Application of the RRKM Theory of Unimolecular Reactions to the Thermal Reactions of Spiropentane

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The RRKM theory of unimolecular reactions is applied to the pyrolysis of spiropentane. The product distribution as a function of pressure, and the overall fall-off curves, are calculated on the basis of two possible detailed mechanisms. Either mechanism is found to fit the experimental data which, with new data presented here, cover the pressure range from 10^{-3} Torr to 1 atm.

A STUDY of the gas-phase reactions of spiropentane [1] has revealed that the rate constant for loss of reactant changes with pressure in a manner that is expected for a true unimolecular process, *i.e.* below pressures of *ca.* 50 Torr (1 Torr = 133 N m^{-2}) the reaction rate declines. There are two reaction paths. One yields methylenecyclobutane (isomerization product) and the other ethylene and allene in equimolar amounts (decomposition products). A particularly interesting feature of the reaction is the observation that the ratio of isomerization to decomposition depends markedly on the total pressure of the system. Qualitative explanation of the results has already been made.[1,2] However in this paper we have attempted to calculate the dependence of product yields on pressure using the Rice–Ramsperger–Kassel–Marcus (RRKM) theory of unimolecular reactions. It was hoped that from such calculations it would be possible to distinguish between possible reaction mechanisms. In particular it was of interest to try to assess

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

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

whether or not there is a direct path from spiropentane to ethylene and allene and, to aid this end, additional experimental work has been carried out extending the pressure range of the earlier study to higher pressures.

EXPERIMENTAL

The apparatus used in the present study was identical to that previously described [3] with the exception that a reaction vessel of 79·5 cm^3 was employed and the gas chromatographic analysis was carried out on a 2 m, $\frac{1}{4}$ in o.d. dinonyl phthalate column held at 40 °C.

The preparation of spiropentane (purity 99·95%) has been previously described.[4] 1,2-Dichloro-1,1,2,2-tetrafluoroethane (Cambrian Chemicals) was used without further purification.

Pyrolyses (15 min duration) were carried out at an indicated 664·0 K. Analyses were performed in either duplicate or triplicate and the first-order rate constants obtained from the data are listed in Table 1 and plotted as filled circles on Figures 1 and 2. The rate constants determined in the pressure region where this study and the study of Burkhardt at 663·2 K overlapped, were in good agreement and no corrections for the apparent temperature differences were made. In order to eliminate the possibility that complicating side reactions were contributing to the reaction rates at the highest pressures some runs were undertaken with 1,2-dichlorotetrafluorethane as added inert gas. The rate constants for these runs (plotted as half-filled circles on Figures 1 and 2) were in good agreement with those in the absence of inert gas but at the same total pressure (*i.e.* experimentally it appears that spiropentane and 1,2-dichlorotetrafluoroethane have the same collisional deactivation efficiencies). The majority of experimental data plotted in Figures 1 and 2 (unfilled symbols) were obtained by Burkhardt.[1]

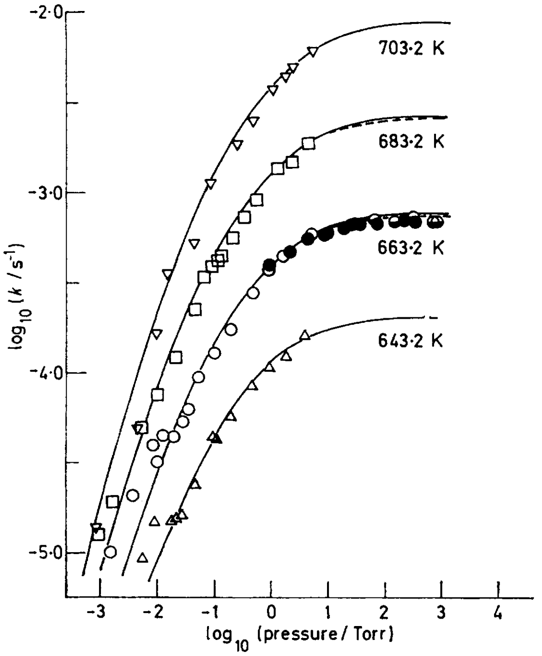

FIGURE 1 Experimental and computed values of k_I as a function of pressure. Open symbols—data of Burkhardt (ref. 1); ● spiropentane alone (this work); ◒ spiropentane + 1,2-dichlorotetrafluoroethane (this work). Dashed curve—Scheme 1; solid curve—Scheme 2

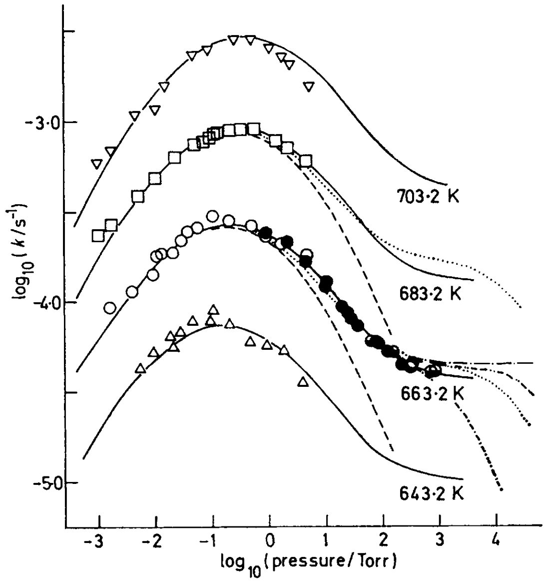

FIGURE 2 Experimental and computed values of k_D as a function of pressure. Open symbols—data of Burkhardt (ref. 1); ● spiropentane alone (this work); ◒ spiropentane + 1,2-dichlorotetrafluoroethane. -·-·- Scheme 1 (E_c = 15 kcal mol^{-1}); · · · · Scheme 1 (E_c = 8 kcal mol^{-1}); —··——··— Scheme 1 (E_c = 5 kcal mol^{-1}); —·—·— Scheme 1 with no direct deactivation of the biradical; — — — Scheme 2 (k_d = 0); —— Scheme 2 including contribution from direct decomposition of spiropentane the ethylene and allene

TABLE 1

Rate constants for isomerization (k_I) and decomposition (k_D) of spiropentane at 664·0 K

Pressure (Torr)			
Spiropentane	CF_2ClCF_2Cl	$10^4k_I/s^{-1}$	$10^4k_D/s^{-1}$
0·9		3·98	2·41
2·1		4·71	2·21
4·5		5·54	1·73
9·6		5·99	1·25
10·0		6·11	1·29
19·0		6·42	0·945
25·4		6·74	0·882
27·7		6·68	0·821
37·6		6·76	0·770
27·7	39·6	6·83	0·601
74·3		7·03	0·592
75·8		6·86	0·600
133		6·78	0·530
28·0	117·1	7·03	0·534
224		7·11	0·457
27·7	289	7·33	0·437
335		7·01	0·458
27·3	715	7·12	0·428
27·7	721	7·12	0·428

REACTION MECHANISMS

Calculations based on two different reaction schemes were attempted. The first, more detailed, scheme is based on the mechanism previously proposed [1-3,5] and involves the intermediate formation of a chemically

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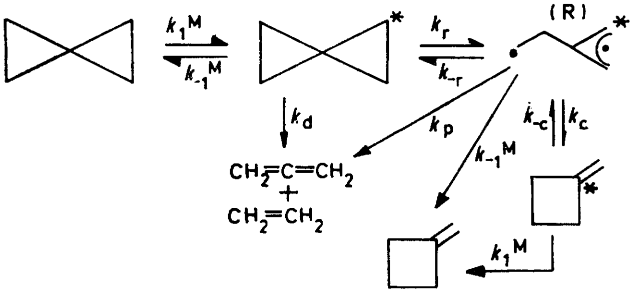
[3] M. C. Flowers and A. R. Gibbons, *J. Chem. Soc.* (*B*), 1971, 612.

[4] M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 1961, 5550.

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

activated, allylically stabilised, biradical intermediate. It is summarised in Scheme 1. M represents the total pressure. Molecules that are energised are indicated by an asterisk. The energy distribution of these energised molecules is governed by the rate of thermal activation of spiropentane, the rates of the various subsequent reactions, and the heats of formation of the products. Direct deactivation of the biradical (R) to methylenecyclobutane is incorporated to take account of the possibility that collisional deactivation of (R), to an energy lower than that required to produce decomposition to ethylene and allene, can occur. Application of the steady-state assumption to all intermediates leads to the following equations for the overall rate constants for isomerization (k_I) and decomposition (k_D) as a function of pressure:



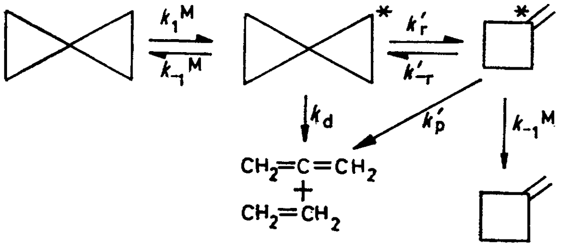
SCHEME 1

$$k_I = \int_{E_a}^{\infty} \frac{k_r}{\left[1 + \frac{(k_{-r} + k_p)}{\omega(1 + \beta)}\right]\left[1 + \frac{(k_d + k_r/\alpha)}{\omega}\right]} \cdot d(k_1/k_{-1}) \quad (1)$$

$$k_D = \int_{E_a}^{\infty} \frac{k_p k_r/\{\omega(1 + \beta) + k_{-r} + k_p\}}{\{1 + (k_d + k_r/\alpha)/\omega\}} \cdot d(k_1/k_{-1}) + \int_{E_a'}^{\infty} \frac{k_d}{\{1 + (k_d + k_r/\alpha)/\omega\}} \cdot d(k_1/k_{-1}) \quad (2)$$

where E_a and E_a' are the critical energies for the isomerization of spiropentane to the biradical (R) and decomposition, respectively; $\omega = k_{-1}$M = collision frequency, $\beta = \omega\{1 + k_c/(k_{-c} + \omega)\}$ and $\alpha = 1 + k_{-r}/(k_p + \beta)$. All rate constants, other than k_{-1}, are energy dependent.

The second reaction scheme conveniently neglects the effect of any intermediates, *i.e.* a single transition state is assumed to govern the rate at which spiropentane is converted into methylenecyclobutane. This is perhaps the simplest scheme that could explain the results. The scheme is summarised below. In this case a steady state treatment leads to the following expressions for the rate constants for formation of products:



SCHEME 2

$$k_I = \int_{E_a}^{\infty} \frac{k_r'}{\gamma[1 + (k_p' + k_{-r}')/\omega]} \cdot d(k_1/k_{-1}) \quad (3)$$

$$k_D = \int_{E_a}^{\infty} \frac{k_p' k_r'}{\gamma(\omega + k_p' + k_{-r}')} \cdot d(k_1/k_{-1}) + \int_{E_a'}^{\infty} \frac{k_d}{\gamma} \cdot d(k_1/k_{-1}) \quad (4)$$

where $\gamma = 1 + [k_d + k_r'\{1 + k_{-r}'/(\omega + k_p')\}]/\omega$.

The initial isomerization step is treated as a reversible reaction in both schemes. The exclusion of the reverse reaction has however no effect on the calculated results. This is to be expected as the reaction to methylenecyclobutane is exothermic by 14 kcal mol^{-1} (1 cal = 4·184 J). Thermal reactivation of stabilised methylenecyclobutane is unimportant under all conditions studied. From the known rate constant for thermal decomposition of methylenecyclobutane [1,6] we have calculated that for a 15-min pyrolysis at 663·2 K, secondary decomposition of methylenecyclobutane would give rise to an apparent first-order rate constant for formation of ethylene and allene of *ca.* 3 × 10^{-7} s^{-1}, *i.e.* more than two orders of magnitude smaller than the observed rate constants at the highest pressure studied.

CALCULATIONS

The RRKM theory [7,8] results in the following equations for $d(k_1/k_{-1})$ and k_x (where x is any of the alphabetic subscripts) in the absence of internal rotations in any of the molecules or transition states:

$$d(k_1/k_{-1}) = \frac{N^*(E^+ + E_a) \,.\, \exp\{-(E^+ + E_a)/RT\}}{P_2} \cdot dE^+ \quad (5)$$

$$k_x = \frac{L_x \sum_{E_v^+ \leqslant E^+} P(E_v^+)}{h \,.\, N^*(E^+ + E_a) \,.\, F} \quad (6)$$

$$F = N^*(E^+ + E_a - cRT\{I^+ - I\}/2I)/N^*(E^+ + E_a) \quad (7)$$

Symbols used are defined as follows: E^+ = energy of the active modes of the transition state in excess of the zero point energies; $N^*(E)$ = density of states of active modes of the excited molecule at energy E; $\sum_{E_v^+ \leqslant E^+} P(E_v^+)$ = sum of states of active modes of the transition state at energy E^+; P_2, P_2^+ = partition function for all active modes of the excited molecules and transition states respectively; L_x statistical factor for reaction k_x; c number of overall rotational degrees of freedom taken as adiabatic; I, I^+ principle moments of inertia of the excited molecule and the transition state respectively;

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[6] R. L. Brandaur, B. Short, and S. M. E. Kellner, *J. Phys. Chem.*, 1961, **65**, 2269; J. P. Chesick, *ibid.*, 1961, **65**, 2170.

[7] R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.*, 1951, **55**, 894; R. A. Marcus, *J. Chem. Phys.*, 1965, **43**, 2658.

[8] R. A. Marcus, *J. Chem. Phys.*, 1965, **43**, 2658.

I_x, I_x^+ moments of inertia of the excited molecule and the activated complex, respectively, along the x axis.

The term F is a correction term for centrifugal effects. At very low pressures the calculated rate for simple unimolecular reactions neglecting this term, will be in error by a factor of 0·8—0·9.[8,9] In the present work the experimental data do not go far into the fall-off region and hence inclusion of this term will have minimal effect. Moreover, in these calculations the vibrational assignments for the transition states were made so that the high-pressure rate constant for overall reactions, given by equation (8), were in agreement with the experimental values.

$$k_\infty = L_x \frac{\boldsymbol{k}T}{h}\left(\frac{I_A{}^+I_B{}^+I_C{}^+}{I_AI_BI_C}\right)^{\frac{1}{2}}\frac{P_2{}^+}{P_2}\exp\left(-E_a/RT\right) \quad (8)$$

Therefore, exclusion of the moments of inertia ratio in equation (8) will entail only slight reassignment of the vibrational frequencies of the transition states and the RRKM theory is known to be insensitive to changes in vibrational frequency assignments.[10] In consequence the value of the ratio of the moments of inertia of the transition state and energised molecule were taken as unity in all cases. With this simplification equation (6) becomes:

$$k_x = \frac{L_x}{h}\cdot\frac{\sum\limits_{E_v{}^+ \leqslant E^+} P(E_v{}^+)}{N^*(E^+ + E_a)} \quad (9)$$

Vibrational assignments for spiropentane[11] and methylenecyclobutane[12] have appeared in the literature. Assignments for the latter molecule were improved by reference to several reported vibrational analyses of cyclobutane[13] and to work on ring-puckering vibrations of methylenecyclobutane.[14] A recent RRKM calculation on the thermal decomposition of methylenecyclobutane has appeared[15] in which slightly different vibrational frequencies are used. However the procedure of fitting the experimental rate constant to equation (8) ensures that the effect of these differences (and of differences in the choice of statistical factors) have a minimal effect on the final answer. Vibrational assignments for the transition states were made with reference to previous assignments for groups similar to those in the complexes presently considered, and to mean values for frequencies associated with normal, partial, and 'three electron' bonds as tabulated by Benson.[16] Hindered rotations were treated as torsional vibrations. All frequencies used are tabulated in the Appendix.

For Scheme 1 the transition states adopted were as follows:

T.S. for isomerization of spiropentane to biradical (R) ($L_r = 4$, $L_{-r} = 1$)

(TSR) [fully allylically stabilised; reaction co-ordinate, C–C–C bend in biradical (R)]

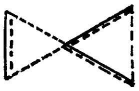
T.S. for cyclization of biradical (R) to methylenecyclobutane ($L_c = L_{-c} = 4$)

(TSC) (fully allylically stabilised; reaction co-ordinate, $\dot{C}H_2CH_2$–allyl torsion)

T.S. for decomposition of biradical (R) ($L_p = 1$)

(TSP) (no allylic stabilisation; reaction co-ordinate, C–C extension)

T.S. for direct decomposition of spiropentane ($L_d = 2$)



(TSD) (no allylic stabilisation).

For Scheme 2 no additional structural assignments of transition states were made. The same vibrational frequencies were adopted for (TSR) and for the transition state for isomerization of spiropentane to methylenecyclobutane, and similarly the vibrational frequencies used for the transition state for decomposition of methylenecyclobutane (TSP′) were the same as those for (TSP).

Vibrational frequencies for (TSR) were chosen so that the rate equation for spiropentane loss, extrapolated to infinite pressure, as measured by Burkhardt[1], *i.e.* $(k_I)_\infty/\text{s}^{-1} = 10^{15\cdot2}\exp(-55{,}500/1\cdot987T)$, gave the same rate constant (at 663·2 K) as calculated from equation (8). Vibrational frequencies for (TSC) were chosen using the rate equation (k_R) measured for the degenerate rearrangement of 2,2-dideuteriomethylenecyclobutane by Doering and Gilbert[2] (see however ref. 17 also).

$$(k_R)_\infty/\text{s}^{-1} = 10^{14\cdot24}\exp(-49{,}880/1\cdot987T)$$

The Arrhenius parameters determined for the decomposition of methylenecyclobutane (k_M) by Burkhardt[1] were used to assign the vibrational frequencies of (TSP). In the latter two instances it was necessary to assume that k_c was much greater than k_p in order to obtain simple

$$(k_M)_\infty/\text{s}^{-1} = 10^{15\cdot8}\exp(-63{,}500/1\cdot987T)$$

expressions for k_∞. With this assumption $k_M = k_{-c}k_p/k_c$

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[9] E. V. Waage and B. S. Rabinovitch, *Chem. Rev.*, 1970, **70**, 377.

[10] M. C. Lin and K. J. Laidler, *Trans. Faraday Soc.*, 1968, **64**, 79; H. M. Frey and B. M. Pope, *ibid.*, 1969, **65**, 441.

[11] D. W. Scott, H. L. Finke, W. N. Hubbard, J. P. McCullough, M. E. Gross, K. D. Williamson, G. Waddington, and H. M. Huffman, *J. Amer. Chem. Soc.*, 1950, **72**, 4664; F. F. Cleveland, M. J. Murray, and W. S. Gallaway, *J. Chem. Phys.*, 1947, **15**, 742.

[12] T. P. Wilson, *J. Chem. Phys.*, 1943, **11**, 369.

[13] G. W. Rathjens, N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Amer. Chem. Soc.*, 1953, **75**, 5634; R. C. Lord and D. G. Rea, *ibid.*, 1957, **79**, 2401; R. C. Lord and I. Nagakawa, *J. Chem. Phys.*, 1963, **39**, 2951.

[14] L. Sharpen and V. W. Laurie, *J. Chem. Phys.*, 1968, **49**, 3041; T. B. Malley, F. Fisher, and R. M. Hedges, *ibid.*, 1970, **52**, 5325.

[15] W. J. Engelbrecht and M. J. De Vries, *J. South African Chem. Inst.*, 1970, **23**, 163, 172, 191.

[16] S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968.

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

and $k_R = k_{-c}$. No experimental data exists for direct decomposition of spiropentane to ethylene and allene and so a minimum value of the pre-exponential factor was selected, *i.e.* $10^{13.9}$ s^{-1}, which at the experimental temperature corresponds to approximately zero entropy of activation.

Heats of formation of spiropentane and methylenecyclobutane were calculated at the experimental temperature from known thermochemical data.[18] The heats of formation of all transition states are defined by the above Arrhenius parameters as

$$\Delta H_f(\mathrm{TSX}) = E_{\mathrm{exp}} - RT \qquad (10)$$

where $\Delta H_f(\mathrm{TSX})$ is the difference in the heats of formation of (TSX) and the reactant molecule at the temperature of the study, and E_{exp} is the experimental activation energy of the reaction. The heat of formation of the biradical (R) was estimated by group additivity.[18] As this value was subject to some uncertainty the effects of changing it were examined. This is equivalent to changing the barrier to cyclization to methylenecyclobutane and to decomposition. All heats of formation used are listed in Table 2.

TABLE 2

Heats of formation and minimum excess energies of species involved in the thermal reactions of spiropentane

	ΔH_f (663 K) [a] (kcal mol^{-1})	$E_{\mathrm{min.}}$ (kcal mol^{-1})
Spiropentane	0	53·2
Methylenecyclobutane	−14·45	67·8
(R)	27·5	28·0
(TSR)	53·7	0
(TSC)	34·1	19·9
(TSP), (TSP′)	47·7	7·5

[a] Relative to spiropentane.

Minimum excess energies ($E_{\mathrm{min.}}$) for each of the energised species, with respect to further reaction, were calculated using equation (11). $\bar{E}_v(\mathrm{TSR})$ and $\bar{E}_v(\mathrm{TSX})$ are the mean thermal vibrational energies of (TSR) and the

$$E_{\mathrm{min.}} = E_{\mathrm{exp}} - \bar{E}_v(\mathrm{TSR}) + \bar{E}_v(\mathrm{TSX}) - RT - \Delta H_f \qquad (11)$$

relevant transition state, respectively. ΔH_f Is the difference between the heats of formation of spiropentane and the reactant molecule or transition state concerned. These values are listed in Table 2. Mean thermal vibrational energies were calculated from equation (12). $E_{\mathrm{min.}}$ Will be numerically equal to E_a, the critical energy

$$\bar{E}_v = \sum_{i=1}^{s} \frac{h\nu_i}{[\exp(h\nu_i/kT) - 1]} \qquad (12)$$

of the initial isomerization, if $\bar{E}_v(\mathrm{TSX})$ is replaced by $\bar{E}_v$(spiropentane) and ΔH_f is set equal to zero in equation (11).

The Whitten and Rabinovitch approximation[19] was used in all cases for evaluation of $N^*(E)$ and for evaluation of $\sum P(E_v^+)$ for transition states that have large minimum excess energies. For the transition state for isomerization of spiropentane to (R) (Scheme 1), or spiropentane to methylenecyclobutane (Scheme 2), where minimum excess energies are zero, the Fowler polynomial method[20] was used. This procedure necessitated the grouping of vibrational frequencies for this transition state into multiples of the lowest frequency. The Whitten and Rabinovitch approximation was used for the transition state for direct decomposition of spiropentane, even though minimum excess energies for this reaction were zero. This reaction is of minor importance and therefore any errors involved in using the approximation were acceptable in the context of the overall calculation.

Values of the rate constants k_x were evaluated from equation (9) at successive intervals of excess energy, E^+, the energy increment being equal to the energy of the lowest frequency of (TSR). The integration of equations (1)—(4) was then carried out by summation, assuming constant values of k_x over each energy range. The summation was terminated at the point where the partition function for (TSR) as computed directly from its vibrational frequencies [equation (12)] was equal to the partition function calculated from the integration of equation (13).

$$P_2^+ = \prod_{i=1}^{s} [1 - \exp(-h\nu_i/kT)]^{-1} \qquad (12)$$

$$P_2^+ = \int_{E^+=0}^{E^+=n\Delta E} \sum P(E_v^+) \exp(-E^+/RT) \,.\, \mathrm{d}(E^+/RT) \qquad (13)$$

k_{-1}M Was taken to be the bimolecular collision frequency with a collision diameter of $5{\cdot}5 \times 10^{-10}$ m; all collisions were assumed to be strong.

RESULTS AND DISCUSSION

Results are summarised in Tables 3 and 4 and Figures 1 and 2. All curves drawn in the figures are based on computed results and have been shifted by 0·6 log units to higher pressures. The computed fall-off curves for loss of spiropentane (not shown) required a similar shift to fit the experimental data, and are identical for both Schemes 1 and 2 as identical transition states were assumed, and the reverse reaction has negligible effect. The shift of 0·6 log units to higher pressures to obtain agreement between theory and experiment is somewhat larger than required in the majority of previous unimolecular reactions studied. It is however similar to that recently obtained for the decomposition of methylenecyclobutane.[15] The reason for this large shift is not clear. Changing frequency assignments of the transition state has very little effect on the position

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[18] 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, *J. Chem. Eng. Data*, 1970, **15**, 266.

[19] G. Z. Whitten and B. S. Rabinovitch, *J. Chem. Phys.*, 1963, **38**, 2466; 1964, **41**, 1883; D. C. Tardy, B. S. Rabinovitch, and G. Z. Whitten, *ibid.*, 1968, **48**, 1427.

[20] R. H. Fowler, 'Statistical Mechanics,' Cambridge University Press, 1936, 2nd edn., ch. 2, pp. 31—33.

of fall-off.[10,15] It is possible that the assumed collision diameter is in error (using a value of $4·5 \times 10^{-10}$ m would shift the curve to higher pressures by 0·2 log units; the collision diameter used in the calculation of the methylenecyclobutane fall-off curve was $5·7 \times 10^{-10}$ m[15]). The assumption of unit collisional deactivation efficiency could well account for part of the residual discrepancy (for a molecule the complexity of spiropentane it is unusual in having no vibrational frequencies below 220 cm^{-1}). Changing the Arrhenius parameters of $k_{\rm I}$, keeping the rate constant fixed at 663·2 K also causes significant changes. Thus increasing the activation energy to 57,330 cal mol^{-1}, with a compensating change of a factor of 4 in the pre-exponential factor, shifts the curve by 0·41 log units to higher pressures. One study of the spiropentane[4] isomerization reported the Arrhenius equation as

$$(k_{\rm I})_\infty/{\rm s}^{-1} = 10^{15·86} \exp(-57{,}570/1·987T)$$

hence it is certainly possible that the 55,500 cal mol^{-1} activation energy used here was somewhat too low. Anharmonicity effects have been concluded to be small for complex molecules[21] but in the absence of quantitative information they may be a contributory cause of the observed shift.

The computed fall-off curves for $k_{\rm I}$ (Figure 1) fit the experimental results for both Schemes 1 and 2. At such pressures that $\omega \ll k_{-{\rm c}}$ the schemes become essentially identical, and when, at higher pressures, this inequality no longer holds the value of $k_{\rm D}$ has already become much smaller than $k_{\rm I}$, and so even quite large fractional changes in decomposition rate do not affect significantly the yields of methylenecyclobutane.

Scheme 1 fits the experimental data for $k_{\rm D}$ well over the entire pressure range, with the rate constant for direct decomposition of spiropentane to ethylene and allene set equal to zero ($k_{\rm d} = 0$). The heats of formation of the biradical (R) as calculated by group additivity and used in the majority of calculations gives an activation energy for cyclization to methylenecyclobutane ($E_{\rm c}$) of 8 kcal mol^{-1}. Changing the heat of formation of (R) so that the barrier is decreased to 5 kcal mol^{-1} shifts the curve for $k_{\rm D}$ on Figure 2, at pressures above 1000 Torr, to higher pressures by *ca.* 0·2 log units. Removal of the direct deactivation of the biradical step is equivalent, for practical purposes, to lowering the activation energy for cyclization to zero. The levelling off of the value of $k_{\rm D}$, at above about 1000 Torr, is due to the rate of loss of the biradical now being governed by the pressure-independent rates of cyclization and decomposition only. At these

TABLE 3

Computed values for $k_{\rm I}$ and $k_{\rm D}$ as a function of pressure at 663·2 K

log (press/Torr)	$-\log_{10}(k_1/{\rm s}^{-1})$					$-\log_{10}(k_{\rm D}/{\rm s}^{-1})$						$(k_{\rm I} + k_{\rm D})/k_\infty$	
	Scheme 1				Scheme 2	Scheme 1				Scheme 2			
	$E_{\rm c} = 5$ kcal mol^{-1}	$E_{\rm c} = 8$ kcal mol^{-1}	$E_{\rm c} = 15$ kcal mol^{-1}	$E_{\rm c} = 8$ kcal mol^{-1} no direct deact. (R)	Without direct decomposition	$E_{\rm c} = 5$ kcal mol^{-1}	$E_{\rm c} = 8$ kcal mol^{-1}	$E_{\rm c} = 15$ kcal mol^{-1}	$E_{\rm c} = 8$ kcal mol^{-1} no direct deact. (R)	No direct decomp.	With direct decomp.	log A = 15·2 (s^{-1}) E = 55·5 kcal mol^{-1}	log A = 15·8 (s^{-1}) E = 57·33 kcal mol^{-1}
5·0	3·108	3·105	3·103	3·129	3·103	5·032	5·431	6·396	4·336	8·815	4·429	1·000	1·000
4·0	3·121	3·115	3·105	3·129	3·103	4·484	4·677	5·437	4·336	7·185	4·428	1·000	1·000
3·0	3·128	3·126	3·114	3·129	3·103	4·350	4·384	4·690	4·333	6·191	4·422	1·000	0·999
2·0	3·132	3·132	3·129	3·132	3·107	4·303	4·307	4·361	4·301	5·235	4·369	0·998	0·994
1·0	3·155	3·155	3·154	3·155	3·134	4·132	4·132	4·140	4·131	5·421	4·128	0·980	0·958
0·0	3·258	3·258	3·258	3·258	3·245	3·809	3·809	3·812	3·809	4·867	3·772	0·896	0·825
−1·0	3·539	3·539	3·538	3·539	3·534	3·606	3·606	3·607	3·606	3·630	3·576	0·680	0·563
−2·0	4·077	4·077	4·076	4·077	4·077	3·655	3·655	3·655	3·655	3·663	3·636	0·387	0·280
−3·0	4·922	4·922	4·922	4·922	4·925	3·949	3·949	3·949	3·949	3·958	3·937	0·158	0·0993
−4·0	6·071	6·070	6·070	6·071	6·076	4·445	4·445	4·445	4·445	4·456	4·438	0·0466	0·0254

TABLE 4

Computed values for $k_{\rm I}$ and $k_{\rm D}$ as a function of pressure at 643·2, 683·2, and 703·2 K (Scheme 1 with $k_{\rm d} = 0$, Scheme **2** with $k_{\rm d}$ as in text)

log (press/Torr)	$-\log_{10}(k_{\rm I}/{\rm s}^{-1})$						$-\log_{10}(k_{\rm D}/{\rm s}^{-1})$					
	643·2 K		683·2 K		703·2 K		643·2 K		683·2 K		703·2 K	
	Scheme		Scheme		Scheme		Scheme		Scheme		Scheme	
	1	2	1	2	1	2	1	2	1	2	1	2
5·0	3·684	3·682	2·560	2·557	2·046	2·043	6·075	5·003	4·823	3·889	4·248	3·381
4·0	3·693	3·682	2·571	2·557	2·058	2·043	5·310	5·002	4·079	3·889	3·515	3·380
3·0	3·704	3·683	2·583	2·558	2·072	2·044	5·007	4·985	3·796	3·880	3·241	3·369
2·0	3·709	3·686	2·586	2·563	2·080	2·050	4·930	4·878	3·718	3·811	3·162	3·284
1·0	3·727	3·707	2·618	2·600	2·114	2·090	4·763	4·561	3·538	3·543	3·978	2·997
0·0	3·817	3·804	2·736	2·722	2·247	2·233	4·423	4·237	3·234	3·201	2·694	2·666
−1·0	4·074	4·069	3·040	3·035	2·574	2·570	4·184	4·132	3·067	3·039	2·563	2·529
−2·0	4·588	4·588	3·602	3·603	3·161	3·161	4·197	4·285	3·150	3·132	2·679	2·622
−3·0	5·413	5·416	4·467	4·470	4·044	4·047	4·463	4·450	3·471	3·460	3·026	3·036
−4·0	6·547	6·553	5·629	5·634	5·219	5·224	4·938	4·931	3·987	3·981	3·561	3·556

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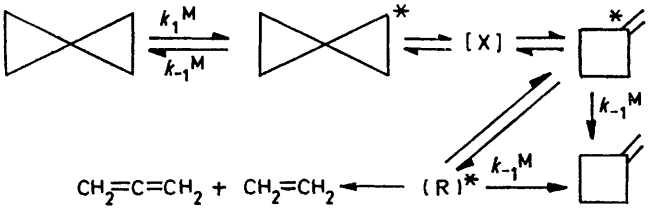
high pressures all methylenecyclobutane molecules, once formed, will be collisionally stabilised. On increasing E_c to 15 kcal mol^{-1} the curve for k_D above 1000 Torr is shifted to lower pressures by *ca.* 1·0 log unit. These changes have essentially no effect on results below 100 Torr. Thus for all reasonable values of E_c a good fit to the experimental data is obtained.

Scheme 2 with k_d set equal to zero produces similar results to Scheme 1 for k_D at the lowest pressures but agreement becomes poor above about 1 Torr. Good agreement was obtained with the experimental results if the following equation for k_d was used:

$$k_d/s^{-1} = 10^{13.9} \exp(-55{,}500/1{\cdot}987T)$$

A modified Scheme 2, in which the allylic biradical mechanism was retained for all reactions of methylenecyclobutane but one in which this biradical was not formed as an intermediate in the conversion of spiropentane into methylenecyclobutane (Scheme 2′) gave virtually identical results to Scheme 2 over the entire pressure range investigated. This scheme could correspond either to a concerted mode of conversion of spiropentane to methylenecyclobutane (the intermediate X is then omitted from the scheme) or, perhaps more reasonably, to the initial formation of a biradical formed by fission of a radial or a peripheral bond of spiropentane, followed by a concerted rearrangement of this biradical to methylenecyclobutane.



SCHEME 2′

Arguments based on the predicted Arrhenius parameters for the spiropentane and methylenecyclobutane reactions support the biradical mechanism.[3,22] Similar calculations for the mechanism based on Scheme 2′ would probably lead to pre-exponential factors for isomerization of spiropentane somewhat smaller than experimentally observed. However the structure of this transition state makes any estimation of the probable pre-exponential factor very unreliable and we have not therefore attempted it.

CONCLUSIONS

Excellent agreement has been obtained between the experimental data and both Scheme 1, with no direct decomposition of spiropentane to allene and ethylene, and Scheme 2, with direct decomposition, over a pressure range spanning six orders of magnitude. A choice between the schemes, merely on the basis of the dependence of the product distribution on pressure, could only be made by studying the reaction at pressures in excess of 10 times those already investigated. At very high pressure Scheme 1 predicts that the rate of decline of k_D as a function of pressure will pass through a minimum and then increase relatively rapidly, whereas Scheme 2 predicts that at very high pressure k_D will become independent of pressure.

APPENDIX

Vibrational frequency assignments (cm^{-1}). Spiropentane: 272, 305(2), 581, 778(2), 852, 870, 872, 896(2), 993, 1033, 1053(2), 1150, 1157(2), 1200(2), 1397, 1430(2), 1500(2), 2990(4), 3050(4).

Methylenecyclobutane: 90, 354, 373, 657, 728(2), 750, 782, 879, 895, 954, 991, 1029, 1059, 1070, 1155, 1167, 1197, 1220, 1248, 1395, 1415, 1425, 1490, 1675, 2826, 2860, 2902, 2921, 2952, 2985(2), 3072.

Biradical (R): 50, 100, 350(2), 420(3), 635, 800(4), 1000(2), 1150(5), 1300(2), 1450(4), 3000(8).

Transition state (TSR): 150, 300(3), 450(2), 600, 750(4), 1050(2), 1200(5), 1350(2), 1500(4), 3000(8).

Transition states (TSP), (TSP′): 25, 225(2), 290, 350(2), 435, 635, 750(4), 1000, 1150(4), 1300(2), 1450(4), 1652, 3000(8).

Transition state (TSC): 150, 300, 350(2), 635, 750(2), 800(2), 900(2), 1000(2), 1150(5), 1300, 1320, 1500(4), 3000(8).

Transition state (TSD): 150, 300(2), 600, 800(2), 896(2), 900(2), 1000(2), 1050(3), 1200(5), 1500(4), 3000(8).

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