible explanation is that (III) undergoes a concerted 1,5-hydrogen shift to give MPD. The low frequency 'puckering' motion of the cyclobutane ring makes close approach of the two centres feasible. However, although the error limits of the measured Arrhenius parameters are large,[1] the pre-exponential factor ($10^{14\cdot16 \mp 1\cdot15}$ s^{-1}) is too high for such a mechanism



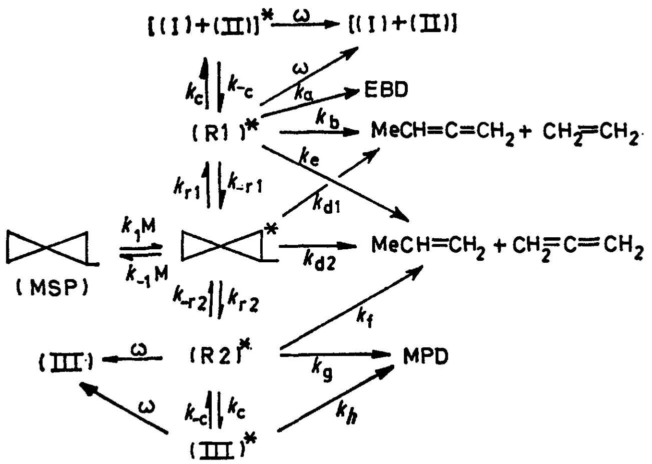
for which log (A/s^{-1}) will be less than 13. It is nevertheless possible that the measured rate is a combination of both concerted and biradical paths.

The relative success of the RRKM theory in predicting the pressure dependence of the product distribution in the analogous spiropentane isomerization[6] led us to

* 1 kcal = 4·184 kJ.

attempt a similar calculation for the more complex methylspiropentane system. It was hoped that these calculations would show whether or not the biradical mechanism is entirely consistent with the experimental data and if direct decomposition of MSP to olefins and allenes, and a concerted rearrangement of (III) to MPD occurs.

Reaction Mechanisms used for RRKM Calculations.— As for the calculations on the reactions of spiropentane two main reaction schemes were adopted. The first scheme (Scheme 4) is based on the above mechanism and involves the intermediate formation of chemically activated, allylically stabilised, biradical intermediates.

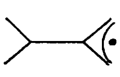


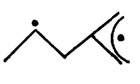
SCHEME 4

As the interconversion of (I) and (II) is too fast, under the conditions of the investigation, to allow the separate rates of decomposition and isomerization of these molecules to be determined, the scheme was simplified for computational purposes by considering only two biradical intermediates. (R1) Therefore represents the biradicals (A)—(C) that can be formed from, and cyclise to, (I) and (II), and (R2) represents the biradical (D) that can only cyclise to (III). No distinction was made either in the rates of cyclization of (R1) and (R2), or in the rates of ring opening of the three methylenecyclobutanes. M represents the total pressure. Molecules that are energised are indicated by an asterisk. The energy distribution of these molecules is governed by the rate of thermal activation of methylspiropentane, the rates of the various subsequent reactions and the heats of formation of the products. Direct deactivation of the biradicals (R1) and (R2) is incorporated to take account of the possibility that collisional deactivation of (R1) and (R2), to energies lower than those required to produce decomposition to an olefin and an allene, or rearrangement to MPD or EBD, can occur. Such stabilised biradicals are assumed to be only capable of cyclizing to the methylenecyclobutanes. Application of the steady-state assumption to all intermediates leads to the following equations for the overall rate constants for isomerization to (I) + (II), (k_{1+2}); (III), (k_3); ethylbutadiene (k_{EBD}) and methylpentadiene (k_{MPD}), and for decomposition to methylallene and ethylene (k_{MA}) and to allene and propylene (k_{AL}):


(A)


(B)


(C)


(D)

$$k_{1+2} = \int_{E_a}^{\infty} \frac{k_{r1}}{\alpha\gamma} \{1 + k_c/(\omega + k_{-c})\} \cdot \mathrm{d}(k_1/k_{-1}) \quad (1)$$

$$k_3 = \int_{E_a}^{\infty} \frac{k_{r2}}{\beta\gamma} \{1 + k_c/(\omega + k_{-c} + k_h)\} \cdot \mathrm{d}(k_1/k_{-1}) \quad (2)$$

$$k_{\mathrm{EBD}} = \frac{1}{\omega}\int_{E_a}^{\infty} \frac{k_a k_{r1}}{\alpha\gamma} \cdot \mathrm{d}(k_1/k_{-1}) \quad (3)$$

$$k_{\mathrm{MPD}} = \frac{1}{\omega}\int_{E_a}^{\infty} \frac{k_{r2}}{\beta\gamma} \cdot \{k_g + k_h k_c/(\omega + k_{-c} + k_h)\} \cdot \mathrm{d}(k_1/k_{-1}) \quad (4)$$

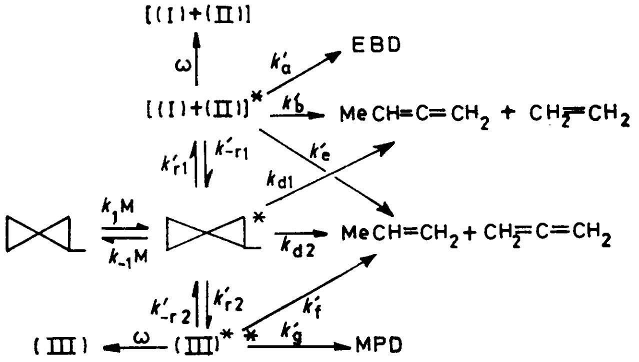
$$k_{\mathrm{MA}} = \frac{1}{\omega}\int_{E_a}^{\infty} \frac{k_b k_{r1}}{\alpha\gamma} \cdot \mathrm{d}(k_1/k_{-1}) + \int_{E_a'}^{\infty} \frac{k_{d1}}{\gamma} \cdot \mathrm{d}(k_1/k_{-1}) \quad (5)$$

$$k_{\mathrm{AL}} = \frac{1}{\omega}\int_{E_a}^{\infty} \left\{\frac{k_e k_{r1}}{\alpha} + \frac{k_f k_{r2}}{\beta}\right\} \cdot \frac{\mathrm{d}(k_1/k_{-1})}{\gamma} + \int_{E_a''}^{\infty} \frac{k_{d2}}{\gamma} \cdot \mathrm{d}(k_1/k_{-1}) \quad (6)$$

where $\alpha = 1 + k_c/(\omega + k_{-c}) + (k_a + k_b + k_e + k_{-r1})/\omega$,
$\beta = 1 + \{k_f + k_g + k_{-r2} + k_c(\omega + k_h)/(\omega + k_{-c} + k_h)\}/\omega$,
and $\gamma = 1 + \{k_{d1} + k_{d2} + k_{r1}(1 - k_{-r1}/\alpha) + k_{r2}(1 - k_{-r2}/\beta)\}/\omega$.

E_a, E_a', and E_a'' are the critical energies for isomerization of MSP to the methylenecyclobutanes [experimentally the activation energies for isomerization to either (I), (II), or (III) were found to be identical[1]] and for direct decomposition to methylallene and to allene, respectively. k_{-1}M Was taken to be the bimolecular collision frequency (ω); all collisions were assumed to be strong and a collision diameter of 6×10^{-10} m was used for each species. Every rate constant, except k_{-1}, will be energy dependent.

The alternative scheme (Scheme 5) neglects the effect of any intermediates. This is perhaps the simplest scheme that could explain the results. It could correspond either to a concerted mode of conversion of MSP to the methylenecyclobutanes or, perhaps more reasonably, to the initial formation of a biradical, formed by fission of a peripheral or a radial bond of MSP, followed by concerted rearrangement of this biradical to the methylenecyclobutanes. Essentially this mechanism requires that if MSP is converted into the methylenecyclobutanes *via* the formation of an intermediate, then this intermediate suffers no effective competing reactions. On the basis of the steady-state assumption, equations for the overall rate constants for formation of the various products can be derived. The computation method employed however, used the same computer programme as written for Scheme 4, but to simulate Scheme 5 biradical (R1)* was replaced by [(I) + (II)]*, biradical (R2)* by (III)*, and k_c was set equal to zero.



Scheme 5

The initial isomerization steps in both Schemes are treated as reversible reactions. The exclusion of the reverse reaction has however no effect on the calculated results. This is to be expected as the reaction to the methylenecyclobutanes is exothermic by some 14 kcal mol^{-1}.

Table 3

Statistical factors and rate equations used to select the transition state vibrational frequencies

Transition state [a]	Statistical factor	Rate equations (s^{-1})	Ref.
TS(r2), (TS(r1))	1 (1·973)	$10^{14\cdot38} \exp(-53{,}723/1\cdot987T)$	This work, 1
TS(a)	1·9	$10^{13\cdot08} \exp(-54{,}650/1\cdot987T)$	2
TS(b)	0·72 (Scheme 4)	$10^{15\cdot25} \exp(-61{,}680/1\cdot987T)$	2
	1·44 (Scheme 5)		
TS(c), TS(−c)	4	$\frac{1}{2} . 10^{14\cdot12} \exp(-49{,}110/1\cdot987T)$	2
TS(d1), TS(d2)	1	$10^{13\cdot6} \exp(-55{,}500/1\cdot987T)$	Assumed [b]
TS(e)	0·28 (Scheme 4)	$10^{14\cdot69} \exp(-62{,}630/1\cdot987T)$	2
	0·56 (Scheme 5)		
TS(f)	1 (Scheme 4)	$10^{15\cdot6} \exp(-59{,}500/1\cdot987T)$	Assumed
	2 (Scheme 5)	$10^{15\cdot9} \exp(-59{,}500/1\cdot987T)$	Assumed
TS(g)	12 (Scheme 4)	$10^{14\cdot16} \exp(-52{,}910/1\cdot987T)$	1 [c]
	6 (Scheme 5)		
TS(h)	3	$10^{12\cdot5} \exp(-48{,}200/1\cdot987T)$	Assumed

[a] Alphanumerics in parentheses are the subscripts of the particular rate constant with which this transition state is associated. In the majority of calculations k_d was set equal to zero. [c] Used only when $k_h = 0$. In calculations where k_h was given by equation above, the assumed rate equation for biradical formation of MPD was $10^{14\cdot16} \exp(-56{,}000/1\cdot987T)$ s^{-1}. This kept the total rate constant at 641·6 K for formation of MPD fixed.

Calculations.—The computation procedures for the evaluation of the integrals, and the expressions used for $d(k_1/k_{-1})$ and for the various energy dependent rate constants have been described previously.[6]

Some simplifications, in addition to those adopted for the spiropentane system (*e.g.* internal rotations were treated as torsional vibrations and the moments of inertia of the transition states and energised reactants were assumed to be equal), were made to aid computation. Thus the same vibrational frequencies were assigned to the transition states for formation of (R1) and (R2) from MSP, to (R1) and (R2) themselves and the heats of formation and rates of cyclization of the biradicals were assumed to be identical. Vibrational frequency assignments for MSP, the methylenecyclobutanes (the same vibrational frequencies were used for each of the methylenecyclobutanes) and the biradicals were made based on those already used in the spiropentane study[6] (see Appendix for the actual values used).

Statistical factors (L_x where x is the subscript of the rate constant) for each rate constant are listed in Table 3. Additional comment is necessary on L_{r1}, L_b, and L_e.

The measured ratio of k_{1+2}/k_3 was 1·973. As the same transition states were used for k_{r1} and k_{r2}, and as L_{r2} is unity, then in order to obtain the experimentally observed rate constant for k_{1+2} a value of L_{r1} equal to 1·973 must be used. For the same reason that, as described earlier, a weighted average of the statistical factors for formation of EBD from (I) and (II) was used, the statistical factors for k_b and k_e were weighted to take account of the fact that presumably (I) can give rise to methylallene and ethylene only, whereas (II) can give rise to these products and to allene and propylene.

The vibrational frequencies of the transition states were initially assigned on the basis of the assumed structures. These frequencies were then arbitrarily modified so that the calculated rate constants for overall reactions [equation (8), ref. 6] agreed with those obtained at 641·6 K using the experimentally determined or assumed Arrhenius equations as listed in Table 3.

The frequencies used for (R1) and (R2) produced a pre-exponential factor for cyclization of $10^{12\cdot4}$ s^{-1}. This is perhaps too low, but the effect of changing the vibrational frequencies of the biradicals, and hence changing the pre-exponential factor, are small and only becomes apparent at pressures above 100 Torr.

No experimental data exists for the rate constant for decomposition of (III). Various rate equations were tried in order to obtain a fit to the experimental data that was similar to that obtained for methylallene from (I) and (II). This necessitated using rate constants approximately an order of magnitude higher for decomposition of (III) compared to the observed values for (I) and (II).

Data for the isomerization of (III) to MPD has only been obtained indirectly [from the secondary decomposition of (III) in the MSP pyrolysis [1]]. The data are therefore presumably subject to rather higher uncertainties than if the reaction had been studied directly. For this reason a variety of Arrhenius parameters were employed. In these instances the same transition-state frequencies were used but with the statistical factor and activation energies changed. In all cases the observed high pressure rate constant at 641·6 K was retained.

TABLE 4

Calculated rate constants based on Schemes 4 and 5

log (pressure/Torr)		3·0	2·0	1·0	0	−1·0	−2·0	−3·0	−4·0
Rate constants [a]									
620·9 K									
$-\log (k_{1+2}/s^{-1})$	(S4)	4·245	4·248	4·249	4·257	4·306	4·468	4·833	5·470
	(S5)	4·228	4·228	4·229	4·239	4·290	4·456	4·824	5·460
$-\log (k_{EBD}/s^{-1})$	(S4)	6·308	6·255	6·241	6·173	5·908	5·544	5·338	5·377
	(S5)	9·757	8·758	7·771	6·845	6·084	5·571	5·334	5·368
$-\log (k_{MA}/s^{-1})$	(S4)	5·788	5·743	5·725	5·634	5·358	5·070	4·994	5·176
	(S5)	9·063	8·065	7·083	6·190	5·506	5·109	5·010	5·188
$-\log (k_3/s^{-1})$	(S4)	4·688	4·707	4·712	4·736	4·859	5·215	5·902	6·890
	(S5)	4·523	4·524	4·534	4·589	4·784	5·226	5·974	6·983
$-\log (k_{MPD}/s^{-1})$	(S4)	5·270	5·230	5·222	5·193	5·087	4·977	5·031	5·282
	(S5)	8·602	7·611	6·667	5·877	5·347	5·115	5·150	5·392
$-\log (k_{AL}/s^{-1})$	(S4)	5·359	5·324	5·315	5·276	5·161	5·082	5·187	5·494
	(S5)	8·215	7·226	6·301	5·562	5·106	4·949	5·050	5·356
641·6 K									
$-\log (k_{1+2}/s^{-1})$	(S4)	3·629	3·631	3·633	3·645	3·704	3·891	4·286	4·952
	(S5)	3·609	3·609	3·611	3·624	3·687	3·878	4·276	4·942
$-\log (k_{EBD}/s^{-1})$	(S4)	5·666	5·617	5·601	5·523	5·254	4·919	4·754	4·831
	(S5)	9·022	8·023	7·039	6·131	5·408	4·942	4·750	4·821
$-\log (k_{MA}/s^{-1})$	(S4)	5·117	5·074	5·054	4·954	4·682	4·432	4·401	4·621
	(S5)	8·300	7·303	6·326	5·455	4·815	4·468	4·416	4·632
	(S5) [b]	5·288	5·284	5·251	5·068	4·701	4·426	4·395	4·620
$-\log (k_3/s^{-1})$	(S4)	4·079	4·097	4·103	4·134	4·274	4·658	5·372	6·379
	(S5)	3·905	3·906	3·918	3·985	4·204	4·675	5·447	6·473
$-\log (k_{MPD}/s^{-1})$	(S4)	4·643	4·606	4·597	4·565	4·462	4·376	4·462	4·740
	(S4) [c]	4·870	4·828	4·819	4·784	4·658	4·525	4·565	4·814
	(S5)	7·874	6·884	5·953	5·195	4·708	4·515	4·582	4·851
$-\log (k_{AL}/s^{-1})$	(S4)	4·705	4·673	4·663	4·621	4·514	4·464	4·603	4·941
	(S4) [c]	4·664	4·630	4·619	4·570	4·444	4·374	4·506	4·849
	(S5)	7·462	6·476	5·567	4·862	4·450	4·333	4·468	4·805
	(S5) [b]	5·286	5·261	5·105	4·726	4·397	4·302	4·444	4·785
660·3 K									
$-\log (k_{1+2}/s^{-1})$	(S4)	3·106	3·108	3·111	3·125	3·197	3·406	3·828	4·520
	(S5)	3·084	3·084	3·087	3·103	3·179	3·393	3·818	4·510
$-\log (k_{EBD}/s^{-1})$	(S4)	5·120	5·074	5·057	4·971	4·701	4·393	4·266	4·375
	(S5)	8·394	7·396	6·416	5·526	4·838	4·413	4·261	4·365
$-\log (k_{MA}/s^{-1})$	(S4)	4·545	4·504	4·483	4·375	4·111	3·896	3·903	4·157
	(S5)	7·650	6·653	5·681	4·832	4·232	3·930	3·918	4·168
$-\log (k_3/s^{-1})$	(S4)	3·563	3·581	3·588	3·624	3·781	4·192	4·928	5·952
	(S5)	3·380	3·381	3·397	3·476	3·716	4·214	5·006	6·047
$-\log (k_{MPD}/s^{-1})$	(S4)	4·110	4·076	4·067	4·033	3·934	3·871	3·984	4·286
	(S5)	7·252	6·265	5·347	4·618	4·168	4·010	4·106	4·399
$-\log (k_{AL}/s^{-1})$	(S4)	4·150	4·120	4·110	4·066	3·967	3·944	4·113	4·479
	(S5)	6·819	5·836	4·942	4·270	3·896	3·814	3·980	4·344

[a] Calculated using the Arrhenius parameters listed in Table 3, but without any direct decomposition to olefins and allenes unless otherwise indicated. No concerted rearrangement of (III) to MPD. S4 and S5 refer to Schemes 4 and 5 respectively. [b] Including direct formation from MSP using Arrhenius equation given in Table 3. [c] With Arrhenius equation for MPD formation from (III) (biradical mechanism) of $10^{13\cdot38} \exp(-51{,}600/1\cdot987T)$ s^{-1}.

For the calculations based on Scheme 5 essentially the same frequencies were used for the transition states associated with the primed rate constants as for the unprimed quantities bearing the same subscript. Small modifications in some instances were necessary to accommodate the use of different statistical factors. In practice the results as quoted in Table 4 would have been unaffected had the original statistical factors and frequencies been retained.

The difference in the heats of formation at 641·6 K of MSP and the methylenecyclobutanes (−14·0 kcal mol^{-1}) was based on the known difference between spiropentane and methylenecyclobutane using group additivity.[7] The heat of formation of the biradicals (27 kcal mol^{-1}

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[7] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279; H. E. O'Neal and S. W. Benson, *Internat. J. Chem. Kinetics*, 1969, **1**, 221; *J. Chem. Eng. Data*, 1970, **15**, 266.

relative to MSP) were calculated by group additivity.[7] Heats of formation of the various transition states were calculated from the activation energies as listed in Table 3 using equation (10) of ref. 6.

COMPUTATIONAL RESULTS

Results are summarised in Table 4 and Figures 3—7. Figure 3 shows the experimental and calculated fall-off curves for the overall reaction. A shift of the calculated curve by 0·8 log units to higher pressures was necessary to fit the experimental data. In consequence all curves plotted in Figures 4—7 are similarly shifted by 0·8 log units. This is 0·2 log units more than the already large shift required in the spiropentane study. Possible explanations for a shift were put forward in the preceding paper;[6] we can however offer no really concrete explanation for the required very large shifts required in these instances. Amongst the explanations was the effect of the variation of the Arrhenius parameters for the isomerization. In this instance increasing the pre-exponential factor four-fold, with compensating changes in the activation energy (1·77 kcal mol^{-1}) shifts the fall-off by 0·34 log units to higher pressures. In contrast changing the two lowest frequencies of TS(r2) from 150 to 75 cm^{-1}, with compensating upward changes of higher vibrational frequencies to maintain a fixed rate constant, changes the position of fall-off by less than 0·02 log units.

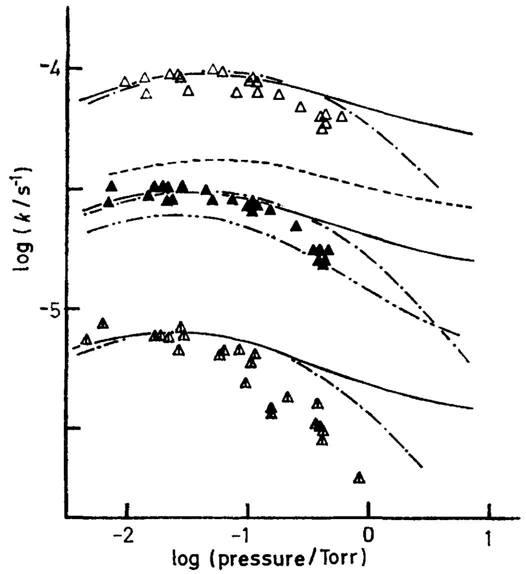

FIGURE 7 Experimental data and computed curves (shifted to higher pressures by 0·8 log units) for 2-methylpenta-1,4-diene. △ 660·3 K; ▲ 641·6 K; ⍋ 620·9 K. Solid curve, Scheme 4 with Arrhenius equation for MPD formation of $10^{13\cdot38} \exp(-51{,}600/1\cdot987T)$ s^{-1}; ---- Scheme 4; —··—··— Scheme 4 with biradical and concerted MPD formation; —·—·— Scheme 5. Arrhenius parameters used were as listed in Table 3 except where otherwise indicated.

The system divides itself conveniently into two separate parts; one involving formation of (I) and (II), and the other, formation of (III). This division is possible because the only products common to both parts, allene and propene, proved to be formed almost exclusively from (III).

Formation of (I) *and* (II).—Although the computed and experimental fall-off curves are not in as close agreement as observed for the reactions of spiropentane, the agreement is quite reasonable for both Schemes 4 and 5 ($k_{d1} = k_{d2} = 0$). Poorest agreement is obtained for the formation of methylallene, but even this is never in error by more than a factor of 0·6. The shapes of the curves obtained from Scheme 4 for formation of methylallene at the higher pressures are perhaps in better agreement than those obtained from the alternative scheme. Inclusion of a direct reaction path in Scheme 5 for formation of methylallene from MSP (using the rate equation given in Table 3) leads however to as good agreement as observed for Scheme 4. Somewhat higher values of k_{d1} would have led to even better agreement with the experimental data. It should be remembered that the shape of the experimental curve for EBD formation at high pressure may have been distorted by the method of extracting the experimental data and therefore the behaviour of this product at the higher pressures cannot be used to distinguish between the proposed schemes. Changing the heats of formation of (R1) by 7 kcal mol^{-1} downwards, or 3 kcal mol^{-1} upwards, produced no effect at the pressures of the experimental study. Significant effects are only observed at pressures well above 100 Torr.

Formation of (III).—Use of Arrhenius parameters, for decomposition of (III) to allene and propene, similar to those for the analogous decomposition of (I) and (II), produced much too low a rate of formation of allene and propene in the low-pressure pyrolysis of MSP. However, using the Arrhenius equation given in Table 3 for this rate constant, and with the experimentally determined Arrhenius equation for isomerization to MPD ($k_h = 0$), the calculated product distribution is plotted in Figures 6 and 7. Agreement with the MPD data using Scheme 4 might be considered reasonable (again bearing in mind that the curve shape for MPD formation at the highest pressures cannot be relied upon). Much better agreement is obtained if the activation energy and pre-exponential factor for this reaction are lowered. Computed curves are plotted for a pre-exponential factor of $10^{13\cdot38}$ s^{-1} and activation energy of 51·6 kcal mol^{-1}. These changes are well within the limits of possible experimental errors. Similarly good agreement can be obtained using both a biradical and a direct mechanism in Scheme 4 for production of MPD (using the Arrhenius equations given in Table 3). Though as there are now essentially two additional adjustable parameters such agreement is perhaps only to be expected.

The curve for allene production is however much too flat in all cases, producing rates too low at the lowest pressures, but too high at the highest. Changing the Arrhenius parameters (keeping the rate constant fixed at 641·6 K) altered the curve shape very little.

An even worse fit would be obtained if a direct decomposition path to allene and propene were included. Again, changing the heats of formation of (R2) by the same amounts as described for (R1) earlier has no effect on the calculated results over the experimental pressure range.

It can be seen however from Figures 6 and 7 that Scheme 5, with a suitable choice of Arrhenius parameters for decomposition and the experimentally determined parameters for isomerization to MPD, will give very good agreement for both allene and MPD yields.

A modified Scheme 5 (Scheme 2′ of the preceding paper [6]) in which decomposition of the methylenecyclobutanes occurs *via* the allylically stabilised biradicals, but in which the initial isomerization does not involve such intermediates, gives identical results to Scheme 5 itself at pressures relevant to this study.

CONCLUSIONS

On the basis of the experimental data from the spiropentane study, no choice between reaction schemes, analogous to 4 and 5 here, could be made.[6] It is unfortunate that the part of the MSP reaction about which rate constants are best known, namely reactions resulting from chemically activated (I) and (II), again provides no positive evidence as to which scheme is to be preferred.

Data from reaction of chemically activated (III) certainly best fit the scheme (Scheme 5) in which the allylic biradical is not an intermediate in the conversion of MSP into (III) [though it still may be an important intermediate in subsequent reactions of (III)]. However without direct data on the rate expressions for decomposition and isomerization of (III), both in the high pressure and fall-off regions, definite conclusions regarding the mechanism cannot be drawn. As discussed in the preceding paper on spiropentane,[6] arguments based on the predicted Arrhenius parameters for the overall reaction [1,8] support the biradical mechanism, though such arguments almost certainly will not exclude the alternative suggested here. The inclusion of biradical and concerted pathways from (III) to MPD, although not inconsistent with the data, must be considered too speculative to warrant further discussion. Whether or not any direct decomposition of MSP to olefins and allenes occurs depends on which scheme, in reality, applies; no direct decomposition is needed with Scheme 4 but direct decomposition is required in Scheme 5 to produce the ' flattening ' of the olefin/allene curves at the highest pressures.

The reason for the inherent difficulty in distinguishing between the mechanisms is the result of two main factors; (i) the long-recognised general lack of sensitivity of RRKM calculations to actual frequency assignments of the transition states [9] and (ii) the fact that distinction between the mechanisms used rests mainly on the competition between the rates of deactivation (ω) and ring opening (k_{-c}) of chemically activated (I), (II), and (III). Only at pressures where the inequality $k_{-c} \gg \omega$ no longer holds (*i.e.* at high pressures) can distinctions between the schemes be drawn. It is therefore somewhat ironic that at the pressures where the effect of chemical activation shows itself most clearly, little evidence can be obtained regarding the precise mechanism of the reaction.

APPENDIX

Vibrational frequency assignments (cm^{-1}) used in the calculations.

Methylspiropentane: 220, 250, 290, 300, 400, 581, 650, 778(2), 780, 852, 870, 872, 896, 912, 920, 993, 1000, 1040, 1053(2), 1150, 1157, 1200(2), 1397, 1430, 1450, 1465, 1500(3), 2950(3), 2990(4), 3050(3).

Methylenecyclobutanes: 80, 220, 354, 373, 400, 500, 650(4), 750, 879, 895, 900, 920, 954, 991, 1040, 1050, 1059, 1070, 1155, 1197, 1220, 1248, 1395, 1415, 1440(2), 1465, 1490, 1675, 2826, 2902, 2921, 2952, 2985, 3000(3), 3072.

Biradicals (R1) and (R2): 50, 100, 300, 350(2), 400(2), 450(2), 750(5), 950, 1000(3), 1150(6), 1300(2), 1450(6), 3000(10).

TS(r1) and TS(r2): 150(2), 300(3), 450(3), 600, 750(3), 900(3), 1050(4), 1200(5), 1350, 1500(6), 3000(10).

TS(a): 350, 400, 450(4), 550, 600, 650, 700(4), 750, 900, 1000(3), 1150(7), 1250, 1300, 1425, 1450(3), 2200, 3000(9).

TS(b)—Scheme 4: 25, 190, 200, 330, 350(2), 400, 410, 450, 550, 640, 700(4), 900, 1000, 1150(5), 1300(2), 1450(6), 1500, 3000(10).

TS(b)—Scheme 5: 25, 200(2), 300, 350(2), 400, 450, 550(2), 650, 750(3), 900, 950, 1000, 1150(5), 1300(2), 1450(6), 1500, 3000(10).

TS(d1) and TS(d2): 150, 300(4), 600(2), 750(3), 900(5), 1050(7), 1200(3), 1350, 1500(5), 3000(10).

TS(e)—Scheme 4: 25, 200(2), 350(3), 400, 450, 465, 550, 650, 700(4), 950, 1000, 1150(4), 1165, 1300(2), 1450(6), 1500, 3000(10).

TS(e)—Scheme 5: 25, 220(2), 350(3), 400, 450, 550(2), 650, 750(3), 900, 950, 1000, 1150(5), 1300(2), 1450(6), 1500, 3000(10).

TS(f)—Schemes 4 and 5: 25, 200(2), 250, 300, 350(2), 400(2), 550, 600, 700(3), 850, 900, 1000, 1150(5), 1300(2), 1450(6), 1500, 3000(10).

TS(g)—Scheme 4: 350, 375, 400(2), 450(3), 540, 600, 700(5), 900, 1000(2), 1010, 1150(7), 1300(2), 1405, 1450(3), 2200, 3000(9).

TS(g)—Scheme 5: 300, 350(2), 400(3), 450(2), 600, 700(5), 900, 1000(2), 1050, 1150(7), 1300(2), 1420, 1450(3), 2200, 3000(9).

TS(h): 400, 500(2), 600(3), 635, 750(7), 900(2), 1000(4), 1150(2), 1200(2), 1300(3), 1450(4), 2200, 3000(9).

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[1/1453 *Received*, 13*th August*, 1971]

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