# Current Aspects of Unimolecular Reactions

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## 1 Introduction

Although a unimolecular reaction is in principle the simplest kind of elementary reaction, work on such reactions both experimental and theoretical, continues to expand at an ever-increasing rate. The RRKM theory, which was the main subject of two books on unimolecular reactions[1,2] published ten years ago, continues to dominate the field largely because of the relative ease of application compared with other theories, although doubts about its applicability in certain cases have been expressed.[3] Modifications to RRKM theory have also proved to be necessary among other things to interpret experiments using crossed molecular beams where dynamical features need to be considered, and to incorporate tunnelling effects.[4]

Reviews covering both the experimental[5,6] and theoretical[7-9] aspects of unimolecular reactions have appeared during the last ten years as well as reviews on unimolecular ion decompositions[10,11] and laser-induced unimolecular reactions.[12,13] The present review is concerned more with experiment than with theory and in keeping with the declared policy of *Chemical Society Reviews* is intended for the non-specialist as well as the specialist in this field. The coverage is selective and examples are chosen to illustrate particular aspects of current research. This inevitably reflects the author's personal interests and for this reason the coverage of thermally induced unimolecular reactions in their high-pressure regions is fairly comprehensive and includes most of the papers

[1] P. J. Robinson and K. A. Holbrook, 'Unimolecular Reactions', Wiley, N. York, 1972.
[2] W. Forst, 'Theory of Unimolecular Reactions', Academic Press, N. York, 1973.
[3] See for example, D. B. Olson and W. C. Gardiner, Jr., *J. Phys. Chem.*, 1979, **83**, 922.
[4] (a) L. Holmlid and K. Rynefors, *Chem. Phys.*, 1981, **60**, 393 and refs. cited therein.
  (b) W. H. Miller, *J. Am. Chem. Soc.*, 1979, **101**, 6810.
[5] P. J. Robinson in 'Reaction Kinetics', A Specialist Periodical Report, ed. P. G. Ashmore, The Chemical Society, London, 1975, Vol. 1, p. 93.
[6] H. M. Frey and R. Walsh in 'Gas Kinetics and Energy Transfer', A Specialist Periodical Report, ed. P. G. Ashmore and R. J. Donovan, The Chemical Society, London, 1978, Vol. 3, p. 1.
[7] M. Quack and J. Troe in 'Gas Kinetics and Energy Transfer', A Specialist Periodical Report, ed. P. G. Ashmore and R. J. Donovan, The Chemical Society, London, 1977, Vol. 2, p. 175.
[8] J. Troe, *Nova Acta Leopold.*, 1979, **49**, 63.
[9] W. L. Hase in 'Potential Energy Surfaces and Dynamics Calculations', ed. D. G. Truhlar, Plenum, N. York, 1981, p. 1.
[10] A. G. Brenton, R. P. Morgan, and J. H. Beynon, *Ann. Rev. Phys. Chem.*, 1979, **30**, 51.
[11] J. L. Franklin in 'Gas Phase Ion Chemistry', ed. M. T. Bowers, Academic Press, N. York, 1979, Vol. 1, p. 273.
[12] N. Bloembergen and E. Yablonovitch in 'Laser-induced Processes in Molecules', ed. K. L. Kompa and S. D. Smith, Springer-Verlag, Berlin, 1979, p. 117.
[13] R. G. Harrison and S. R. Butcher, *Cont. Phys.*, 1980, **21**, 19.

appearing between 1978 (covered by the review of Frey and Walsh[6]) and about the middle of 1981. The format of this review follows that of the earlier reviews on this subject, which are cited above, and like those is restricted largely to reactions of neutral gas phase species.

## 2 Theoretical Aspects

An energized molecule A* can decompose unimolecularly (reaction 1)

$$A^* \xrightarrow{\ k(E)\ } \text{Products} \tag{1}$$

or be de-energized by collision with another molecule M (where M may be a reactant molecule or molecule of an added unreactive gas) (reaction 2).

$$A^* + M \xrightarrow{\ k_2\ } A + M \tag{2}$$

Energized molecules A* may be produced thermally (with a Boltzmann distribution of energies) or by non-thermal methods such as chemical activation, photoactivation, and more recently multiphoton (laser) excitation. For a thermally energized reaction the overall unimolecular rate constant $k_{uni}$ is given by the expression

$$k_{uni} = \int_{E_0}^{\infty} \frac{k(E)}{1 + k(E)/k_2[M]} \cdot f(E)\,dE \tag{3}$$

where $E_0$ is the critical energy for the reaction, $f(E)\,dE$ is the thermal Boltzmann distribution function given by

$$f(E)\,dE = \frac{N(E)e^{-E/RT}\,dE}{\int_0^{\infty} N(E)e^{-E/RT}\,dE} \tag{4}$$

and the microscopic rate constant $k(E)$ at energy $E$ may be calculated from the RRKM expression
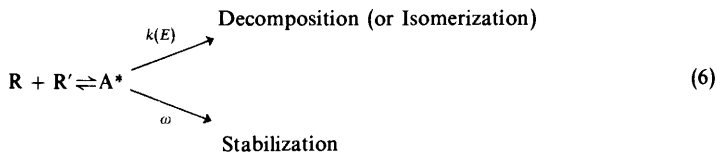
$$k(E) = \frac{L^+ \Sigma P(E_{vr}^+)}{\hbar F N(E)} \tag{5}$$

in which $L^+$ is reaction path degeneracy, $\Sigma P(E_{vr}^+)$ is the sum of the vibrational-rotational states of the activated complex, $N(E)$ is the density of such states for the energized molecule, and $F$ is a correction factor for adiabatic rotations.[14] Computer programs exist which permit the evaluation of the energy quantities $\Sigma P(E_{vr}^+)$ and $N(E)$ provided that a prior assignment of vibration frequencies to the activated complex and the energized molecule can be made.[15]

In a chemically activated system, an energized molecule is produced with

[14] See ref. 1, Chapter 4.
[15] See ref. 1, Chapter 6 for details, also W. L. Hase and D. L. Bunker, Quantum Chemistry Program Exchange Cat. No. QCPE-234; S. E. Stein and B. S. Rabinovitch, *J. Chem. Phys.*, 1973, **58**, 2438; S. E. Stein and B. S. Rabinovitch, *Chem. Phys. Lett.*, 1977, **49**, 183.

sufficient energy to enable it to undergo subsequent unimolecular isomerization or decomposition, for example by an exothermic recombination of two radicals

$$R + R' \rightleftharpoons A^* \quad \begin{array}{c} \xrightarrow{k(E)} \text{Decomposition (or Isomerization)} \\ \\ \xrightarrow{\omega} \text{Stabilization} \end{array} \qquad (6)$$

where $\omega$ is the gas-kinetic collision frequency. RRKM treatment of the reaction scheme above, including the postulation of an activated complex for the process of producing $A^*$, leads to an expression permitting the calculation of the energy distribution function $f(E)dE$. The results show that chemically activated molecules are produced with a very much narrower spread of energies than those produced by thermal energization.[16]

Recently, many unimolecular reactions have been studied in which the energized reactant molecules have been produced by multiphoton absorption of infrared laser radiation.[17] There is at present a lack of agreement about the form of the distribution function applicable to the molecules energized in this way. Thus, Jenson, Steinfeld, and Levine[18] have concluded that a model based on maximal entropy can produce either a Poisson or a Boltzmann distribution of vibrational energy following multiple photon excitation and Colussi, Benson, Hwang, and Tiee have found a very narrow energy distribution in the multiphoton dissociation of $CH_2DCH_2Cl$.[19]

As an alternative to the RRKM formulation of $k(E)$ in equation (5), Forst[20] showed how this rate constant could be recovered by the process of deconvolution from the high pressure rate constant $k_\infty$. This leads to equation (7),

$$k(E) = \frac{A_\infty N(E - E_\infty)}{N(E)} \qquad \text{for} \qquad E > E_0 \qquad (7)$$

where $A_\infty$ and $E_\infty$ are the high pressure Arrhenius parameters. This equation has proved to be extremely useful in enabling the fall-off curves to be predicted without any assumed model of the activated complex and Forst has recently[21] listed a number of papers including applications of his method. The method is only strictly valid in the upper regions of the fall-off curve and requires accurate calculation of the energy densities involved. In its original form it also assumes that $A_\infty$ and $E_\infty$ are independent of temperature, which in principle they are not, but in practice the deviation may not be important. Yau and Pritchard[22] have tested the Forst procedure by comparing the predicted

[16] See ref. 1, p. 274.

[17] R. V. Ambartzumian and V. S. Letokhov 'Chemical and Biochemical Applications of Lasers', ed. C. B. Moore, Academic Press, N. York, 1977, vol. 3.

[18] C. C. Jenson, J. I. Steinfeld, and R. D. Levine, *J. Chem. Phys.*, 1978, **69**, 1432.

[19] A. J. Colussi, S. W. Benson, R. J. Hwang, and J. J. Tiee, *Chem. Phys. Lett.*, 1977, **52**, 349.

[20] W. Forst, *J. Phys. Chem.*, 1972, **76**, 342.

[21] W. Forst, *J. Phys. Chem.*, 1979, **83**, 100.

[22] A. W. Yau and H. O. Pritchard, *Can. J. Chem.*, 1979, **57**, 2458.

reaction rates with theoretical calculations for the reactions $N_2O \rightarrow N_2 + O$ and $CO_2 \rightarrow CO + O$. For these reactions, which adhere well to the Arrhenius law, the approximations in the Forst procedure were considered to be reasonable. The situation may be different at high temperatures such as those involved in shock tube experiments. Forst[21] has taken some data of Tsang[23] for the decomposition of n-butane into two ethyl radicals and fitted them to the expression

$$k_\infty = A'_\infty (\mathbf{k}T)^n e^{-E'_\infty/\mathbf{k}T} \tag{8}$$

In a more recent paper, Forst and Turrell[24] have fitted the same data to the expression

$$k_\infty = A'_\infty e^{B\mathbf{k}T} e^{-E'_\infty/\mathbf{k}T} \tag{9}$$

where $B$ is a constant, found to be negative. The exponential expression leads to a larger temperature dependence of $A'_\infty$ and $E'_\infty$ and calculations for a temperature of 2500 K (actually well above the range of Tsang's experiments) produces a $k_\infty$ value smaller by a factor of 4.5 than that from the normal Arrhenius equation. The implications for the fall-off curves, *i.e.* log $(k_{uni}/k_\infty)$ *versus* log pressure, deduced from such temperature-dependent parameters are discussed. Use of expression (9) produces more curvature in the fall-off plot and a bigger decline of activation energy with pressure. Forst has drawn attention to the need for consideration of these points in extrapolating values of high pressure Arrhenius parameters from measurements made in the fall-off region. Many such examples are quoted later in this review.

Much recent work on unimolecular reactions has involved the formulation of the processes involved in terms of the so-called master equation. This involves writing the steady state concentration of molecules in the $i^{th}$ energy level $(n_i)$ as the equation

$$\frac{dn_i}{dt} = R_i + \Sigma_j z_j P_{ij} n_j - \Sigma_j z_i P_{ji} n_i - k_i n_i = 0 \tag{10}$$

where the first two terms on the right-hand side refer to the rate of non-collisional input and collisional input respectively into level $i$, and the last two terms represent collisional transfer from level $i$ to level $j$ and unimolecular reaction with the microscopic rate constant $k_i$. The complete master equation represents a series of equations of type (10) one for each energy level $i$ which must hold simultaneously subject to the overall conditions

$$\Sigma_j P_{ji} = 1 \tag{11}$$

and

$$\frac{P_{ji}}{P_{ij}} = \frac{n_j}{n_i} = \frac{g_j}{g_i} \exp[-(E_j - E_i)/\mathbf{k}T] \tag{12}$$

[23] W. Tsang, *Int. J. Chem. Kinet.*, 1978, **10**, 821.
[24] W. Forst and S. Turrell, *Int. J. Chem. Kinet.*, 1981, **13**, 283.

The quantity $P_{ji}$ represents the collisional transfer probability from level $i$ into level $j$ and hence equation (11) represents the condition that all transitions from level $i$ must end in some other level $j$ and equation (12) represents the condition for equilibrium between a given pair of levels $i$ and $j$ for which $g$ represents degeneracy and $E$ energy of the appropriate levels. In principle, the complete master equation can be solved by matrix methods and the steady state populations $n_1, n_2, \ldots, n_n$ and the rate of reaction can be calculated. In practice, to simplify the solution of the large matrices involved, the energy levels are 'grained' into blocks and are often solved by iterative methods for different models of the transition probabilities. This approach has proved to be necessary in particular to take into account 'weak collisions'. Such collisions may be defined as those in which a colliding partner removes an amount of energy less than $kT$, and these are particularly important for highly energized molecules produced by non-thermal energization methods where many collisions may be needed to reduce the energy of the molecule to a value below the critical energy $E_0$. For further details the reader is referred to reference 1 (Chapter 10 and the references cited therein).

In addition to the necessity of formulating the master equation in order to consider weak collisions, there are many other applications where this approach is necessary, particularly for non-thermal energization processes. Recent treatments of multiphoton absorption processes are for example similarly formulated in terms of rate equations which in this case incorporate absorption and stimulated emission processes between the various levels.[25-27]

Yau and Pritchard have now provided some analytical solutions to their master equation version of unimolecular reaction theory[28,29] for particular transition probability models[30] and Singh and Pritchard[31] have recently derived an improved equation for the unimolecular rate constant which should prove easier to use than the original version.

Troe has extended his reformulation of the statistical adiabatic channel model of unimolecular reactions to cover thermal reactions at high pressures.[32] This simplified version of the earlier theory presented by Quack and Troe[33-35] is based on a two-parameter characterization of the potential energy surface, and calculations for the high-pressure reverse-recombination rate constants are shown to be in reasonable agreement both with experiment and with calculations based on the exact theory. To facilitate further application of the theory, full details of the calculations for the $C_2H_6 \rightleftharpoons 2CH_3$ system are given.

[25] E. R. Grant, P. A. Schulz, Aa. S. Sudbo, and Y. T. Lee, *Phys. Rev. Lett.*, 1978, **40**, 115.
[26] M. Quack, *J. Chem. Phys.*, 1978, **69**, 1282.
[27] M. Quack, *Ber. Bunsenges. Phys. Chem.*, 1979, **83**, 757.
[28] A. W. Yau and H. O. Pritchard, *Can. J. Chem.*, 1978, **56**, 1389.
[29] A. W. Yau and H. O. Pritchard, *Can. J. Chem.*, 1980, **58**, 626.
[30] A. W. Yau and H. O. Pritchard, *Can. J. Chem.*, 1979, **57**, 1723.
[31] S. R. Singh and H. O. Pritchard, *Chem. Phys. Lett.*, 1980, **73**, 191.
[32] J. Troe, *J. Chem. Phys.*, 1981, **75**, 226.
[33] M. Quack and J. Troe, *Ber. Bunsenges. Phys. Chem.*, 1974, **78**, 240.
[34] M. Quack and J. Troe, *Ber. Bunsenges. Phys. Chem.*, 1975, **79**, 170.
[35] M. Quack and J. Troe, *Ber. Bunsenges. Phys. Chem.*, 1975, **79**, 469.

This theory is particularly relevant to bond-fission reactions and the reverse radical recombinations.

Troe[36] has also presented a simplified treatment of reactions in the fall-off region between high and low pressure limits in terms of reduced fall-off curves of $k/k_\infty$ *versus* $k_0/k_\infty$ where $k$ is the general-pressure first-order rate constant and $k_0$ and $k_\infty$ are its limiting forms at low and high pressures. According to Lindemann–Hinshelwood theory, $k/k_\infty$ is a function of $k_0/k_\infty$, *i.e.*

$$k/k_\infty = F_{LH}(k_0/k_\infty) = \frac{k_0/k_\infty}{1 + k_0/k_\infty} \qquad (13)$$

Fall-off curves predicted by the Kassel theory are broader (*i.e.* show more gradual change of curvature) than those from the simple expression above and can be represented by introduction of a broadening factor assuming strong collisions, $F_{SC}(k_0/k_\infty)$ (see Figure 5 of reference 36). A further broadening is caused by weak collisions represented by the factor $F_{WC}(k_0/k_\infty)$.

Hence $$k/k_\infty = F_{LH}(k_0/k_\infty)F_{SC}(k_0/k_\infty)F_{WC}(k_0/k_\infty) \qquad (14)$$

Troe has given expressions for $F_{SC}(k_0/k_\infty)$ and $F_{WC}(k_0/k_\infty)$ which can be derived from experimentally accessible parameters such as the high and low pressure activation energies and the collision efficiency $\beta_c$ (see Section 4). A further correction can be made in order to represent the shape expected from a full RRKM fall-off calculation. Illustrative examples which show the ease with which such calculations can be done are given in reference 36. This method has also been used in a recent compilation of rate constants for combination/dissociation processes.[37]

Theoretical calculations of potential energy surfaces, activation energy barriers, and transition state structures have continued to be of interest to quantum chemists. New techniques are being devised to locate the saddle point on the potential energy surface[38,39] and some progress is claimed in the estimation of vibration frequencies from *ab initio* calculations of the activated complex in the isomerization of methyl isocyanide.[40] Calculations[41] of a similar kind for the decomposition of formaldehyde coupled with experimental measurements of the rate of decomposition of photoexcited formaldehyde* have shown that decomposition occurs at energies about 20—40 kJ mol$^{-1}$ below the most accurate *ab initio* calculation of the activation barrier, implying that the reaction occurs almost entirely by tunnelling. Tunnelling has also been studied theoretically in the isomerization of HNC to HCN.[42] Kato and Morokuma have carried

* $H_2CO \rightarrow H_2 + CO$

[36] J. Troe, *J. Phys. Chem.*, 1979, **83**, 114.
[37] D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, *J. Phys. Chem. Ref. Data*, 1980, **9**, 295.
[38] P. Pulay in 'Application of Electronic Structure Theory' (Modern Theoretical Chemistry, Vol. 4, ed. H. F. Schaefer), Plenum, N. York, 1977, p. 153.
[39] M. J. Rothman and L. Lohr, Jr., *Chem. Phys. Lett.*, 1980, **70**, 405.
[40] P. Saxe, Y. Yamaguchi, P. Pulay, and H. F. Schaefer III, *J. Am. Chem. Soc.*, 1980, **102**, 3718.
[41] S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaefer III, *J. Am. Chem. Soc.*, 1981, **103**. 1900.
[42] S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaefer III, *J. Chem. Phys.*, 1980, **73**, 2733.

out a series of extensive studies using *ab initio* molecular orbital methods to determine the geometries of reactants, products, and transition states. Normal mode analysis of these, when allied to RRKM calculations, enabled predictions of rate constants and energy partitioning among the products. In this way they have examined the decompositions of ethyl fluoride,[43] vinyl fluoride,[44] and the fluoroethyl radical.[45]

Although it is clear that quantum mechanical calculations of the complete multidimensional potential energy surface for a polyatomic molecule and precise determinations of activation energies are still a long way off, the methods employed by these authors in concentrating upon particularly important regions of the potential energy surface are clearly yielding some valuable results. A recent selective review of *ab initio* methods of calculation of potential barriers in unimolecular rearrangements highlights some of the current problems.[46]

Recent work on the theory of unimolecular reactions can be broadly classified into attempts to modify the RRKM theory or to produce forms applicable to particular purposes, and attempts to devise new theories. Apart from those RRKM modifications already mentioned, Doll[47] has described a method for making anharmonic corrections to RRKM theory using Monte Carlo techniques and has also[48] used Monte Carlo methods to calculate unimolecular rate constants by a method reminiscent of early Slater theory[49] although without the restrictive conditions. Pritchard *et al.*[50] have interestingly gone back to a fore-runner of Slater theory, namely the dynamical theory of Polanyi and Wigner[51] and recast it in quantum terms. In this theory, reaction occurs when a critical amount of energy accumulates in a particular oscillator; if it does so, then decomposition will occur within the vibrational period of that oscillator. For either a harmonic or a Morse oscillator this is given by

$$\tau = (2c v_r)^{-1} \qquad (15)$$

where $c$ is the velocity of light and $v_r$ the wave number for the particular oscillator.

The microscopic rate constant $k(E)$ is then given by

$$k(E) = 2c v_r \alpha(E) \qquad (16)$$

where $\alpha(E)$ is the fraction of molecular states decomposing within the period $\tau$. This fraction can be calculated statistically from the energy densities of the molecule and the 'sub-molecule' with oscillator $r$ removed.

This simple theory can be extended to s oscillators and Pritchard *et al.* have

[43] S. Kato and K. Morokuma, *J. Chem. Phys.*, 1980, **73**, 3900.
[44] S. Kato and K. Morokuma, *J. Chem. Phys.*, 1981, **74**, 6285.
[45] S. Kato and K. Morokuma, *J. Chem. Phys.*, 1980, **72**, 206.
[46] C. E. Dykstra, *Ann. Rev. Phys. Chem.*, 1981, **32**, 25.
[47] J. D. Doll, *Chem. Phys. Lett.*, 1980, **72**, 139.
[48] J. D. Doll, *J. Chem. Phys.*, 1981, **74**, 1074.
[49] See ref. 1, Chapter 2.
[50] H. O. Pritchard, G. M. Diker, and A. W. Yau, *Can. J. Chem.*, 1980, **58**, 1516.
[51] M. Polanyi and E. Wigner, *Z. Phys. Chem.*, 1928, **139**, 439.

shown that $k(E)$ values thus calculated can agree well with those predicted by more elaborate calculations for the methyl isocyanide isomerization. Calculations using the present procedure are very sensitive to the choice of the reactive oscillator or oscillators and, as realized by the authors, this can be both an advantage and a disadvantage. Clearly more work on the factors governing this choice is necessary if the method is to have wider application.

The quantum version of RRK theory has also received some attention lately, particularly in connection with the interpretation of multiphoton dissociation experiments where the experiments do not permit a distinction between RRK and RRKM predictions.[52,53]

Other contributions to unimolecular theory have been made by Lindenberg *et al.*[54] and by Kay[55] and the absolute-rate theory (or transition-state theory) has also been re-assessed.[56]

**3 Intramolecular Energy Transfer**
A key assumption of statistical unimolecular theories such as the RRKM theory is that following excitation, rapid intramolecular vibrational and rotational energy redistribution occurs in a time which is short compared with the time for dissociation or isomerization.

This assumption has been tested in the past by chemical activation experiments which produce initially a non-random distribution of energy. The subsequent rate of randomization (or relaxation) was then measured (in carefully designed experiments) relative to the rate of de-energization by collision. In such experiments for example, Rabinovitch and co-workers[57-59] by assuming an exponential rate of energy randomization found a relaxation constant of about $10^{12}$ s$^{-1}$ and it is now customary to assume that randomization normally occurs within $10^{-11}$ to $10^{-12}$ seconds.[5,6]

The question of whether intramolecular energization processes are rapid or not nevertheless continues to be raised and probed by a variety of experimental techniques. An excellent review of recent experimental work has been given by Oref and Rabinovitch[60] who have concluded that little evidence for non-statistical behaviour exists, particularly for polyatomic species with moderate to high levels of excitation.

A molecule which obeys the assumption of RRKM theory stated above is variously described as an RRKM-type molecule or a 'statistical' molecule and its behaviour loosely as RRKM-like, statistical, random, stochastic, or ergodic

[52] E. Thiele, J. Stone, and M. F. Goodman, *Chem. Phys. Lett.*, 1980, **76**, 579.
[53] J. Stone, E. Thiele, M. F. Goodman, J. C. Stephenson, and D. S. King, *J. Chem. Phys.*, 1980, **73**, 2259.
[54] V. Seshadri, B. J. West, and K. Lindenberg, *J. Chem. Phys.*, 1980, **72**, 1145.
[55] K. G. Kay, *J. Chem. Phys.*, 1978, **69**, 434.
[56] D. M. Golden, *J. Phys. Chem.*, 1979, **83**, 108.
[57] J. D. Rynbrandt and B. S. Rabinovitch, *J. Phys. Chem.*, 1971, **75**, 2164.
[58] B. S. Rabinovitch, J. F. Meagher, K. J. Chao, and J. R. Barker, *J. Chem. Phys.*, 1974, **60**, 2932.
[59] A. N. Ko, B. S. Rabinovitch, and K. J. Chao, *J. Chem. Phys.*, 1977, **66**, 1374.
[60] I. Oref and B. S. Rabinovitch, *Acc. Chem. Res.*, 1979, **12**, 166.

although the precise meanings of these terms differ. Hase and Bunker[61] originally defined non-RRKM-behaviour as either apparent or intrinsic. Apparent non-RRKM-behaviour can arise when the reaction time is particularly short, but such a molecule might well show RRKM-behaviour towards a different reaction channel if one were available. Intrinsic non-RRKM-behaviour on the other hand can never lead to RRKM-behaviour since there is an inherent weak coupling between the oscillators in the molecule (or, in phase-space parlance, a 'bottleneck' to the energy flow). Some of the early discussion on whether $CH_3NC$ is a non-RRKM molecule or not has now been resolved.[60]

Richardson and Simons[62] have described experiments on energy randomization in a molecule they regard as 'more typical' than that studied by Rynbrandt and Rabinovitch.[57] Methylene ($CH_2{}^1A_1$) was made to react with methyl [$^2H_3$]silane to give [$^2H_1$]methyl methyl [$^2H_2$]silane (Scheme 1). Because of its mode of

$$CH_3SiD_2CH_2D$$

$$\omega$$

$$CH_3SiD_2CH_2D^*$$

and/or

$$CH_2D_2 + :Si$$

$$CH_3D + :Si$$
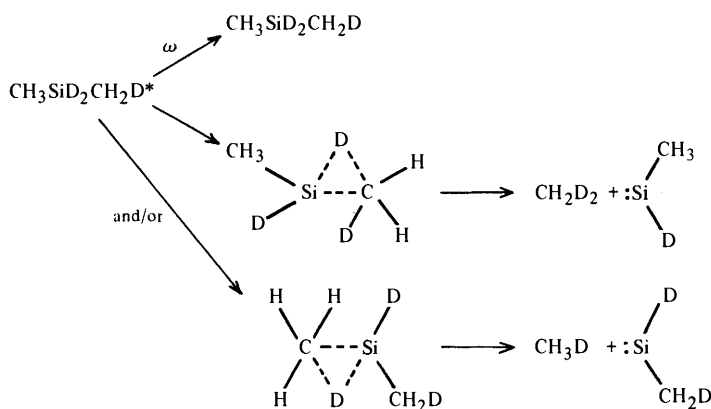
**Scheme 1**

formation, excess energy initially would be expected to be located in the $CH_2D$ part of the molecule. At high pressures, assuming strong collisions, excess energy would be removed before energy randomization could occur and any product would result from elimination of $CH_2D$ leading to $CH_2D_2$. Randomization of energy would also produce elimination of $CH_3$ to give $CH_3D$. The ratio of $CH_3D$ to $CH_2D_2$ was found to be reasonably constant with pressures up to 4 atmospheres, corresponding to a lifetime of $1.7 \times 10^{-11}$ seconds, thus indicating virtual complete randomization within this time.

In contrast to this, work on another type of reaction, the 1—5 H-atom shift in the isomerization of *cis*-3-methyl-[1,2-$^2H_2$]penta-1,3-diene has provided some evidence for non-randomization with a relaxation constant of about $4 \times 10^{-11}$ seconds.[63] This molecule was generated from the cross-combination of

[61] W. L. Hase and D. L. Bunker, *J. Chem. Phys.*, 1973, **59**, 4621.

[62] T. H. Richardson and J. W. Simons, *Int. J. Chem. Kinet.*, 1978, **10**, 1055.

[63] T. Ibuki and S. Sugita, *J. Chem. Phys.*, 1979, **70**, 3989.

$CH_3CH{=}CCH_3$ and $CD{=}CHD$ radicals which produces the *cis*-isomer having about $512 \, kJ \, mol^{-1}$ excitation energy. The rate constant for isomerization to *cis*-3-methyl-[4,5-$^2H_2$]penta-1,3-diene was measured relative to the rate of collisional stabilization at pressures up to 2006 Torr. At low pressures ($\sim 216$ Torr) the rate constants agreed with RRKM calculations of $k(E)$ based on known high pressure Arrhenius parameters, but at high pressures a fall in rate constant for isomerization was observed. It was argued that at these collision times the excitation energy cannot reach the isomerizing $C{-}H$ bond before collisional stabilization occurs.

Oref and Rabinovitch[60] have pointed out that non-randomization is more likely to be observed at lower levels of excitation when the relaxation constant is lower and may no longer compete with the rate of unimolecular reaction. In this connection it is interesting to note the recent experiments of Bauer and True[64] on a low energy process ($E_a \simeq 42 \, kJ \, mol^{-1}$), the conformational $syn \rightleftharpoons anti$ isomerization of methyl nitrite. This process was followed by n.m.r. line-width measurements at pressures up to 100 Torr. Under these conditions the reaction is unimolecular in its second-order region as predicted by theory. The rate determining step is the rate of energization and experimental values for the rate constant of this process were compared with the predictions of RRKM and Slater theories. Agreement was obtained with the RRKM calculations which could be taken to imply rapid randomization of energy even for molecules with low energy barriers and low densities of states.

Some specific evidence for non-randomization of energy has come from experiments using non-thermal energization. Hamer and Huber[65] for example have recently reported evidence that photoactivated cyclic aliphatic ketones such as cyclopentanone and cycloheptanone undergo dissociation from higher vibrational levels of the lowest triplet-state faster than relaxation occurs from this state. Reddy and Berry[66] have photoactivated allyl isocyanide at selective sites in the molecule using a CW dye laser producing CH stretch overtone excitations. Rate constants (determined from the slopes of Stern–Volmer plots) showed deviation from RRKM calculated values at the appropriate energy and depended on the mode of excitation. This last example is a rare example of 'mode-selective' behaviour which has been the motivation for much experimental work in the field of multiphoton infrared excitation. Other possible examples of mode-specific chemistry have been observed by Zare and co-workers[67] and by Hall and Kaldor.[68]

The criteria governing mode specificity and the related problem of intramolecular energy randomization have been clearly explained by Waite and Miller in a recent paper.[69] In this paper they show that the question of intramolecular

[64] S. H. Bauer and N. S. True, *J. Phys. Chem.*, 1980, **84**, 2507.

[65] E. Hamer and J. R. Huber, *Chem. Phys. Lett.*, 1978, **55**, 543.

[66] K. V. Reddy and M. J. Berry, *Chem. Phys. Lett.*, 1979, **66**, 223.

[67] R. Naaman, D. M. Lubman, and R. N. Zare, *J. Chem. Phys.*, 1979, **71**, 4192.

[68] R. B. Hall and A. Kaldor, *J. Chem. Phys.*, 1979, **70**, 4027.

[69] B. A. Waite and W. H. Miller, *J. Chem. Phys.*, 1980, **73**, 3713.

energy randomization as such, is not the prime factor of interest and state that 'what matters for mode specificity is the rate of intramolecular energy transfer compared to the rate of the chemistry of interest, not the question of ergodicity in an infinite time limit'. In a subsequent paper[70] the same authors have calculated energies and lifetimes by quantum mechanical methods for metastable states of a particular potential energy surface (the Henon–Heiles P.E. surface). This is a surface for which the classical dynamics is known to change from quasi-periodic at low energies to ergodic at high energies. Despite this it was found that rate constants for unimolecular decay were well represented by RRKM calculations over the entire energy range, confirming the view that mode specificity is not solely determined by the degree of ergodicity of the intra-molecular dynamical behaviour.

Dynamical behaviour has, however, been the subject of much study of classical trajectories on various potential energy surfaces. For example, Wolf and Hase[71] have used classical trajectories to investigate the internal dynamics of the model molecule $H-C-C$. Two different anharmonic potential energy surfaces were studied which exhibited intrinsic non-RRKM lifetimes and gave a large number of quasi-periodic trajectories at energies above the threshold for $H-C-C \rightarrow H + C=C$. Trajectory studies have also been used to study energy partitioning, in this case the distribution of translational energy among the product fragments. Hase[72] found that for classical trajectory calculations on the molecule $Cl-C\equiv C-H$ it was possible with random or non-random excitation of either HCC or ClCC modes to produce random (*i.e.* RRKM) or non-RRKM lifetime distributions.[73] Despite this, the average translational energies were the same, irrespective of the type of excitation, indicating that observation of statistical relative translational energy distributions does not necessarily imply complete intramolecular vibrational energy transfer. Relatively few quantum dynamical studies of energy transfer have been made compared with classical studies. One problem is the definition of ergodicity from a quantum standpoint, and this has received some attention in recent papers.[74–76]

In conclusion, the generally confusing picture of the intramolecular energy-transfer process which has arisen from a variety of experimental techniques over the last few years is gradually being clarified. This is an area in which careful planning of experiments is particularly necessary in order to avoid ambiguity of interpretation. The role of collisions in assisting intramolecular energy randomization is still unclear and may be circumvented by excitation under suitable collision-free conditions, *e.g.* in laser-induced reactions at sufficiently

[70] B. A. Waite and W. H. Miller, *J. Chem. Phys.*, 1981, **74**, 3910.

[71] R. J. Wolf and W. L. Hase, *J. Chem. Phys.*, 1980, **73**, 3779.

[72] W. L. Hase, *Chem. Phys. Lett.*, 1979, **67**, 263.

[73] For an excellent illustration of the difference, see the review by W. J. Chesnavitch and M. T. Bowers in 'Gas Phase Ion Chemistry', ed. M. T. Bowers, Academic Press, N. York, 1979, Vol. 1, p. 119.

[74] E. J. Heller, *J. Chem. Phys.*, 1980, **72**, 1337.

[75] D. W. Noid, M. L. Koszykowski, M. Tabor, and R. A. Marcus, *J. Chem. Phys.*, 1980, **72**, 6169.

[76] D. W. Noid, M. L. Koszykowski, and R. A. Marcus, *Ann. Rev. Phys. Chem.*, 1981, **32**, 267.

low pressures, or in molecular beam experiments. Energy distribution in the unimolecular decompositions of ions has been recently reviewed,[11] as has the production of ions in selected internal energy states, by the method of photoion–photoelectron coincidence,[77] and some non-statistical energy distributions have been reported.

It is to be hoped that as more data on measured relaxation constants are obtained, it will be possible to establish more clearly their dependence on the energy content and structure of the excited molecules as Oref and Rabinovitch[60] have done with the limited data available at present.

### 4 Intermolecular Energy Transfer

The rate-determining step in a unimolecular reaction at low pressures with thermal energization is the second-order collisional process

$$A + M \rightarrow A^* + M \qquad (-2)$$

Direct measurements of the rate of reaction in this region enable the collisional efficiencies of various bath gas molecules M to be determined. The collisional efficiency per unit collision, $\beta_c$, can then be defined by the equation

$$k_0 = \beta_c k_0{}^{sc} \qquad (17)$$

where $k_0$ is the limiting value of the first-order rate constant $k_{uni}$ at low pressures, and $k_0{}^{sc}$ is the 'strong collision' value of this rate constant which is obtained from equation (3) by writing $k_2[M] \ll k(E)$ and $k_2[M] =$ collision frequency $\omega$, hence

$$k_0{}^{sc} = \omega \int_{E = E_0}^{\infty} f(E)dE \qquad (18)$$

where $f(E)dE$ is given as previously by equation (4). To avoid calculation of $k_0{}^{sc}$ from equation (18), which requires knowledge of collision diameters and other molecular parameters, relative collisional efficiencies are often measured assuming that the reactant molecule A is a strong collider $(\beta_c = 1)$. For weak colliders $\beta_c < 1$ and from the values of $\beta_c$ it is possible to obtain values of $\langle \Delta E_d \rangle$ *i.e.* the average energy transferred per deactivating collision. Tardy and Rabinovitch[78] have shown that a 'quasi-universal' relationship exists between $\beta_c$ and $\langle \Delta E_d \rangle / \langle E^+ \rangle$ where $\langle E^+ \rangle$ is the Boltzmann average energy of the reacting molecules. The exact relationship depends, according to this treatment, on the model assumed for the transition probabilities in the weak collision master equation, *i.e.* whether step-ladder, exponential, or some other distribution such as Gaussian or Poisson.

In an alternative treatment of weak collisions, Troe[79,80] developed an

[77] T. Baer in ref. 73, p. 153.
[78] D. C. Tardy and B. S. Rabinovitch, *J. Chem. Phys.*, 1968, **48**, 1282.
[79] J. Troe, *J. Chem. Phys.*, 1977, **66**, 4745.
[80] J. Troe, *J. Chem. Phys.*, 1977, **66**, 4758.

analytical solution of the master equation for an exponential model of collisional transition probabilities. This leads to equation (19).

$$\frac{\beta_c}{1 - \sqrt{\beta_c}} \simeq \frac{-\langle \Delta E \rangle}{F_E k T} \qquad (19)$$

This involves a different energy quantity *viz.* $\langle \Delta E \rangle$ which is defined as the average energy transferred per activating or deactivating collision, and $F_E$ is defined by the equation

$$F_E = \int_{E_0}^{\infty} \frac{f(E) \mathrm{d}E}{f(E_0) k T} \qquad (20)$$

where $f(E)\mathrm{d}E$ is given by equation (4).

The relationships between the energy quantities $\langle \Delta E_d \rangle$ and $\langle \Delta E \rangle$ and their implications for the expected temperature-dependence of $\langle \Delta E_d \rangle$, $\langle \Delta E \rangle$, and $\beta_c$ have now been discussed in several reviews.[6,7,78] In general $\beta_c$ is found experimentally to have a slight inverse temperature dependence and $\langle \Delta E_d \rangle$ and $\langle \Delta E \rangle$ also usually decline with increase in temperature. When studied over a sufficiently large temperature range, *e.g.* in shock-tube experiments combined with lower temperature thermal studies, the decline of $\beta_c$ with temperature could in principle lead to a reduced observed activation energy at the higher temperatures.

The results of some recent studies of intermolecular energy transfer in unimolecular reactions are collected in Table 1. Many of the data have been obtained from chemical activation work when $\beta_c$ is calculated from the observed ratio of decomposition $(D)$ and stabilization $(S)$ products (equation 21).

$$k_a = \beta_c \omega (D/S) \qquad (21)$$

From the chemical activation results in Table 1 it will be seen that there is general agreement with previous expectations[5,78] that $\Delta E$ values vary from about 2 kJ mol$^{-1}$ for the smallest bath-gas molecules to about 40—60 kJ mol$^{-1}$ for the large polyatomic molecules, and that the former are fitted better by an exponential and the latter by a stepladder distribution.
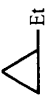
There is less agreement at present about whether collisional energy transfer depends upon the molecular parameters of the reactant (substrate) molecules. For example, McCluskey and Carr[81] have presented some tentative evidence, based on their work on chemically activated alkylcyclopropanes, which shows a possible decrease in $\langle \Delta E_d \rangle$ with increasing size of the reactant molecule. On the other hand, Richmond and Setser,[82] in comparing recent results for chemically activated $C_2H_5F$ and $C_2H_4F_2$ with previous results on $CH_3CF_3$ have found that differences in the efficiencies of $N_2$ and $CO_2$ as deactivators are not due to differences in internal properties of the excited molecules but are more likely due to differences in interaction potentials between these various molecules and the bath gas. This explanation is in accord with the idea of a collision complex $A - M^*$ proposed by Lin and Rabinovitch.[83]

[81] R. J. McCluskey and R. W. Carr, Jr., *J. Phys. Chem.*, 1978, **82**, 2637.

[82] G. Richmond and D. W. Setser, *J. Phys. Chem.*, 1980, **84**, 2699.

[83] Y. N. Lin and B. S. Rabinovitch, *J. Phys. Chem.*, 1970, **74**, 3151.

**Table 1**  Studies of intermolecular energy transfer

| Energized species | $\langle E^* \rangle$/kJ mol$^{-1}$ | $\langle E_0 \rangle$/kJ mol$^{-1}$ | Bath gas | $\Delta E$/kJ mol$^{-1}$ | $\beta_c$ | T/K | Comments and Ref. |
|---|---|---|---|---|---|---|---|
| *Chemical Activation* | | | | | | | |
| $C_3H_8$ | 426.7 | | $CH_2N_2$–$C_2H_6$–$SiMe_4$–$O_2$ | 20.9—83.7 | | | Step-ladder model (S.L.) [a] |
| $C_4H_{10}$ | 431.8 | | $CH_2N_2$–$C_3H_8$–$SiMe_4$–$O_2$ | 20.9—83.7 | | | S.L. [a] |
| [Me-cyclobutane] | 441.4 | 248.2 | Cyclobutane | 16.7 | | | S.L. [b] |
| | | | Cyclobutane | 42.0 ± 8.0 | | | S.L. [q] |
| $MeCF_3$ | 426.8 | | He | 4.2 (Exp) | | | [c] |
| | | | $CO_2$ | 8.4 (Exp) | | | |
| | | | MeCl | 16.8 (SL) | | | |
| | | | $C_2F_6$ | 25.1 (SL) | | 300 | |
| | | | n-$C_8F_{18}$ | 42.0 (SL) | | | |
| [F-cyclopentane] | 355.6 | 230.1 | $CO_2$ | | 0.3 | 393 | [d] |
| | | | $N_2$ | | 0.1 | | |
| [Cl,Cl-cyclopropane] | 386—400 | 233 | $C_3F_8$ | 30—60 | | | S.L. [e] |
| [T-cyclobutane] | | | Cyclobutane | 41.8 | | | |
| | | | He | 2.1 | | | |
| | | | $N_2$ | 8.4 | | | S.L. [p] |
| | | | $CO_2$ | 20.9 | | | |
| [cyclopropane] | 436.8 | | n-$C_5H_{12}$ | 35.9 | | | S.L. [f] |
| [Me-cyclopropane] | 432.6 | | n-$C_5H_{12}$ | 16.7 or 26.4 | | | S.L. [f] |
| [Et-cyclopropane] | 438.5 | | But-1-ene | 30.9 | | | S.L. [f] |

| Molecule | E | M | (col) | (col) | T/K | Model / Method | Ref |
|---|---|---|---|---|---|---|---|
| EtF | 380.7 | He | 4.2 | 0.19 | | Exponential Model (EXP)  S.L. | g |
| | | N$_2$ | 10.5 | 0.55 | | S.L. | |
| | | CO$_2$ | 8.4 | 0.47 | | S.L. | |
| | | SF$_6$ | 21.0 | 1.0 | | EXP | |
| 1,2-C$_2$H$_4$F$_2$ | 387.0 | He | 4.2 | 0.19 | | S.L. | g |
| | | N$_2$ | 10.5 | 0.85 | | S.L. | |
| | | CO$_2$ | 10.5 | 0.58 | | S.L. | |
| | | SF$_6$ | 21.0 | 1.0 | | S.L. | |
| Vinyl radical | 167.4 | He | | 0.078 | 300 | Modified RRKM including tunnelling | h |
| | | | | 0.21 | | RRKM | |

*Thermal Energization in Shock Waves*

| Molecule | | M | (col) | (col) | T/K | Method | Ref |
|---|---|---|---|---|---|---|---|
| $\triangle$ | | Ar | | 0.05 | 1038—1208 | | i |
| | | He | | 0.04 | | | |
| CD$_4$ | | Ar | | 0.25 | 500 | S.L. | j |
| | | | | 0.01 | 2500 | | |
| MeCl | | Ar | ~0.70 | 0.02 | 1800—2100 | | k |
| MeI | | Ar | 0.29 | 0.02 | 1050—1500 | | l |
| NO$_2$ | | Ar | 3.0 | 0.12 | 1800 | | |
| ClNO | | Ar | 1.2 | 0.09 | 1000 | | m |
| O$_3$ | | Ar | 0.16 | 0.019 | 800 | | |
| N$_2$O | | Ar | 0.51 | 0.022 | 2000 | | |

*Thermal Energization at Low Pressures*

| Molecule | | M | (col) | (col) | T/K | Method | Ref |
|---|---|---|---|---|---|---|---|
| $\triangle$ | | He | 4.6 | 0.075 | 770 | (Measured at $k/k_\infty = 0.015$) (EXP) | n |
| | | He | 2.2 | 0.01 | 973 | EXP | |
| | | | 2.27 ± 0.59 | 0.01 | 975 | EXP | |
| | | He | 1.92 ± 0.59 | 0.006 | 1175 | S.L. | |
| | | H$_2$ | 1.79 ± 0.72 | 0.009 | 975 | EXP | |
| | | | 1.07 | 0.002 | 1175 | S.L. | |
| $\triangle$ | | N$_2$ | 5.39 ± 1.79 | 0.02 | 975 | EXP | o |
| | | | 5.39 ± 1.79 | | 1175 | S.L. | |
| | | | 4.19 ± 1.79 | 0.013 | 1175 | S.L. | |

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Table 1—continued

| Energized species | $\langle E^* \rangle$/kJ mol$^{-1}$ | $\langle E_0 \rangle$/kJ mol$^{-1}$ | Bath gas | $\Delta E$/kJ mol$^{-1}$ | $\beta_c$ | $T$/K | Comments and Ref. |
|---|---|---|---|---|---|---|---|
| △ | | | CO$_2$ | 13.2 ± 1.92 | 0.09 | 975 | S.L. |
| | | | | 5.39 ± 1.79 | 0.022 | 1175 | S.L. |
| Wall-Energization | | | | | $\beta_w$ | | |
| | | | | 47.9 | 0.65 | 775 | r |
| | | | | 40.7 | 0.50 | 975 | |
| | | | | 14.1 | 0.35 | 1175 | |
| Cycloheptatriene | | | | (35.9) | (0.5) | 800 | r |
| Cl (structure) | | | | 53.8 | 0.4 | 1100 | r |
| | | | | 59.9 | 0.8 | 930 | r |
| | | | | 41.9 | 0.4 | 1150 | r |

[a] R. J. Wolf and W. L. Hase, *J. Phys. Chem.*, 1978, **82**, 1850. [b] T. H. Richardson and J. W. Simons, *J. Am. Chem. Soc.*, 1978, **100**, 1062. [c] P. J. Marcoux and D. W. Setser, *J. Phys. Chem*, 1978, **82**, 97. Representative values only given. See ref. for a comprehensive list of 17 bath gases at 300 K and 5 bath gases at 195 K. [d] G. O. Pritchard and J. P. Gute, *Int. J. Chem. Kinet.*, 1978, **10**, 759 $\beta$ values relative to $\beta$-fluorocyclohexane = 1. [e] Ref. 106. The parameters quoted relate to the major channel leading to 2,3-dichloropropene. A concurrent process produces 1,1-dichloropropene ($\sim 5\%$ total products). [f] Ref. 81. Ethyl cyclopropane values uncertain due to lack of precise thermal Arrhenius parameters. Representative values of the data given. [g] Ref. 82. [h] K. Kowari, K. Sugawara, S. Sato, and S. Nagase, *Bull. Chem. Soc. Jpn*, 1981, **54**, 1222. [i] D. K. Lewis, S. E. Giesler, and M. S. Brown, *Int. J. Chem. Kinet.*, 1978, **10**, 277. [j] C. C. Chiang, J. A. Barker, and G. B. Skinner, *J. Phys. Chem.*, 1980, **84**, 939. [k] O. Kondo, K. Saito, and I. Murakami, *Bull. Chem. Soc. Jpn*, 1980, **53**, 2133. [l] K. Saito, H. Tahara, O. Kondo, T. Yokubo, T. Higashihara, and I. Murakami, *Bull. Chem. Soc. Jpn*, 1980, **53**, 1335. [m] Ref. 86. See this reference for $\beta_c$ and $\Delta E$ values also for nine other bath gases. [n] Ref. 84. Values are relative to $\beta_c (\Delta) = 1.0$ $\Delta E > 42$ kJ mol$^{-1}$ (770 K) and $\beta_c(\Delta) = 0.5$ $\Delta E > 21.8$ kJ mol$^{-1}$ (973 K). [o] Ref. 85. [p] M. B. Callahan and L. D. Spicer, *J. Phys. Chem*, 1979, **83**, 1013. [q] W. S. Kolln, M. Johnson, D. E. Peebles, and J. W. Simons, *Chem. Phys. Lett.*, 1979, **65**, 85. [r] Ref. 100. Data for $\Delta d_2$ were recalculated from Ref. 88. Data for cycloheptatriene based on earlier work of D. C. Astholtz, J. Troe, and W. Wieters, *J. Chem. Phys*, 1979, **70**, 5107. Values of $\beta_w$ and $\Delta E$ for this compound at the lower temperature are uncertain.

Evidence for the decline of $\beta_c$ and $\langle \Delta E_d \rangle$ with temperature has come from work on thermally energized cyclopropane.[84,85] In one of these studies[85] the new technique known as the diffusion cloud method in which the reactant diffuses from a point source at low pressure into a flowing gas stream was used. The concentration of reactant at some point distant from the source depends on the diffusion constant, the velocity profile, and the unimolecular rate constant. Although absolute rate constant measurements would be difficult by this technique, the 'calibration' of many unknown parameters by the use of a reactant such as cyclopropane with a well known thermal isomerization rate constant makes it possible to obtain relative collisional efficiencies for different flow gases. The method is particularly valuable in yielding data for these at temperatures close to those attainable in shock tubes.

Shock tube studies often involve small molecules since large polyatomics are too easily decomposed at the high temperatures involved. Care is needed in comparing the values of $\langle \Delta E \rangle$ and $\beta_c$ for small molecules with those for large polyatomic molecules although the same temperature dependence can often be observed. Endo, Glänzer, and Troe[86] have drawn attention to the particularly low value of $\langle \Delta E \rangle$ observed for the $O_3$ molecule which could be related to its low density of vibrational states. Stace and Murrell[87] have confirmed the temperature dependence of $\beta_c$ for the ozone molecule by some classical trajectory studies of $O_3$ collisions with He, Ar, and Xe in the range 300—2500 K. Calculations on a model system approximating to the non steady-state conditions applicable to cyclopropane isomerization in a shock tube have been recently described by Mallins and Tardy.[88]

An important topic which has received much attention in the last few years is that of collisional energization by the wall of the reaction vessel. This is particularly important for very low-pressure pyrolysis experiments (VLPP) where until recently it was assumed that the collisional efficiency for wall energization $\beta_w$ was unity.[89] An ingenious method for the direct study of gas–wall vibrational energy transfer known as the Variable Encounter Method has been devised by Rabinovitch and co-workers.[90-99] This method allows the study of vibrational energy transfer from the hot walls of a reactor to an

[84] B. S. Rabinovitch and I. E. Klein, *J. Phys. Chem.*, 1978, **82**, 243.
[85] E. Kamaratos, J. F. Burkhalter, D. G. Keil, and B. S. Rabinovitch, *J. Phys. Chem.*, 1979, **83**, 984.
[86] H. Endo, K. Glänzer, and J. Troe, *J. Phys. Chem.*, 1979, **83**, 2083.
[87] A. J. Stace and J. N. Murrell, *J. Chem. Phys.*, 1978, **68**, 3028.
[88] R. J. Mallins and D. C. Tardy, *Int. J. Chem. Kinet.*, 1979, **11**, 1007.
[89] K. D. King, *Int. J. Chem. Kinet.*, 1981, **13**, 273.
[90] D. F. Kelley, B. D. Barton, L. Zalotai, and B. S. Rabinovitch, *J. Chem. Phys.*, 1979, **71**, 538.
[91] D. F. Kelley, L. Zalotai, and B. S. Rabinovitch, *Chem. Phys.*, 1980, **46**, 379.
[92] M. C. Flowers, F. C. Wolters, B. D. Barton, and B. S. Rabinovitch, *Chem. Phys.*, 1980, **47**, 189.
[93] B. D. Barton, D. F. Kelley, and B. S. Rabinovitch, *J. Phys. Chem.*, 1980, **84**, 1299.
[94] M. C. Flowers, F. C. Wolters, D. F. Kelley, and B. S. Rabinovitch, *Chem. Phys. Lett.*, 1980, **69**, 543.
[95] D. F. Kelley, T. Kasai, and B. S. Rabinovitch, *J. Chem. Phys.*, 1980, **73**, 5611.
[96] F. C. Wolters, M. C. Flowers, and B. S. Rabinovitch, *J. Phys. Chem.*, 1981, **85**, 589.
[97] M. C. Flowers, F. C. Wolters, D. F. Kelley, and B. S. Rabinovitch, *J. Phys. Chem.*, 1981, **85**, 849.
[98] D. F. Kelley, T. Kasai, and B. S. Rabinovitch, *J. Phys. Chem.*, 1981, **85**, 1100.
[99] T. Kasai, D. F. Kelley, and B. S. Rabinovitch, *Chem. Phys. Lett.*, 1981, **81**, 126.

initially cold gas *i.e.* during the transient region of a unimolecular reaction. The reaction (for example the isomerization of cyclopropane to propene) can be followed by sampling after a variable number of collisions between the gas molecules and the reactor wall. The average probability of reaction per collision is then compared with calculations based on various distributions of energy transfer probabilities. The results have shown that whereas gas–wall collisions are more efficient than gas–gas collisions and $\beta_w = 1$ for low temperatures ($<400$ K), at higher temperatures $\beta_w$ and $\langle \Delta E_d \rangle$ decline with temperature as found for homogeneous gas phase intermolecular energy transfer.

VLPP experiments have been carried out by Gilbert and King[100] on the decomposition of chlorocyclobutane which occurs *via* two different reaction channels (see ref. *e*, Table 2). It was found possible to derive data relating both to gas–gas and gas–wall energy transfer processes from the pressure and temperature variation of the rate constant for the two channels. The results showed a decline of $\beta_w$ and $\langle \Delta E_d \rangle$ from 930 K to 1150 K in agreement with previous work on single channel decompositions of cycloheptatriene and $[^2H_2]$cyclopropane.

Interest in non-thermal unimolecular reactions such as those induced by laser irradiation has stimulated some recent model calculations involving solution of a master equation for non-equilibrium conditions and a range of collisional energy transfer models.[101]

**5 Other Non-thermal Energization Studies**
In addition to the chemical activation, photoactivation, and laser-induced unimolecular reaction experiments already described in connection with intra- and inter-molecular energy transfer, many others have been reported where the principal aims have been to obtain other kinds of information.

Among examples of recently studied chemically activated systems is a comprehensive study[102] of 1-, 2-, and 3-methyl chlorocyclobutanes prepared by the insertion of singlet methylene ($CH_2 {}^1A_1$) into chlorocyclobutane. Chlorine abstraction can also produce chloromethyl and cyclobutyl radicals, which subsequently combine to produce chemically activated chloromethylcyclobutane (Scheme 2). All these chemically activated species can undergo both HCl elimination and ring rupture reactions. Estimated *A* factors for the relevant reactions have been used to assign vibration frequencies and hence perform standard RRKM calculations with a view to determining threshold energies for the various processes by matching calculated and observed $k_E$ values. It was found that reasonable agreement between these $k_E$ values was possible for the methylchlorocyclobutanes if a value of $\Delta H_f^0(CH_2 {}^1A_1)$ of 422 kJ mol$^{-1}$ was assumed. This value is within the error limits of the most recently accepted[103,104] value of $414 \pm 8$ kJ mol$^{-1}$.

[100] R. G. Gilbert and K. D. King, *Chem. Phys.*, 1980, **49**, 367.
[101] R. J. Mallins and D. C. Tardy, *J. Phys. Chem.*, 1979, **83**, 1017.
[102] B. E. Holmes and D. W. Setser, *J. Phys. Chem.*, 1978, **82**, 2450.
[103] R. K. Lengel and R. N. Zare, *J. Am. Chem. Soc.*, 1978, **100**, 7495.
[104] L. B. Harding and W. A. Goddard, *Chem. Phys. Lett.*, 1978, **55**, 217.

*cis + trans*    *cis + trans*
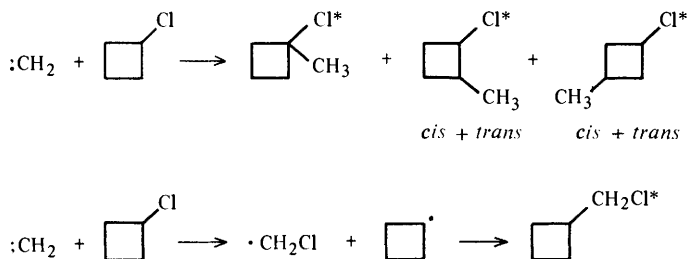


**Scheme 2**

In a subsequent paper[105] Holmes and Setser have studied vibrational energy partitioning in the 1- and 3-methylcyclobutenes produced from the corresponding methylcyclobutanes by HCl elimination. These molecules are formed with sufficient energy to undergo further rearrangement to butadienes. The conclusions are that the methylcyclobutenes acquire a relatively low percentage (32%) of the potential energy available. This type of study is complementary to other methods of measuring energy disposal such as i.r. chemiluminescence.

Further chemical activation studies reported include work on 1,1-dichloro-cyclopropane,[106] methylamine,[107] and thiirane.[108]

Chemically activated species sometimes arise as a result of photoactivation, thus Tschuikow-Roux and Yano[109] have applied RRKM theory to halogenoethyl radicals produced by chlorine-atom addition to olefins in secondary reactions following the vacuum u.v. photolysis of 1,1,2-trichloro-2,2-difluoroethane. The photoactivation of butene isomers at similar wavelengths was studied by Collin and Wieckowski[110] who measured the production of allene from vibrationally excited allyl radicals produced by the sequence of reactions

$$C_4H_8 + h\nu \rightarrow C_4H_8^{**} \rightarrow C_3H_5^* + CH_3$$

$$C_3H_5^* \rightarrow CH_2=C=CH_2 + H$$
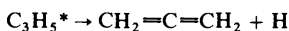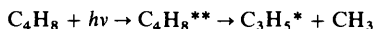
Rate constants were measured for three different photon energies and the results when compared with a simple RRK treatment indicate a non-random distribution of the excess photon energy with the majority of the energy residing in the heavier fragment ($C_3H_5^*$ radical). In an extension of this work to various $C_4$ and $C_5$ olefins[111] it was found that RRKM calculations on a strong-collision basis compared with experimental data led to similar conclusions regarding the vibrational energy content of butenyl radicals.

[105] B. E. Holmes and D. W. Setser, *J. Phys. Chem.*, 1978, **82**, 2461.

[106] K. Eichler and H. Heydtmann, *Int. J. Chem. Kinet.*, 1981, **13**, 1107.

[107] K. J. Chao, C. L. Lin, M. Hsu, and S. Y. Ho, *J. Phys. Chem.*, 1979, **83**, 1241.

[108] A. G. Sherwood, I. Safarik, B. Verkoczy, G. Almadi, H. A. Wiebe, and O. P. Strausz, *J. Am. Chem. Soc.*, 1979, **101**, 3000.

[109] T. Yano and E. Tschuikow-Roux, *J. Chem. Phys.*, 1980, **72**, 3401.

[110] G. J. Collin and A. Wieckowski, *Can. J. Chem.*, 1978, **56**, 2630.

[111] G. J. Collin and H. Deslauriers, *Int. J. Chem. Kinet.*, 1980, **12**, 17.

Energy partitioning has also been studied in photoactivated trimethylene sulphoxide[112] which produces vibrationally excited cyclopropane and sulphur monoxide with an initial non-random distribution of energy.

## 6 Infrared Laser-induced Unimolecular Reactions

The study of chemical reactions induced by infrared multiphoton absorption (IRMPA) is a rapidly growing area spanning many established research disciplines. The implications of this work for the chemical kinetics of unimolecular reactions are obvious but even a restricted survey of the numerous papers which have appeared in this field in the last few years is beyond the scope of the present review. The highly selective nature of the present section is therefore intended to draw attention to some of the current topics of interest.

Since the photon of infrared radiation of a typical frequency of $3 \times 10^{13}$ s$^{-1}$ corresponds to about 12 kJ mol$^{-1}$, dissociation of a molecule with an activation energy of 240 kJ mol$^{-1}$ would require absorption of 20 photons. The mechanism by which this may be achieved *via* the quasi-continuum of absorbing states of a molecule is dealt with in many recent reviews.[113,13,114-116] Particular attention to chemical problems in infrared multiphoton dissociation (IRMPD) experiments of relevance to unimolecular reactions is given in the reviews of Ashfold and Hancock[115] and Danen and Jang.[117]

The motivation for much early research into the use of lasers to promote unimolecular reactions was the hope of achieving mode-selective chemistry *i.e.* the hope that energy initially deposited by a specific exciting wavelength might remain isolated in a particular mode which was closely related to the reaction coordinate in the Slater sense. This topic has been mentioned earlier in connection with intramolecular energy transfer since rapid intramolecular energy relaxation would make mode specificity impossible. The whole question has become one of degree, *i.e.* how fast or how slow can intramolecular energy transfer be made in relation to the rate of particular unimolecular reactions? Particular examples continue to promote discussion. One such example is the work of Hall and Kaldor[68] on the irradiation of cyclopropane using two lasers with widely different frequencies. Two possible reaction channels are a high energy fragmentation into ethene and methylene and a lower energy isomerization to propene.

$$\Delta \rightarrow CH_2=CH_2 + :CH_2$$
$$\Delta \rightarrow C_3H_6$$
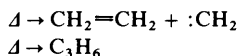
[112] F. H. Dorer and K. E. Salomon, *J. Phys. Chem.*, 1980, **84**, 3024.

[113] N. Bloembergen and E. Yablonovitch, *Physics Today*, 1978, **31**(5), 23.

[114] H. W. Galbraith and J. R. Ackerhalt in 'Laser-induced Chemical Processes', ed. J. I. Steinfeld, Plenum, N. York, 1981, p.1.

[115] M. N. R. Ashford and G. Hancock in 'Gas Kinetics and Energy Transfer', A Specialist Periodical Report, ed. P. G. Ashmore and R. J. Donovan, Royal Society of Chemistry, London, 1980, Vol. 4, p. 73.

[116] P. A. Schulz, Aa. S. Sudbø, D. J. Krajnovich, H. S. Kwok, Y. R. Shen, and Y. T. Lee, *Ann. Rev. Phys. Chem.*, 1979, **30**, 379.

[117] W. C. Danen and J. C. Jang in 'Laser-induced Chemical Processes', ed. J. I. Steinfeld, Plenum, N. York, 1981, p. 45.

Irradiation causing excitation of the $C-H$ asymmetric stretch ($3.22\,\mu m$) produced propene with almost no fragmentation whereas excitation of the $CH_2$ wag ($9.50\,\mu m$) produced roughly equal yields of $C_3H_6$ and fragmentation products. The authors interpreted their results in terms of a selective mechanism. Argon was found to increase the yield of fragmentation products when $3.22\,\mu m$ radiation was used and this was thought to assist the intra-molecular energy transfer process.

Thiele, Goodman, and Stone[118] have developed a theory of intramolecular vibrational relaxation and unimolecular decay in which the former process occurs at a restricted rate. It was concluded that a low relaxation rate (possibly two orders of magnitude less than the $10^{12}\,s^{-1}$ deduced from the experiments of Rabinovitch and co-workers) could well account for Hall and Kaldor's observations. An alternative view of these experiments is taken by Ashfold and Hancock[115] who point out the possibility that the higher intensity of the $CO_2$ laser pulse ($9.50\,\mu m$) could be responsible for the access to the higher energy reaction channel rather than any mode selectivity.

The need for careful reporting of laser parameters such as pressure, wavelength, pulse shape, fluence variation within the cell and mode quality of the laser beam has recently been emphasized by Jang and Setser.[119] Without this, comparison between work in different laboratories is difficult to make. These authors found as an example that inert gas effects on $CO_2$ laser-induced elimination of HF from $CH_3CH_2F$ and $CH_3CF_3$ were related to laser pulse length. Brenner[120] earlier found that product branching ratios for two different unimolecular channels for the decomposition of ethyl vinyl ether could be varied by changing the pulse duration. The higher energy channel was favoured by shorter more intense pulses.

In contrast, Danen, Koster, and Zitter[121] attempted to force the laser-induced reaction of *cis*-3,4-dichlorocyclobutene to follow the non-allowed channel (2) instead of the channel (1) predicted by the Woodward-Hofmann rules of conservation of orbital symmetry for a thermally-allowed ground-state conrotatory ring-opening reaction (Scheme 3). Despite the use of relatively short laser pulses the non-allowed process (2) could not be made competitive and *cis,trans*-1,4-dichlorobuta-1,3-diene was the sole product. This system has recently been re-investigated by Gordon and co-workers[122] who have found increased amounts of the 'symmetry-forbidden' products at fluences greater than those employed by Danen and co-workers. It is not however considered likely that the disrotatory concerted process (2) occurs on the ground electronic surface contrary to the Woodward–Hofmann rules. A more likely explanation

[118] (a) E. Thiele, M. F. Goodman, and J. Stone, *Chem. Phys. Lett.*, 1980, **69**, 18.
    (b) E. Thiele, M. F. Goodman, and J. Stone, *Opt. Eng.*, 1980, **19**, 10.
[119] J. C. Jang and D. W. Setser, *J. Phys. Chem.*, 1979, **83**, 2809.
[120] D. M. Brenner, *Chem. Phys. Lett.*, 1978, **57**, 357.
[121] W. C. Danen, D. F. Koster, and R. N. Zitter, *J. Am. Chem. Soc.*, 1979, **101**, 4281.
[122] Chung-Rei Mao, N. Presser, Lian-Shun John, R. M. Moriarty, and R. J. Gordon, *J. Am. Chem. Soc.*, 1981, **103**, 2105.
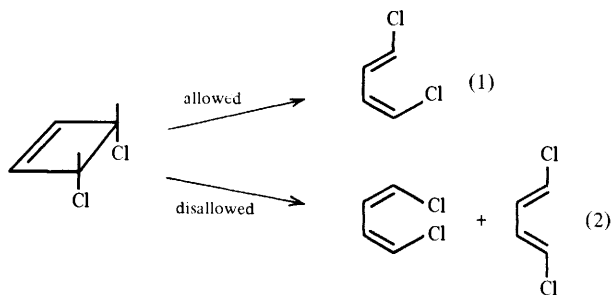
**Scheme 3**

is the direct formation of these products from a biradical intermediate or by secondary isomerization of the vibrationally hot product from reaction (1).

Other examples of systems involving competing reaction channels have been the decompositions of methanol[123] and of cyclobutanone.[124,125] In the former, product analysis suggested that the primary process is

$$CH_3OH \rightarrow CH_3 + OH$$
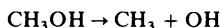
irrespective of whether the initial excitation is of a CO stretch (9.7 $\mu$m CO$_2$ laser) or OH stretch (2.7 $\mu$m HF laser). In the CO$_2$ laser-induced decomposition of cyclobutanone, a low energy pathway produces ethene and a higher energy pathway produces cyclopropane. Conflicting results have been reported with one set of workers[124] finding the high energy path enhanced and another[125] finding the low energy path enhanced at low pressures. Higher pressures would normally be expected to favour thermal equilibration and a Boltzmann-type energy distribution. Under these conditions it is possible in principle to use the RRKM theory to calculate specific rate constants for the unimolecular reactions of the energized species and hence to compare calculated and experimental rate constants for different forms of the energy distribution function. Calculations of this kind have been made for example by Steinfeld and co-workers[126] for the decompositions of halogenated ethylenes and by Benson and co-workers[19] for the decomposition of ethyl chloride. Although the data are fitted in general by RRKM-theory, in both cases the form of the distribution function cannot be determined unambiguously without independent measurements of absorbed energy.

Despite the difficulties of interpretation, experiments on laser-induced reactions are clearly increasing and theoretical papers (not referred to here) are appearing in increasing numbers. In a purely practical sense, although mode selectivity may only be rarely possible, laser initiation may for other reasons often provide a

[123] R. Bhatnagar, P. E. Dyer, and G. A. Oldershaw, *Chem. Phys. Lett.*, 1979, **61**, 339.
[124] M. H. Back and R. A. Back, *Can. J. Chem.*, 1979, **57**, 1511.
[125] R. G. Harrison, H. L. Hawkins, R. M. Leo, and P. John, *Chem. Phys. Lett.*, 1980, **70**, 555.
[126] C. Reiser, F. M. Lussier, C. C. Jenson, and J. I. Steinfeld, *J. Am. Chem. Soc.*, 1979, **101**, 350.

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preferred route to a particular product and may often produce entirely different products from the comparable thermal reaction. The laser-induced decomposition of vinyl chloride, for example,[126] is a concerted elimination to give HCl and acetylene, whereas thermal studies in a flow system at 500—600 °C give dimerization to chloroprene. D. M. Golden and co-workers[127] have used a CW infrared laser to heat an unreactive bath gas which then transfers energy by collision to the substrate. This technique − 'laser powered homogeneous pyrolysis' − pioneered by Shaub and Bauer[128] is useful in the study of reactions which under normal conditions follow a rapid heterogeneous path. It was also claimed that laser-induced, $SiF_4$-sensitized retro-Diels–Alder reactions carried out at room temperature by 'cold pyrolysis' enabled these reactions to proceed with fewer side-products than under normal thermal energization.[129]

## 7 Thermal Unimolecular Reactions at High Pressures

This section includes a fairly comprehensive compilation of the Arrhenius parameters for the major types of unimolecular reactions considered in the book by Robinson and Holbrook[1] and in subsequent reviews. The author is well aware that this is not an 'evaluation' in the sense described by Baulch and Montague,[130] although comments are made on some values where appropriate and some of the more interesting mechanistic aspects of recent work are discussed. An excellent contribution to a Symposium on the current status of the kinetics of elementary gas reactions by Cvetanovic, Singleton, and Paraskevopoulos[131] deals with recommended methods for the evaluation of temperature coefficients of rate constants. Although a common procedure for reporting the reproducibility of measured Arrhenius parameters does not exist and the procedure used by particular authors is frequently not stated, error limits are usually calculated from a least-squares treatment of the logarithmic form of the Arrhenius equation and most often correspond to the 95% confidence limits. In the tables which follow, the error limits quoted by the authors are listed and reference to the original papers must be made if their precise significance is important.

The high pressure Arrhenius parameters $A_\infty$ and $E_\infty$ given in the tables must be assessed in relation to the type of unimolecular reaction involved. In many cases it is helpful to make comparisons with the parameters for the 'parent compound' such as cyclopropane or cyclobutane for small-ring alicyclic compounds, cyclobutene for the isomerizations of cyclic olefins, and ethyl chloride for four-centred decomposition reactions. Absolute rate-theory predicts a value of $10^{13}$—$10^{14}$ s$^{-1}$ for the pre-exponential factor of a unimolecular reaction whose activated complex resembles the initial state. Higher values can often be attributed to 'loose' activated complexes resembling more the product state, for example reactions with biradical intermediates and bond fissions

[127] K. E. Lewis, D. F. McMillen, and D. M. Golden, *J. Phys. Chem.*, 1980, **84**, 226.

[128] W. M. Shaub and S. H. Bauer, *Int. J. Chem. Kinet.*, 1975, **7**, 509.

[129] D. Garcia and P. M. Keehn, *J. Am. Chem. Soc.*, 1978, **100**, 6111.

[130] D. L. Baulch and D. C. Montague, *J. Phys. Chem.*, 1979, **83**, 42.

[131] R. J. Cvetanovic, D. L. Singleton, and G. Paraskevopoulos, *J. Phys. Chem.*, 1979, **83**, 50.

producing complex radicals. Activation energies are not so easy to predict but much progress has been made by the judicious application of Benson's rules to the estimation of the enthalpies of reactants and activated complexes. Those readers unfamiliar with the details of such calculations should consult 'Thermochemical Kinetics' by S. W. Benson (J. Wiley, N. York, 2nd Edn. 1976).

**A. Small Alicyclic Compounds and their Derivatives (Table 2).**—Work on substituted cyclopropanes has clarified some of the details of earlier reports of these reactions. Heydtmann and Körbitzer[132] have re-investigated the thermolysis of 1,1-dichlorocyclopropane and established that a small fraction of the isomerization occurs to give 1,1-dichloropropene, a product undetected by earlier workers. Eichler and Heydtmann[106] have reported slightly different Arrhenius parameters, for formation of this product, which fit well all the previous thermal and chemical activation studies of 1,1-dichlorocyclopropane. Robinson and Waller[133] have confirmed the strong accelerating effect of methyl substitution into chlorinated cyclopropanes found by Holbrook and co-workers[134] in a comprehensive study of *cis-* and *trans*-1-chloro-2,3-dimethyl-cyclopropanes. Isomerization reactions occur to give *cis-* or *trans*-4-chloropent-2-ene, as well as a 6-centred elimination (from the *cis* compound) producing pentadiene and HCl.

Fluorine substitution in the cyclopropane ring is known to produce a decrease in activation energy and an enhancement of the rate of isomerization. *gem*-Difluoro-substitution has been studied by Ferrero and Staricco[135] in 1,2-bis(trifluoromethyl)-1,2,3,3-tetra-fluorocyclopropane and found to lead to elimination of $CF_2$ instead of isomerization to propenes. The evidence appears to favour a concerted process for this elimination although a biradical path cannot be excluded.

The analogous elimination of a methylene radical from a substituted cyclopropane has been observed in photochemical studies of alkyl-substituted cyclopropanes.[136] Theoretical calculations by Rossi[137] have supported the view that this process occurs by a two-step mechanism *via* the biradical (Scheme 4).
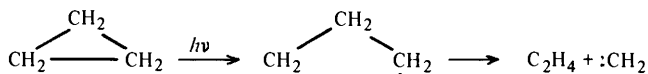


**Scheme 4**

Some of the uncertainty in the postulation of biradical pathways for cyclopropane and other alicyclic systems arises from lack of knowledge of barriers to internal rotation in biradicals. Molecular orbital calculations by Lipscomb and co-

[132] H. Heydtmann and B. Körbitzer, *Z. Phys. Chem. (Frankfurt)*, 1981, **125**, 255.

[133] P. J. Robinson and M. J. Waller, *Int. J. Chem. Kinet.*, 1979, **11**, 937.

[134] (a) K. A. Holbrook and K. A. W. Parry, *J. Chem. Soc.*, 1970, 1019.
   (b) R. P. Clifford and K. A. Holbrook, *J. Chem. Soc., Perkin 2*, 1972, 1972.

[135] J. C. Ferrero and E. H. Staricco, *Int. J. Chem. Kinet.*, 1979, **11**, 1287.

[136] J. C. Ferrero and E. H. Staricco, *J. Am. Chem. Soc.*, 1978, **100**, 7089.

[137] A. Rossi, *J. Phys. Chem.*, 1979, **83**, 2554.

workers[138] for the methylene cyclopropane rearrangement have predicted a low energy barrier to ring-closure of $13.8 \text{ kJ mol}^{-1}$ for the biradical intermediate involved. This value is, however, comparable with the difference between the theoretically predicted and observed activation energies for this isomerization.

Doubts expressed by Berson about the validity of thermochemical estimates underlying the biradical mechanism have been amplified in a recent review.[139] Despite numerous experimental attempts to distinguish whether rotation at the biradical centres occurs simultaneously or independently, Berson concludes that questions still remain to be resolved which will require new experimental approaches.

Direct measurements on the relative rates of rotation, cleavage, and closure of tetramethylene biradicals which are relevant to the thermolysis of cyclobutane derivatives have been reported by Dervan and Santilli.[140] Deuterated tetramethylene radicals were generated by the thermal decomposition of [*cis*-3,4-$^2$H$_2$]-3,4,5,6-tetrahydropyridazine and these underwent rotation, cleavage, and closure reactions as in Scheme 5. From the results it was found that
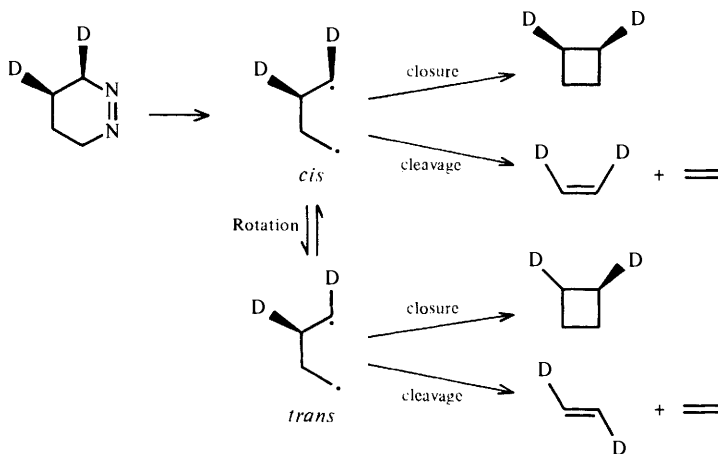


**Scheme 5**

$k_{\text{cleavage}}/k_{\text{closure}} = 2.2 \pm 0.2$ and $k_{\text{rotation}}/k_{\text{closure}} = 12 \pm 3$, hence rotation is much faster than closure or cleavage under these conditions (439 °C). The rate constants for closure and cleavage were taken to be the same for the *cis* and *trans* reactants. Comparison with the results of other workers shows that increasing methyl substitution at the biradical centre slows the rate of rotation relative to cleavage as would be expected from the increased moments of inertia.

[138] D. A. Dixon, R. Foster, T. A. Halgren, and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1978, **100**, 1359.
[139] J. A. Berson in 'Rearrangements in Ground and Excited States', ed. P. de Mayo, Academic Press, N. York, 1980, p. 311.
[140] P. B. Dervan and D. S. Santilli, *J. Am. Chem. Soc.*, 1980, **102**, 3863.

High-pressure Arrhenius parameters for the decompositions of chloro-cyclobutane by alternative paths to vinyl chloride and ethene or buta-1,3-diene and HCl were obtained by King and co-workers[141] from VLPP data using RRKM theory and assuming that gas–wall collisions are strong. In a more recent publication, Gilbert and King[100] have shown that this assumption needs revision for the higher temperatures employed when $\beta_\omega$ deviates considerably from unity (See Section 4).

Bromocyclobutane was also studied by these authors[142] who found no evidence for the expected path leading to vinyl bromide but only the path producing elimination of HBr.

Among other cyclobutane derivatives studied, the decomposition of vinyl cyclobutane is of interest. Frey and Pottinger[143] found that this compound undergoes a ring expansion reaction (as does vinyl cyclopropane) in addition to decomposition to ethene and buta-1,3-diene. Both reaction paths were interpreted in terms of biradical intermediates which are stabilized by allylic resonance.

The unimolecular reactions of substituted cyclopentanes and higher alicyclics are receiving more attention. Among mechanistic studies are those of Gajewski and Salazar[144] on the ring-opening reactions of some methyl-substituted 1,3-dimethylenecyclopentanes. The results suggest that in these cases the biradical intermediates formed may reclose faster than they undergo rotation, with the consequence of partial stereospecificity in the reaction products.

**B. Polycyclic Systems (Table 3).**—The relatively few studies of polycyclic systems yielding kinetic parameters in this review period are listed in Table 3. The effects observed are generally those predicted from the similar reactions in comparable monocyclic systems. Two *gem*-fluorine substituents in a cyclopropane ring are found to produce considerable rate enhancement and this is also true for substituted spiropentane.[145] The observations have been rationalized in terms of biradical intermediates. For 1,1,2,2-tetrafluorospiropentane, a $CF_2$ extrusion reaction occurs with similar Arrhenius parameters to that of the comparable reaction for 1,1,2,2-tetrafluorocyclopropane.

Huybrechts and co-workers[146] have studied the Diels–Alder addition of ethene and cyclohexa-1,3-diene to bicyclo[2.2.2]oct-2-ene and the reverse thermolysis at 548—632 K. The Arrhenius parameters are in good agreement with those found by Cocks and Frey[147] for the reaction at higher temperatures (649—718 K) and can be explained in terms of a biradical intermediate with little or no activation energy to ring closure.

[141] K. D. King, B. J. Gaynor, and R. G. Gilbert, *Int. J. Chem. Kinet.*, 1979, **11**, 11.
[142] K. D. King and R. G. Gilbert, *Int. J. Chem. Kinet.*, 1980, **12**, 339.
[143] H. M. Frey and R. Pottinger, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 1827.
[144] J. J. Gajewski and J. Salazar, *J. Am. Chem. Soc.*, 1979, **101**, 2739, 2740.
[145] W. R. Dolbier, Jr., S. F. Sellers, B. H. Al-Sader, and T. H. Fuller, *J. Am. Chem. Soc.*, 1981, **103**, 717.
[146] G. Huybrechts, D. Rigaux, J. Vankeerberghen, and B. van der Mele, *Int. J. Chem. Kinet.*, 1980, **12**, 253.
[147] A. T. Cocks and H. M. Frey, *J. Chem. Soc. (A)*, 1971, 1661.

# Table 2  *High-pressure Arrhenius parameters for small alicyclic compounds and their derivatives*
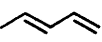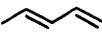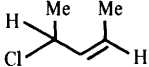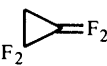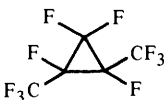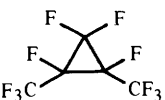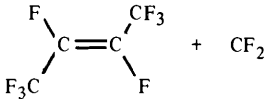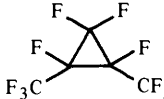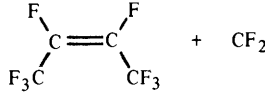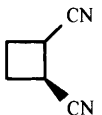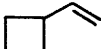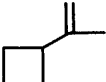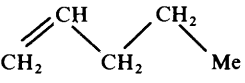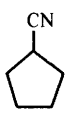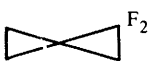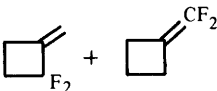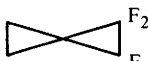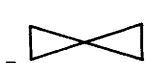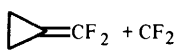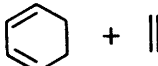
| Reactant | Product(s) | $\log_{10}(A_\infty/\text{s}^{-1})$ | $E_\infty/\text{kJ mol}^{-1}$ | Ref. |
|---|---|---|---|---|
| 1,1-dichlorocyclopropane (Cl, Cl) | $CH_2ClCCl=CH_2$ | $15.13^* \pm 0.1$ | $241.9^* \pm 1.3$ | |
| | $MeCH=CCl_2$ | $14.50 \pm 0.38$ | $250 \pm 5$ | a |
| 1-chloro-2,2-dimethylcyclopropane (Cl; Me, Me) | HCl + (butadiene) | $13.92 \pm 0.08$ | $199.6 \pm 0.9$ | b |
| 1-chloro-2-methyl... (Cl, Me; Me) | HCl + (butadiene) | $13.8 \pm 0.4$ | $190.2 \pm 4$ | b |
| | H–C(Me)=... Me / Cl ... H | $14.6 \pm 0.4$ | $199.5 \pm 4$ | b |
| (perfluoro methylenecyclopropane, $F_2$, $F_2$) = | ($F_2$ cyclopropane) $=F_2$ | $12.6 \pm 0.5$ | $123.8 \pm 4$ | c |
| (F, F; F, CF$_3$; F$_3$C, F) | (F, F; F, F; F$_3$C, CF$_3$) | $15.15 \pm 0.16$ | $186.2 \pm 1.7$ | d |
| | $F$,$CF_3$ C=C $F_3C$,$F$ + $CF_2$ | $15.14 \pm 0.28$ | $195.4 \pm 2.9$ | d |
| (F, F; F, F; F$_3$C, CF$_3$) | (F, F; F, CF$_3$; F$_3$C, F) | $15.35 \pm 0.19$ | $181.6 \pm 1.7$ | d |
| | $F$,$F$ C=C $F_3C$,$CF_3$ + $CF_2$ | $15.39 \pm 0.26$ | $194.9 \pm 2.5$ | d |
| chlorocyclobutane (Cl) | $C_2H_4 + CH_2=CHCl$ | $14.8 \pm 0.3$ | $255.6 \pm 4.2$ | e |
| | (butadiene) + HCl | $13.6 \pm 0.3$ | $233.0 \pm 4.2$ | e |
| bromocyclobutane (Br) | (butadiene) + HBr | $13.6 \pm 0.3$ | $217.6 \pm 4.2$ | f |
| 1,2-dicyanocyclobutane (CN, CN) | $2\ CH_2=CHC\overset{\bullet}{N}$ | $16.0 \pm 0.3$ | $221.3 \pm 3.3$ | g |

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**Table 2**—*continued*

| Reactant | Product(s) | $\log_{10}(A_\infty/\mathrm{s}^{-1})$ | $E_\infty/\mathrm{kJ\,mol}^{-1}$ | Ref. |
|---|---|---|---|---|
| | $C_2H_4 + CH_2{=}CF_2$ | $15.60 \pm 0.13$ | $289.7 \pm 1.8$ | $h$ |
| | $2\,CH_2{=}CF_2$ | $15.34 \pm 0.05$ | $292.0 \pm 0.8$ | $i$ |
| | $CH_2{=}CH_2 + CF_2{=}CF_2$ | $15.27 \pm 0.06$ | $308.0 \pm 0.9$ | $i$ |
| | $+ C_2H_4$ | $14.87 \pm 0.07$ | $212.2 \pm 0.8$ | $j$ |
| | | $13.86 \pm 0.13$ | $203.5 \pm 1.5$ | $j$ |
| | $+ C_2H_4$ | $15.22 \pm 0.15$ | $219.02 \pm 1.77$ | $j$ |
| | | $13.76 \pm 0.20$ | $204.81 \pm 2.31$ | $j$ |
| | $CH_2{=}CH-CH_2-CH_2-CH_2$Me | $16.1$ | $354.9$ | $k$ |
| | $\triangle + C_2H_4$ | $16.25$ | $397.6$ | $k$ |
| $k_1$ | $+ HCN$ | $12.8^* \pm 0.3$ | $274.5^* \pm 5.4$ | |
| | | $12.8^\dagger \pm 0.3$ | $283.7^\dagger \pm 10.5$ | |
| $k_2$ | $C_2H_3CN + C_3H_6$ | $16.0^* \pm 0.3$ | $334.7^* \pm 4.6$ | $l$ |
| $k_3$ | $C_3H_5CN + C_2H_4$ | $16.3^\ddagger \pm 0.3$ | $335.1\ddagger \pm 8.4$ | |
| | $Bu^nCH{=}CH_2$ | $16.7$ | $369.1$ | $m$ |

$^a$ Ref. 132. For a better fit to both thermal and chemical activation data see ref. 106. *Values taken from previous work, see *Trans. Faraday Soc.*, 1970, **66**, 869. $^b$ Ref. 133. $^c$ W. R. Dolbier, S. F. Sellers, B. H. Al-Sader, and B. E. Smart, *J. Am. Chem. Soc.*, 1980, **102**, 5398. $^d$ Ref. 135. $^e$ Ref. 141. $^f$ Ref. 142. $^g$ K. D. King and R. D. Goddard, *Int. J. Chem. Kinet.*, 1978, **10**, 453. $^h$ H. M. Frey and R. T. Conlin, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 2556. $^i$ H. M. Frey and R. T. Conlin, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 322. $^j$ Ref. 143. $^k$ W. Tsang, *Int. J. Chem. Kinet.*, 1978, **10**, 599; see also B. L. Kalra, S. A. Feinstein, and D. K. Lewis, *Can. J. Chem.*, 1979, **57**, 1324. $^l$ Ref. 175. *Stirred-flow reactor, $^\dagger$VLPP extrapolated by RRKM, $^\ddagger$parameters for $(k_2 + k_3)$ from VLPP. $^m$ W. Tsang, *Int. J. Chem. Kinet.*, 1978, **10**, 1119.

**Table 3** *High-pressure Arrhenius parameters for reactions of polycyclic compounds*

| Reactant | Product | $\log_{10}(A_\infty/\text{s}^{-1})$ | $E_\infty/\text{kJ mol}^{-1}$ | Ref. |
|---|---|---|---|---|
| (structure, $F_2$) | (structures, $CF_2$ / $F_2$) | $16.1 \pm 0.2$ | $242.7 \pm 2.1$ | *a* |
| (structure, $F_2$, $F_2$) | (structure, $F_2$ / $CF_2$) | $13.8 \pm 0.1$ | $189.5 \pm 1.3$ | *b* |
| | (structure) $=CF_2 + CF_2$ | $15.2 \pm 0.2$ | $203.3 \pm 1.7$ | *b* |
| (structure, $F_2$, $F_2$) | (structure, $F_2$, $F_2$) | $14.8 \pm 0.2$ | $216.3 \pm 2.5$ | *b* |
| (bicyclic structure) | (structures) + ‖ | $15.12 \pm 0.04$ | $239.7 \pm 0.4$ | *c* |

[a] W. R. Dolbier, Jr., S. F. Sellers, B. H. Al-Sader, and S. Elaheimer, *J. Am. Chem. Soc.*, 1981, **103**, 715.
[b] Ref. 145. [c] Ref. 146.

**C. Cyclic Olefins (Table 4).**—Some recent kinetic results on reactions of cyclic olefins are given in Table 4.

The elimination of hydrogen from cyclopentene to give pentadiene is believed, from previous work, to be a unimolecular process occurring *via* a concerted symmetry-allowed 1,4-transition state. King[148] has re-investigated this compound by VLPP and on the basis of a 1,4-$H_2$ elimination transition state and an assumed $A_\infty$ value based on the results of previous workers he derived the $E_\infty$ value 255.2 kJ mol$^{-1}$ by the use of RRKM theory.

Lewis[149] and co-workers have carried out some shock-tube experiments using deuterium-labelled cyclopentene and have shown that at high temperatures (1100—1300 K) both the 'symmetry allowed' [1,4] and 'symmetry disallowed' [1,2] eliminations occur, although the former is favoured by a ratio of 2:1. The results lead to an apparent difference in activation energies of $\simeq 34$ kJ mol$^{-1}$ for the two paths. The authors point out the need for laser-induced experiments purporting to produce preferential 'disallowed' products to be compared with thermally activated systems at comparable temperatures.
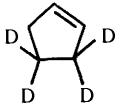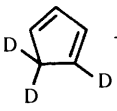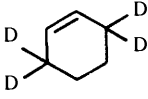
Rather similar experiments have been carried out by Tardy[150] and co-workers

[148] K. D. King, *Int. J. Chem. Kinet.*, 1978, **10**, 117.
[149] D. K. Lewis, M. Greaney, and E. L. Sibert, *J. Phys. Chem.*, 1981, **85**, 1783.
[150] D. C. Tardy, R. Ireton, and A. S. Gordon, *J. Am. Chem. Soc.*, 1979, **101**, 1508.

**Table 4** *High-pressure Arrhenius parameters for reactions of cyclic olefins*

| Reactant | Product(s) | $\log_{10}(A_\infty/\text{s}^{-1})$ | $E_\infty/\text{kJ mol}^{-1}$ | Ref. |
|---|---|---|---|---|
| | $+ D_2$ | 14.1 | 277 | a |
| | $+ HD$ | 12.8 | 243 | a |
| $D_2C =\!\!=CH-CH=\!\!=CD_2$ | $+\ \ \ \text{C}=\text{C}$ | $14.93 \pm 0.79$ | $272.8 \pm 11.7$ | b |
| | $+ D_2$ | $12.63 \pm 0.76$ | $257.7 \pm 11.3$ | b |
| | $\parallel$ | 15.57 | 290.9 | c |
| | $+ H_2$ | 13.35 | 255.2 | d |

$^a$ Ref. 149.  $^b$ Ref. 150. Also minor amounts of symmetry-forbidden products. Only 3 temperatures studied.  $^c$ J. M. Simmie, *Int. J. Chem. Kinet.*, 1978, **10**, 227. (Retro-Diels–Alder.)  $^d$ Ref. 148.

on deuterium-labelled cyclohexene in a conventional static thermolysis apparatus at lower temperatures (750—800 K). Here the activation energy difference between 'allowed' and 'disallowed' $D_2$ or $(HD + H_2)$ elimination reactions was $(25 \pm 12)$ kJ mol$^{-1}$. The primary reaction for this compound however is the retro Diels–Alder reaction to ethene and buta-1,3-diene.

**D. Heterocyclic Compounds (Table 5).**—The high-pressure Arrhenius parameters for some recently studied thermolyses of heterocyclic compounds are shown in Table 5. Among the oxetanes studied, the effect of a vinyl group in the ring in *cis*-2,4-dimethyl-*trans*-3-vinyloxetane[151] produced the expected lowering of the activation energy for reaction to penta-1,3-diene and ethanal, presumably by allylic stabilization of the biradical intermediate.

Although symmetrically-substituted oxetanes show Arrhenius parameters similar to those of oxetane itself, it has previously been observed[152] that alkyl substituents in the 2-position lead to lower $A$-factors and activation energies.

[151] H. A. J. Carless, A. K. Maitra, R. Pottinger, and H. M. Frey, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 1849.

[152] M. J. Clarke and K. A. Holbrook, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 1890.

In the case of the recently studied thermolysis of 2,2-dimethyloxetane[153] this lowering occurs to such an extent for the path leading to formation of the more highly alkylated olefin (isobutene) that a biradical mechanism does not appear able to account for the experimental observations. Imai and Nishida[154] likewise concluded that their observations on the solution thermolyses of some 3-alkyl-2-phenyloxetanes, in particular the *trans* isomers could best be explained by concurrent concerted fragmentation and a biradical process. The concerted process for these $[2 + 2]$ eliminations would necessarily involve a twisted transition state $[\sigma_{2_s} + \sigma_{2_a}]$ from orbital symmetry considerations. This is normally excluded on energetic grounds but such a mechanism would explain the preference for the more highly alkylated olefinic product found both in the case of 2,2-dimethyloxetane and of the 3-alkyl-2-phenyloxetanes.

Further work is in progress in the author's laboratory to extend these ideas to other substituted oxetanes.

**E. Alkyl Halides (Table 6).**—The unimolecular decompositions of alkyl halides are known to occur *via* 4-centred transition states and recent work has been involved with confirming the model proposed initially by Maccoll and Thomas[155] and quantitatively treated by Benson, Bose, and Haugen.[156,157] Maccoll and co-workers[158,159] have recently investigated the involvement of the Cl atom in the transition state for ethyl chloride and some secondary and tertiary chloride decompositions by measurement of the relative $k(^{35}Cl)$ and $k(^{37}Cl)$ ratios and their temperature dependence. Chuchani and co-workers[160] on the other hand have studied the enhancement of rate due to stabilization of the polar transition state produced by anchimeric assistance of polarizable groups substituted in the $\beta$ position.

Neopentyl halides are unable to decompose molecularly *via* 4-centred transition states since they lack a $\beta$ hydrogen atom. Recent work by Shapiro and co-workers[161,162] has, however, shown that molecular elimination can occur *via* 3- or 5-membered transition states when neopentyl chloride or bromide is decomposed in the presence of cyclohexene inhibitor. The elimination reactions which occur can be explained by formation of an ion-pair type of transition state followed by highly polar cyclic transition states in which the halogen atom removes an $\alpha$- or $\gamma$-hydrogen atom.

**F. Esters (Table 7).**—The unimolecular decompositions of esters are known to occur *via* a 6-centred transition state. These decompositions have recently been

[153] P. Hammonds and K. A. Holbrook, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 2195.
[154] T. Imai and S. Nishida, *Chem. Lett. (Japan)*, 1980, **1**, 41.
[155] A. Maccoll and P. J. Thomas, *Nature*, 1955, **176**, 392.
[156] S. W. Benson and A. N. Bose, *J. Chem. Phys.*, 1963, **39**, 3463.
[157] S. W. Benson and G. R. Haugen, *J. Am. Chem. Soc.*, 1965, **87**, 4036.
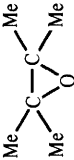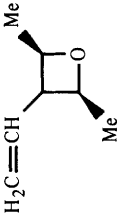[158] A. Maccoll and M. N. Mruzek, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 2714.
[159] A. Maccoll, M. N. Mruzek, and M. A. Baldwin, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 838.
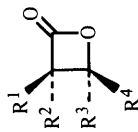[160] G. Chuchani, I. Martin, G. Martin, and D. Bigley, *Int. J. Chem. Kinet.*, 1979, **11**, 109.
[161] R. L. Failes, Y. Mollah, and J. S. Shapiro, *Int. J. Chem. Kinet.*, 1981, **13**, 7.
[162] R. L. Failes, Y. Mollah, and J. S. Shapiro, *Int. J. Chem. Kinet.*, 1979, **11**, 1271.

**Table 5** *High-pressure Arrhenius parameters for the thermolysis of some heterocyclic compounds*

| Reactant | Product(s) | $\log_{10}(A_\infty/\mathrm{s}^{-1})$ | $E_\infty/\mathrm{kJ\,mol^{-1}}$ | Ref. |
|---|---|---|---|---|
| (oxirane with $CF_3$ substituent) | $CF_3COMe$<br>$CF_3CH_2CHO$ | $13.15 \pm 0.57$<br>$14.49 \pm 0.68$ | $239.7 \pm 7.6$<br>$259.0 \pm 9.4$ | a |
| (dioxolane: Me, Me, Me, Me ring structure) | $Me_3CCOMe$<br>$MeC(=CH_2)OCHMe_2$<br>$(\rightarrow Me_2CO + MeCH=CH_2)$<br>$MeC(=CH_2)C(OH)Me_2$ | $13.57 \pm 0.46$<br><br>$13.55 \pm 0.34$<br>$11.81 \pm 0.94$ | $233.4 \pm 6.2$<br><br>$235.0 \pm 4.5$<br>$209.8 \pm 12.5$ | b |
| $H_2C\!\!=\!\!CH$ (oxetane with two Me groups) | $MeCHO + MeCH=CHCH=CH_2$ | $13.42 \pm 0.60$ | $200.3 \pm 7.5$ | c |
| (oxetane with Me group) | $MeCH=CH_2 + CH_2O$<br>$MeCHO + C_2H_4$ | $14.64 \pm 0.36$<br>$14.53 \pm 0.36$ | $249.8 \pm 4.7$<br>$249.8 \pm 4.7$ | d |
| (oxetane with two Me groups) | $Me_2CH=CH_2 + CH_2O$<br>$Me_2CO \qquad + C_2H_4$ | $13.48 \pm 0.25$<br>$15.56 \pm 0.34$ | $222.1 \pm 2.9$<br>$270.6 \pm 4.4$ | d |

| | | | | |
|---|---|---|---|---|
| | | R² = R³ = H  R⁴ = Ph | 12.89 | 138.7 |
| | | R² = R⁴ = H  R³ = Ph | 12.42 | 126.5 |
| | R¹ = Me | R² = R³ = H  R⁴ = Ph | 12.79 | 142.0 |
| | R¹ = Pr$^i$ | R² = R⁴ = H  R³ = Ph | 12.92 | 133.6 |
| | R¹ = Pr$^i$ | R² = R³ = H  R⁴ = Ph | 12.46 | 147.9 |
| | R¹ = Bu$^t$ | R² = R⁴ = H  R³ = Ph | 12.81 | 135.3 |

R¹ = Me, R² = R³ = H  R⁴ = Ph — $e$

| Reaction | log | $E$ | ref |
|---|---|---|---|
| $CH_2=CCH=CH_2 + CH_2O$ (with Me) | $14.62 \pm 0.03$ | $209.5 \pm 0.4$ | $g$ |
| $CH_2=CHCH=CH_2 + CH_2O$ | $14.31 \pm 0.14$ | $208.1 \pm 1.7$ | $h$ |
| $MeCHO + MeCH=CHCH=CH_2$ | $13.91 \pm 0.1$ | $196.3 \pm 1.2$ | $i$ |
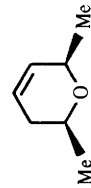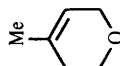
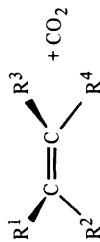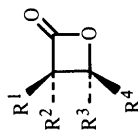[a] M. C. Flowers and M. R. Honeyman, J. Chem. Soc., Faraday Trans. 1, 1980, 76, 2290. [b] M. C. Flowers and M. R. Honeyman, J. Chem. Soc., Faraday Trans. 1, 1981, 77, 1923. [c] Ref. 151. [d] Ref. 153. [e] T. Imai and S. Nishida, J. Org. Chem., 1980, 45, 2354. Arrhenius parameters calc from $\Delta H^\neq$, $\Delta S^\neq$ values at 150 °C. Reactions studied in tetramethylene diamine solvent. [f] H. M. Frey and H. P. Watts, Int. J. Chem. Kinet., 1981, 13, 729. [h] H. M. Frey and S. P. Lodge, J. Chem. Soc., Perkin Trans. 2, 1979, 1463. [i] H. M. Frey, R. Pottinger, H. A. J. Carless, and D. J. Lingley, J. Chem. Soc., Perkin Trans. 2, 1979, 1460.

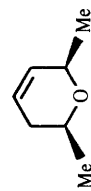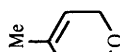**Table 6** *High-pressure Arrhenius parameters for some alkyl halide eliminations*

| Reactant | Product(s) | $\log_{10}(A_\infty/\text{s}^{-1})$ | $E_\infty/\text{kJ mol}^{-1}$ | Ref. |
|---|---|---|---|---|
| EtCl | $C_2H_4 + HCl$ | $13.84 \pm 0.2$ | $241.8 \pm 4.2$ | a |
| $CH_2DCH_2Cl$ | $CHD{=}CH_2 + HCl$ | $13.33 \pm 0.1$ | $239.2 \pm 2.09$ | b |
| | $C_2H_4 + DCl$ | | | |
| EtF | $C_2H_4 + HF$ | $13.65 \pm 0.2$ | $248.9 \pm 4.2$ | c |
| EtBr | $C_2H_4 + HBr$ | $12.5$ | $216.3$ | d |
| $Pr^nCl$ | $C_3H_6 + HCl$ | $13.49 \pm 0.24$ | $227.6 \pm 4.6$ | a |
| | | $13.44 \pm 0.28$ | $229.3 \pm 5.4$ | c |

*β-substituted ethyl chlorides*

| Reactant | Product(s) | $\log_{10}(A_\infty/\text{s}^{-1})$ | $E_\infty/\text{kJ mol}^{-1}$ | Ref. |
|---|---|---|---|---|
| $X^1X^2CHCH_2Cl$ | $X^1X^2C{=}CH_2 + HCl$ | | | |
| $X^1 = H\ X^2 = Me_2N$ | | $13.22 \pm 0.17$ | $203.7 \pm 2.1$ | e |
| $X^1 = H\ X^2 = MeO$ | | $14.06 \pm 0.53$ | $244.7 \pm 7.1$ | e |
| $X^1 = H\ X^2 = Me_2CH$ | | $14.12 \pm 0.05$ | $235.3 \pm 0.7$ | f |
| $X^1 = H\ X^2 = Me_3C$ | | $13.08 \pm 0.19$ | $218.8 \pm 2.5$ | f |
| $X^1 = H\ X^2 = CN$ | | $13.20 \pm 0.3$ | $241.0 \pm 4.0$ | g |
| $X^1 = Me\ X^2 = CN$ | | $13.49 \pm 0.25$ | $241.2 \pm 3.5$ | h |
| $X^1 = H\ X^2 = Ph$ | | $13.07 \pm 0.35$ | $220.9 \pm 4.6$ | i |
| $X^1 = H\ X^2 = PhOMe$ | | $13.81 \pm 0.34$ | $228.4 \pm 4.6$ | i |
| $MeC(Me)ClEt$ | $Me_2C{=}CHMe + HCl$ | $13.77 \pm 0.25$ | $184.1 \pm 2.6$ | j |
| $MeC(Me)ClCHMe_2$ | $Me_2C{=}CMe_2 + HCl$ | $13.33 \pm 0.18$ | $175.3 \pm 1.9$ | j |

R¹R²C=CR³R⁴ + CO₂

(from cyclobutanone structure with R¹, R², R³, R⁴ and O)

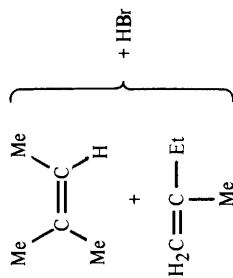| | | $\log A$ | $E_a$ | |
|---|---|---|---|---|
| R¹ = Me | R² = R³ = H R⁴ = Ph | 12.89 | 138.7 | |
| R¹ = Me | R² = R⁴ = H R³ = Ph | 12.42 | 126.5 | |
| R¹ = Prⁱ | R² = R³ = H R⁴ = Ph | 12.79 | 142.0 | |
| R¹ = Prⁱ | R² = R⁴ = H R³ = Ph | 12.92 | 133.6 | |
| R¹ = Buᵗ | R² = R³ = H R⁴ = Ph | 12.46 | 147.9 | |
| R¹ = Buᵗ | R² = R⁴ = H R³ = Ph | 12.81 | 135.3 | e |
| (4-methyl-3,6-dihydro-2H-pyran) | $CH_2=CCH=CH_2 + CH_2O$ (Me) | 14.62 ± 0.03 | 209.5 ± 0.4 | g |
| (3,6-dihydro-2H-pyran) | $CH_2=CHCH=CH_2 + CH_2O$ | 14.31 ± 0.14 | 208.1 ± 1.7 | h |
| (2,6-dimethyl-3,6-dihydro-2H-pyran) | $MeCHO + MeCH=CHCH=CH_2$ | 13.91 ± 0.1 | 196.3 ± 1.2 | i |

[a] M. C. Flowers and M. R. Honeyman, J. Chem. Soc., Faraday Trans. 1, 1980, 76, 2290. [b] M. C. Flowers and M. R. Honeyman, J. Chem. Soc., Faraday Trans. 1, 1981, 77, 1923. [c] Ref. 151. [d] Ref. 153. [e] T. Imai and S. Nishida, J. Org. Chem., 1980, 45, 2354. Arrhenius parameters calc from ΔH‡, ΔS‡ values at 150 °C. Reactions studied in tetramethylene diamine solvent. [f] H. M. Frey and H. P. Watts, Int. J. Chem. Kinet., 1981, 13, 729. [h] H. M. Frey and S. P. Lodge, J. Chem. Soc. Perkin Trans. 2, 1979, 1463. [i] H. M. Frey, R. Pottinger, H. A. J. Carless, and D. J. Lingley, J. Chem. Soc., Perkin Trans. 2, 1979, 1460.
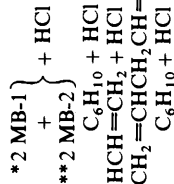
| Reaction | | | |
|---|---|---|---|
| CMe₃CH₂Br → $\left.\begin{array}{c}\text{Me}_2\text{C=CMe}_2 \\ + \\ \text{H}_2\text{C=C(Me)Et}\end{array}\right\}$ + HBr | 14.2 ± 0.3 | 247 ± 5 | k |
| CMe₃CH₂Cl → $\left.\begin{array}{c}\text{*2 MB-1} \\ + \\ \text{**2 MB-2}\end{array}\right\}$ + HCl | 13.78 ± 0.6 | 258.7 ± 8.4 | l |
| Me₂C=CH(CH₂)₂Cl → C₆H₁₀ + HCl | 13.43 ± 0.3 | 215.0 ± 3.7 | m |
| CH₂=CH(CH₂)₂Cl → CH₂=CHCH=CH₂ + HCl | 13.79 ± 0.17 | 223.8 ± 2.1 | n |
| CH₂=CH(CH₂)₃Cl → CH₂=CHCH₂CH=CH₂ + HCl | 14.25 ± 1.20 | 238.4 ± 12.7 | n |
| CH₂=CH(CH₂)₄Cl → C₆H₁₀ + HCl | 12.38 ± 0.22 | 209.6 ± 2.9 | n |

* 2-methylbut-1-ene.   ** 2-methylbut-2-ene.   a P. J. Evans, T. Ichimura, and E. Tschuikow-Roux, Int. J. Chem. Kinet., 1978, 10, 855.   b P. J. Papagiannakopoulos and S. W. Benson, Int. J. Chem. Kinet., 1982, 14, 63. Overall parameters.   c K. Okada, E. Tschuikow-Roux, and P. J. Evans, J. Phys. Chem., 1980, 84, 467.   d T. J. Park and K. H. Jung, Bull. Korean Chem. Soc, 1980, 1, 30.   e Ref. 160.   f G. Chuchani, J. Phys. Chem, 1978, 82, 2767.   g K. D. King, J. Chem. Soc., Faraday Trans. 1, 1978, 74, 912.   h G. Chuchani and A. Rotinov, React. Kinet. Catal. Lett., 1979, 12, 333.   i J. A. Hernández A and G. Chuchani, Int. J. Chem. Kinet., 1978, 10, 923; see also G. Chuchani, J. D. Medina, I. Martin, and J. A. Hernández A, J. Phys. Chem, 1981, 85, 3900.   j G. Chuchani and I. Martin, J. Phys. Chem, 1980, 84, 3188.   k Ref. 161. Maximum inhibition by cyclohexene.   l Ref. 162. Experiments with [²H₂]neopentyl chloride have confirmed the molecular eliminations occurring for maximal inhibition by cyclohexene.   m G. Chuchani, I. Martin, M. E. Alonso, and P. Jano, Int. J. Chem. Kinet., 1981, 13, 1.   n G. Chuchani, J. A. Hernández A, and I. Martin, Int. J. Chem. Kinet., 1979, 11, 1279. For some other examples of neighbouring-group participation see G. Chuchani, A. Rotinov, A. Hernández A, and R. M. Domínguez, Int. J. Chem. Kinet., 1982, 14, 381.

*Substitution at C-3*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| H | H | H | H | H | Pr$^i$ | 12.73 ± 0.29 | 202.5 ± 3.8 | g |
| H | H | H | H | H | Bu$^t$ | 12.34 ± 0.35 | 194.1 ± 4.2 | g |
| H | H | H | H | H | Bu$^s$ | 13.62 ± 0.09 | 211.9 ± 1.2 | h |
| H | H | H | H | H | Bu$^i$ | 12.82 ± 0.05 | 203.1 ± 0.6 | h |
| H | H | H | H | H | cC$_6$H$_{11}$ | 13.20 ± 0.26 | 207.4 ± 3.2 | h |
| H | H | H | H | H | cC$_5$H$_9$ | 13.30 ± 0.28 | 208.1 ± 3.4 | h |
| H | H | H | H | H | Me$_2$N | 13.90 ± 0.30 | 220.4 ± 3.8 | i |
| H | H | H | H | H | MeO | 12.04 ± 0.24 | 203.7 ± 2.9 | i |
| H | H | H | H | H | MeS | 11.27 ± 0.39 | 179.0 ± 4.6 | i |
| H | H | H | H | H | Cl | 12.14 ± 0.66 | 202.0 ± 8.4 | i |
| H | H | H | H | H | F | 12.68 ± 0.60 | 211.2 ± 7.1 | i |
| H | H | H | H | H | CN | 11.51 ± 0.13 | 171.9 ± 1.7 | i |
| H | H | H | H | Me | Bu$^t$ | 12.87 ± 0.31 | 181.2 ± 3.4 | j |
| H | H | H | H | H | CH=CH$_2$ | 13.20 ± 0.17 | 200.8 ± 2.1 | k |
| H | H | H | H | H | CH$_2$CH=CH$_2$ | 12.81 ± 0.36 | 204.0 ± 4.5 | k |
| H | H | H | H | H | (CH$_2$)$_2$CH=CH$_2$ | 12.43 ± 0.14 | 197.5 ± 1.8 | k |
| H | H | H | Me | H | CH=CH$_2$ | 12.34 ± 0.25 | 178.2 ± 2.9 | k |
| H | H | Me | Me | H | CH=CH$_2$ | 13.59 ± 0.30 | 169.9 ± 2.9 | k |
| H | H | H | H | H | Me$_2$C=CH | 13.21 ± 0.14 | 199.6 ± 1.7 | l |
| H | H | H | H | H | o-MeC$_6$H$_4$— | 12.47 ± 0.28 | 192.5 ± 3.5 | m |
| H | H | H | H | H | o-MeOC$_6$H$_4$— | 12.49 ± 0.20 | 193.0 ± 2.4 | m |

[a] G. Chuchani, I. Martin, G. Fraile, O. Lingstuyl, and M. J. Diaz, *Int. J. Chem. Kinet.*, 1978, **10**, 893. [b] M. A. G. Sarmiento, R. M. Dominguez, and G. Chuchani, *J. Phys. Chem.*, 1980, **84**, 2531. [c] G. Chuchani, J. L. Triana, A. Rotinov, D. F. Caraballo, *J. Phys. Chem.*, 1981, **85**, 1243. [d] P. G. Blake and B. F. Sharydeh, *Int. J. Kinet.*, 1981, **13**, 463. [e] G. Chuchani and J. L. Triana, *React. Kinet. Catal. Lett.*, 1981, **18**, 433. [f] I. Martin, G. Chuchani, I. Avila, A. Rotinov, and R. Olmos, *J. Phys. Chem.*, 1980, **84**, 9. [g] G. Chuchani, I. Martin, and I. Avila, *Int. J. Chem. Kinet.*, 1979, **11**, 561. [h] I. Martin and G. Chuchani, *J. Phys. Chem.*, 1981, **85**, 3902. [i] G. Chuchani, I. Martin, J. A. Hernández A, A. Rotinov, and G. Fraile, and D. B. Bigley, *J. Phys. Chem.*, 1980, **84**, 944. [j] G. Chuchani and R. M. Dominguez, *Int. J. Chem. Kinet.*, 1981, **13**, 577. Individual Arrhenius parameters for the formation of various pentene products are given. [k] I. Martin, J. A. Hernández A, A. Rotinov, and G. Chuchani, *J. Phys. Chem.*, 1979, **83**, 3070. [l] G. Chuchani, I. Martin, and M. E. Alonso, *J. Phys. Chem.*, 1981, **85**, 1241. Reaction inhibited by propene. [m] G. Chuchani, A. Rotinov, D. F. Caraballo, and J. D. Medina, *React. Kinet. Catal. Lett.*, 1980, **13**, 173. Reactions in presence of cyclohexene inhibitor.

reviewed by Taylor.[163] The table summarizes recent experimental work (largely by Chuchani and co-workers) concerning the decompositions of esters substituted at the C-1, C-2, or C-3 positions (see Table 7) in the parent molecule.

The principal conclusions are that for substitution at C-1, electron-withdrawing substituents enhance the rate of elimination whereas electron-releasing substituents decrease it; many substituents at C-2 enhance the rate by steric acceleration; at C-3, branched alkyl-substituents cause slight steric acceleration and anchimeric assistance appears not to occur.

The results confirm, in general, the semi-polar semi-concerted transition state which is considerably less heterolytic than that for alkyl halides. The Arrhenius parameters reported in Table 7 are in line with those found in earlier work.

**G. Other Six-centred Elimination Reactions (Table 8).**—Arrhenius parameters for some other six-centred elimination reactions are listed in Table 8. Included are the molecular retro-ene decompositions of a number of unsaturated hydrocarbons. When studied under normal static thermolysis conditions these are often accompanied by free radical processes, as for example was found by Richard, Scacchi, and Back[164] who estimated Arrhenius parameters for 3-methylpentene decomposition from measured rate constants for the reverse addition of ethene to but-2-ene and the known equilibrium constant. King[165] and co-workers have used the technique of VLPP to study the competing processes of retro-ene reaction and $C-C$ bond fission for a number of alkenes and alkynes. For alkynes it is found that the retro-ene pathway is faster relative to bond fission than for alkenes. For hex-1-yne, the $A$ factor found by Tsang[166] for the molecular retro-ene reaction was assumed and $E_\infty$ found from the VLPP data by RRKM calculations. The gas–wall collisional energy transfer efficiency $\beta_w$ was assumed to vary with temperature in the manner found for chlorocyclobutane.

All of the $A$ factors shown in Table 8 lie within the limits of $10^{11.5 \pm 1.5}$ predicted by O'Neal and Benson[167] for reactions with six-centred transition states.

**H. Bond Fission Reactions (Table 9).**— Probably the most-studied unimolecular bond fission reaction in recent years has been the decomposition of ethane into two methyl radicals. Two recent determinations of the high pressure Arrhenius parameters are quoted in Table 9. From a survey of the experimental data on this reaction and the reverse methyl radical recombination, Baulch and Duxbury[168] have given the following recommended rate expressions:

$$\log(k^\infty_{\text{decomp}}/s^{-1}) = (16.38 \pm 0.5) - (44010 \pm 3170/2.303[T/K])$$

[163] R. Taylor in 'The Chemistry of the Functional Groups' Suppl. Vol. B 'Acid Derivatives', ed. S. Patai, Wiley, London, 1979, p. 859.
[164] C. Richard, G. Scacchi, and M. H. Back, *Int. J. Chem. Kinet.*, 1978, **10**, 307.
[165] K. D. King, *Int. J. Chem. Kinet.*, 1979, **11**, 1071, and other refs. following Table 8.
[166] W. Tsang, *Int. J. Chem. Kinet.*, 1978, **10**, 687.
[167] H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 1967, **71**, 2903.
[168] D. L. Baulch and J. Duxbury, *Combustion and Flame*, 1980, **37**, 313.
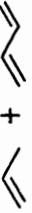
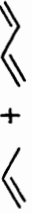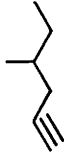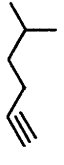**Table 8**  *High-pressure Arrhenius parameters for some other 6-centred eliminations*

| Reactant | Product(s) | $\log_{10}(A_\infty/\mathrm{s}^{-1})$ | $E_\infty/\mathrm{kJ\,mol^{-1}}$ | Ref. |
|---|---|---|---|---|
| *Alkenes* | | | | |
| (structure) | (structure) + (CH₂=CH₂) | $11.97 \pm 0.3$ | $229.3 \pm 4.2$ | a |
| | (structure) + (CH₂=CH₂) | $11.43 \pm 0.3$ | $228.9 \pm 4.2$ | b |
| (structure) | 2 (structure) | $12.6 \pm 0.2$ | $241.4 \pm 6.3$ | c |
| | | $12.6$ | $240.3$ | |
| *Dienes* | | | | |
| (structure) | (structure) + (structure) | $11.3 \pm 0.4$ | $197.1 \pm 4.2$ | d |
| *Alkynes and Diynes* | | | | |
| (structure) | $CH_2{=}C{=}CH_2 + C_2H_4$ | $12.8 \pm 0.4$ | $238.5 \pm 8.4$ | e |
| (structure) | $CH_2{=}C{=}CH_2 + C_3H_6$ | $12.7$ | $236.1$ | f |
| (structure) | | $12.7 \pm 0.4$ | $236.0 \pm 4.2$ | g |

**Table 8**—*continued*

| Reactant | Product(s) | $\log_{10}(A_\infty/\text{s}^{-1})$ | $E_\infty/\text{kJ mol}^{-1}$ | Ref. |
|---|---|---|---|---|
|  | $CH_2{=}C{=}CH_2 + CH_2{=}CHC{\equiv}CH$ | $12.6 \pm 0.4$ | $216.3 \pm 4.2$ | d |
|  | $CH_2{=}C{=}CH_2 + C_4H_8$ | 12.9 | 232.8 | f |
|  | $CH_2{=}C{=}CH_2 + \text{i-}C_4H_8$ | 12.3 | 228.6 | f |
|  | $MeCH{=}C{=}CH_2 + \text{i-}C_4H_8$ | 12.3 | 238.6 | f |

*Vinyl ethers*

| Reactant | Product(s) | $\log_{10}(A_\infty/\text{s}^{-1})$ | $E_\infty/\text{kJ mol}^{-1}$ | Ref. |
|---|---|---|---|---|
|  | $C_2H_4 + MeCHO$ | $11.47 \pm 0.25$ | $181.6 \pm 4.2$ | h |
|  | $+\ MeCHO$ | $12.00 \pm 0.27$ | $160.7 \pm 4.2$ | h |
|  | $+\ Me_2CO$ | $11.98 \pm 0.46$ | $168.1 \pm 5.1$ | i |

| Compound | Products | $\log A$ | $E$ | Ref. |
|---|---|---|---|---|
| *Carbamates* | | | | |
| Me(H)NCO$_2$Et | MeNH$_2$ + CO$_2$ + C$_2$H$_4$ | 12.47 | 192.5 | j |
| | MeNCO + EtOH | 12.39 | 197.6 | j |
| *Sulphides* | | | | |
| Me–S–CH$_2$=CHCH$_2$ | MeCH=CH$_2$ + CH$_2$=S | 11.23 ± 0.25 | 160 ± 3 | k |
| (CH$_2$=CHCH$_2$)$_2$S | CH$_2$=CHCH=S + C$_3$H$_6$ | 11.01 ± 0.06 | 138.2 ± 0.7 | k |
| PhCH$_2$–S–CH$_2$=CHCH$_2$ | PhCH=S + C$_3$H$_6$ | 10.93 ± 0.18 | 141 ± 2.0 | k |
| Bu$^n$–S–CH$_2$=CHCH$_2$ | PrCH=S + C$_3$H$_6$ | 11.42 ± 0.28 | 155 ± 3 | l |

[a] Ref. 164. [b] Ref. 165. [c] W. Tsang, *Int. J. Chem. Kinet.*, 1978, **10**, 1119. [d] K. D. King, *J. Phys. Chem.*, 1980, **84**, 2517. [e] K. D. King, *Int. J. Chem. Kinet.*, 1981, **13**, 245. [f] Ref. 166. [g] K. D. King, *Int. J. Chem. Kinet.*, 1981, **13**, 273. [h] M. Rossi and D. M. Golden, *Int. J. Chem. Kinet.*, 1979, **11**, 715. [i] M. C. Flowers and M. R. Honeyman, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 1921. [j] N. J. Daly and F. Ziolkowski, *Int. J. Chem. Kinet.*, 1980, **12**, 241. [k] G. Martin, M. Ropero, and R. Avila, *Phosphorus and Sulfur*, 1982, **13**, 213. [l] G. Martin, A. Drayer, M. Ropero, M. E. Alonso, *Int. J. Chem. Kinet.*, 1982, **14**, 131.

for the range 750—1500 K and

$$\log(k_{\text{recomb}}^{\infty}/\text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}) = (13.38 \pm 0.08)$$

for the range 250—420 K.

A computer simulation of ethane decomposition under shock-tube conditions at high temperatures has been reported.[169]

The Arrhenius parameters for bond fission reactions at high pressures are expected to give activation energies close to the bond-dissociation energies and high $A$ factors characteristic of loose transition states. The difficulty of applying transition-state theory to such reactions has been discussed by Golden[56] and some examples of the application of RRKM theory to a modified Gorin model have been discussed by Baldwin, Lewis, and Golden.[170]

## 8 Thermal Reactions in the Low-pressure and Fall-off Regions (Table 10)

Relatively few conventional studies of unimolecular reactions of moderately complex molecules in their fall-off regions have been reported recently. Bailey and Frey[171] have studied the decomposition of 1,1,2,2-tetrafluorocyclobutane at pressures down to 0.03 Torr and have measured the ratio of rate constants for the two decomposition channels. The results were explained using a step-ladder energy transfer model with $\Delta E = 12$ kJ mol$^{-1}$. Flowers[172] has re-examined the RRKM treatment of the fall-off for the various decomposition channels of fluorocyclopropane. Although there has been some criticism of the original data, it seems that the experiments are consistent with RRKM theory despite an earlier report to the contrary.

Márta and co-workers[173] have recently examined the fall-off behaviour of oxetane and [2,2-$^2$H$_2$]oxetane and have refined earlier RRKM calculations for the former.[174]

The technique of very low pressure pyrolysis (VLPP) has been extensively used especially by King and co-workers[175] and the data obtained extrapolated by RRKM theory to obtain $k_{\infty}$ values. These data are reported in the appropriate tables in Section 7.

Most of the data given in Table 10 refer to small molecules, the decompositions of which are in, or close to, their second-order regions. Extrapolations can often be made with the aid of theory to obtain the rate constants $k_{\text{bim}}$.

Studies in which the prime objective has been to obtain vibrational energy transfer parameters are listed in Table 1, and some fall-off studies concerned with radical decompositions will be referred to in Section 9.

[169] W. M. Lee and C. T. Yeh, *J. Phys. Chem.*, 1979, **83**, 771.
[170] A. C. Baldwin, K. E. Lewis, and D. M. Golden, *Int. J. Chem. Kinet.*, 1979, **11**, 529.
[171] I. M. Bailey and H. M. Frey, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 709.
[172] M. C. Flowers, *Can. J. Chem.*, 1978, **56**, 29.
[173] L. Zalotai, Zs. Hunyadi-Zoltan, T. Bérces, and F. Márta, *Int. J. Chem. Kinet.* Submitted for publication.
[174] K. A. Holbrook and R. A. Scott, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 1849.
[175] See for example K. D. King and R. D. Goddard, *Int. J. Chem. Kinet.*, 1981, **13**, 755.

**Table 9** *High-pressure Arrhenius parameters for some bond-fission reactions*

| Reactant | Product(s) | $\log_{10}(A_\infty/s^{-1})$ | $E_\infty/kJ\,mol^{-1}$ | Ref. |
|---|---|---|---|---|
| *Carbon–carbon bonds* | | | | |
| $C_2H_6$ | 2Me | 16.85 | 377.2 | a |
| | | $16.72 \pm 0.17$ | $371.7 \pm 2.8$ | b |
| $i\text{-}C_4H_{10}$ | $Pr^i$ + Me | 15.92 | 357.4 | c |
| $CMe_4$ | $Bu^t$ + Me | 17.3 | 338.1 | d |
| $Pr^nCH_2CH{=}CH_2$ | $CH_2{=}CHCH_2^{\cdot}$ + $Pr^n$ | $15.9 \pm 0.2$ | $296.2 \pm 4.2$ | e |
| | | 15.9 | 295.9 | f |
| $CH_2{=}CHCH{=}CHCH_2Me$ | $CH_2{=}CHCH{=}CHCH_2^{\cdot}$ + Me | $15.92 \pm 0.17$ | $277.7 \pm 3.5$ | g |
| $MeCH_2C{\equiv}CH$ | $HC{\equiv}CCH_2^{\cdot}$ + Me | $15.5 \pm 0.3$ | $310.4 \pm 8.4$ | h |
| $MeC(Me)_2C{\equiv}CH$ | $HC{\equiv}C\dot{C}Me_2$ + Me | 15.8 | 296.2 | i |
| $PhCH_2CH_2C{\equiv}CH$ | $HC{\equiv}C\dot{C}H_2$ + $PhCH_2$ | $14.6 \pm 0.4$ | $252.3 \pm 8.4$ | j |
| $MeC{\equiv}CCHMe_2$ | $MeC{\equiv}C\dot{C}HMe$ + Me | $16.2 \pm 0.3$ | $311.3 \pm 6.3$ | k |
| $MeC{\equiv}CCMe_3$ | $MeC{\equiv}C\dot{C}Me_2$ + Me | $16.4 \pm 0.3$ | $298.7 \pm 6.3$ | k |
| $Pr^nCH_2C{\equiv}CH$ | $CH{\equiv}C\dot{C}H_2$ + $Pr^n$ | $15.9 \pm 0.3$ | $295.8 \pm 8.4$ | l |
| $PhCH_2Me$ | $PhCH_2$ + Me | 15.3 | 304.2 | m |
| | | 15.85 | 312.5 | n |
| $PhCH_2Et$ | $PhCH_2$ + Et | 15.30 | 291.2 | o |
| $PhCHMe_2$ | $Ph\dot{C}HMe$ + Me | 15.8 | 298.3 | m |
| $PhCH_2Pr^i$ | $PhCH_2$ + $Pr^i$ | 15.6 | 283.7 | o |
| $PhCMe_3$ | $Ph\dot{C}Me_2$ + Me | 15.9 | 289.1 | m |
| $PhCH_2Bu^t$ | $PhCH_2$ + $Bu^t$ | 15.5 | 269.0 | o |
| $Ph(C_6H_4)CH_2Me$ | $Ph(C_6H_4)CH_2$ + Me | 15.65 | 300.4 | n |
| $Ph(C_6H_4)_2CH_2Me$ | $Ph(C_6H_4)_2CH_2$ + Me | 15.60 | 278.2 | n |
| $EtCMe_2NM_2$ | Et + $CMe_2NH_2$ | 16.5 | 320.1 | p |
| $o\text{-}C_6H_4NCH_2Me$ | $o\text{-}C_6H_4NCH_2^{\cdot}$ + Me | 15.0 | $307 \pm 12$ | q |
| $m\text{-}C_6H_4NCH_2Me$ | $m\text{-}C_6H_4NCH_2^{\cdot}$ + Me | 15.0 | $300 \pm 11$ | q |
| $p\text{-}C_6H_4NCH_2Me$ | $p\text{-}C_6H_4NCH_2^{\cdot}$ + Me | 15.0 | $303 \pm 11$ | q |
| *Other C—X bonds* | | | | |
| $\begin{array}{c} CH_2 \\ \| \\ MeCOMe \end{array}$ | $\begin{array}{c} CH_2 \\ \mid \\ Me{-}C{-}\ddot{O} + Me \end{array}$ | 15.8 | 277.4 | r |
| $PhCH_2OCH{=}CH_2$ | $PhCH_2$ + $^{\cdot}CH_2CHO$ | $16.6 \pm 0.3$ | $224.8 \pm 4.2$ | s |
| $MeCOCH_2Br$ | $MeCOCH_2^{\cdot}$ + Br | 16.0 | 261.5 | r |
| $MeCl$ | Me + Cl | 13.86 | 383 | t |
| $SiMe_4$ | $SiMe_3$ + Me | $14.1 \pm 0.2$ | $301.2 \pm 2.9$ | u |
| $GeMe_4$ | $GeMe_3$ + Me | 15.1* | 288.7* | u |
| | | 12.1** | 213.4** | u |
| $SnMe_4$ | $SnMe_3$ + Me | $13.9 \pm 0.4$ | $231.8 \pm 5.9$ | u |
| | | 17.3 | 291.6 | d |
| $GaEt_3$ | $GaEt_2$ + Et | $15.7 \pm 0.2$ | $194.6 \pm 2.4$ | v |
| $t\text{-}C_5H_{11}NH_2$ | $t\text{-}C_5H_{11}$ + $NH_2$ | 15.9 | 330.1 | p |
| $PhN(Me)H$ | $Ph\dot{N}H$ + Me | $15.1 \pm 0.3$ | 279.1 | w |
| $PhNMe_2$ | $Ph\dot{N}Me$ + Me | $15.1 \pm 0.3$ | 270.7 | w |
| $MeNH_2$ | Me + $NH_2$ | 10.84 | 201.5 | x |

**Table 9**—*continued*

| Reactant | Product(s) | $\log_{10}(A_\infty/\text{s}^{-1})$ | $E_\infty/\text{kJ mol}^{-1}$ | Ref. |
|---|---|---|---|---|
| *Azo-compounds* | | | | |
| $RN{=}NR'$ | $R + R' + N_2$ | | | |
| $R = R' = Et$ | | $15.8 \pm 0.1$ | $205.1 \pm 1.5$ | $y$ |
| $R = R' = Pr^i$ | | $16.2 \pm 0.3$ | $196.8 \pm 2.6$ | $y$ |
| $R = R' = Ph$ | | $12.6$ | $223.4 \pm 12$ | $z$ |

*a* D. B. Olson and W. C. Gardiner, Jr., *J. Phys. Chem.*, 1979, **83**, 922; see also D. B. Olson, T. Tanzawa, and W. C. Gardiner, *Int. J. Chem. Kinet.*, 1979, **11**, 23. *b* A. B. Trenwith, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 614. *c* G. Pratt and D. Rogers, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 1694. (Wall-less reactor pyrolysis.) *d* Ref. 170; *A* factors estimated. *e* K. D. King, *Int. J. Chem. Kinet.*, 1979, **11**, 1071. *f* W. Tsang, *Int. J. Chem. Kinet.*, 1978, **10**, 1119. *g* A. B. Trenwith, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 266. *h* K. D. King, *Int. J. Chem. Kinet.*, 1978, **10**, 545. *i* K. D. King, *Int. J. Chem. Kinet.*, 1977, **9**, 907. *j* K. D. King and T. T. Nguyen, *J. Phys. Chem.*, 1979, **83**, 1940. *k* K. D. King, *Int. J. Chem. Kinet.*, 1981, **13**, 255. *l* K. D. King, *Int. J. Chem. Kinet.*, 1981, **13**, 273. *m* D. A. Robaugh and S. E. Stein, *Int. J. Chem. Kinet.*, 1981, **13**, 445. *n* D. F. McMillen, P. L. Trevor, and D. M. Golden, *J. Am. Chem. Soc.*, 1980, **102**, 7400. *E* value for ethyl benzene assumed. *A* values for 1-ethylnaphthalene and 9-ethylanthracene derived by adjustment of the value found for ethylbenzene. *o* D. A. Robaugh, B. D. Barton, and S. E. Stein, *J. Phys. Chem.*, 1981, **85**, 2378. *A* factor for neopentylbenzene estimated. *p* W. Tsang, *Int. J. Chem. Kinet.*, 1978, **10**, 40. *q* B. D. Barton and S. E. Stein, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 1755. *A* factors assumed. *r* F. Zabel, S. W. Benson, and D. M. Golden, *Int. J. Chem. Kinet.*, 1978, **10**, 295. *s* M. Rossi and D. M. Golden, *Int. J. Chem. Kinet.*, 1979, **11**, 715. *t* O. Kondo, K. Saito, and I. Murakami, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2133. Extrapolated by RRKM from shock-tube data (See Table 10). *u* J. E. Taylor and T. S. Milazzo, *J. Phys. Chem.*, 1978, **82**, 847. *above 710 °C; **below 710 °C. *v* M. C. Paputa and S. J. W. Price, *Can. J. Chem.*, 1979, **57**, 3178. *w* A. J. Colussi and S. W. Benson, *Int. J. Chem. Kinet.*, 1978, **10**, 1139. *x* E. A. Dorko, N. R. Pchelkin, J. C. Wert III, and G. W. Mueller, *J. Phys. Chem.*, 1979, **83**, 297. Extrapolated by H–L theory from shock-tube data (See Table 10). *y* G. Ács, A. Peter, and P. Huhn, *Int. J. Chem. Kinet.*, 1980, **12**, 992. *z* A. Leiba and I. Oref, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 2694.

## 9 Radical Decompositions (Table 11)

A useful review has appeared listing free-radical reactions occurring during the low-temperature thermolysis of n-alkanes.[176] Included are many recommended values of Arrhenius parameters for alkyl radical decompositions from a survey of the published data. These are too numerous to list in Table 11, which includes some more recently published data for alkyl radicals and also the extensive results of Batt and co-workers[177] on alkoxy-radical decompositions. The latter have been recently assessed by Choo and Benson.[178]

Attention is drawn to the work on the t-butoxy-radical decomposition in which the fall-off curve has been obtained for the first time. A detailed study of the fall-off curve for the decomposition of the 1,2-dichloroethyl radical has been made by Ashmore, Owen, and Robinson.[179] RRKM calculations incorporat-

[176] D. L. Allara and R. Shaw, *J. Phys. Chem. Ref. Data*, 1980, **9**, 523.
[177] L. Batt, *Int. J. Chem. Kinet.*, 1979, **11**, 977, and refs. cited therein.
[178] K. Y. Choo and S. W. Benson, *Int. J. Chem. Kinet.*, 1981, **13**, 833.
[179] P. G. Ashmore, A. J. Owen, and P. J. Robinson, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 677.

**Table 10** *Unimolecular reactions in the low pressure and fall-off regions*

| Reactant | Product(s) | Kinetic data* | Theory used | Ref. |
|---|---|---|---|---|
| MeCl ($+M$) | Me + Cl ($+M$) | $\log k_{bim} = 15.56 - 247/\theta$ [M = Ar] | RRKM | a |
| MeI ($+M$) | Me + I ($+M$) | $\log k_{bim} = 15.40 - 178.1/\theta$ [M = Ar] | | b |
| $CH_4$ ($+M$) | Me + H ($+M$) | $\log k_{bim} = 17.00 - 358.9/\theta$ [M = Ar] | | c |
| $CD_4$ ($+M$) | $CD_3 + D$ ($+M$) | $\log k_{bim} = 16.32 - 355.2/\theta$ [M = Ar] | RRKM | d |
| $HN_3$ ($+M$) | $NH_3(^3\Sigma^-) + N_2$ ($+M$) | $\log k_{bim} = 13.77 - 128.0/\theta$ [M = Ar] | RRKM | e |
| $MeNH_2$ ($+M$) | Me + $NH_2$ ($+M$) | $\log k_{bim} = 13.50 - 147.0/\theta$ [M = Kr] | H-L | f |
| $C_2H_6$ ($+M$) | 2Me ($+M$) | $\log k_{bim} = 111.29 - 25.26 \log T - 667.8/\theta$ [M = $C_2H_6$ or Ar] | RRK | g |

* '$\log k_{bim}' \equiv \log_{10}(k_{bim}/cm^3 mol^{-1} s^{-1})$, $\theta = 19.147 \times 10^{-3} T/K$. [a] O. Kondo, K. Saito, and I. Murakami, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2133. (See also Table 9). [b] K. Saito, H. Tahara, O. Kondo, T. Yokubo, T. Higashihara, and I. Murakami, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1335. (See also Table 9) [c] K. Tabayahi and S. H. Bauer, *Combustion and Flame*, 1979, **34**, 63. [d] C. C. Chiang, J. A. Baker, and G. B. Skinner, *J. Phys. Chem.*, 1980, **84**, 939. [e] O. Kajimoto, T. Yamamoto, and T. Fueno, *J. Phys. Chem.*, 1979, **83**, 429. [f] J. E. Dove and W. S. Nip, *Can. J. Chem.*, 1979, **57**, 689. [g] D. B. Olson, T. Tanzawa, and W. C. Gardiner, *Int. J. Chem. Kinet.*, 1979, **11**, 23.

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**Table 11**  *High-pressure Arrhenius parameters for some decompositions of radicals*

| Radical | Product(s) | $\log_{10}(A_\infty/s^{-1})$ | $E_\infty/kJ\ mol^{-1}$ | Ref. |
|---|---|---|---|---|
| Et | $C_2H_4 + H$ | $13.5 \pm 0.7$ | $175 \pm 12$ | *a* |
| Bu$^i$ | $Me + C_3H_6$ | — | $136.5 \pm 4.8$ | *b* |
| Bu$^t$ | $i$-$C_4H_8 + H$ | $14.67$ | $164.8$ | *c* |
| Bu$^t$CH(Me)CH$_2$ | $Bu^tCH{=}CH_2 + Me$ | $13.8 \pm 0.5$ | $130 \pm 7$ | *d* |
| Bu$^t$CH(Me)CH$_2$ | $C_3H_6 + Bu^t$ | $13.8 \pm 0.5$ | $111 \pm 7$ | *d* |
| Me$_2$C(CH$_2$)Pr$^i$ | $CH_2{=}C(Me)Pr^i + Me$ | $13.8 \pm 0.5$ | $121 \pm 7$ | *d* |
| Me$_2$C(CH$_2$)Pr$^i$ | $Me_2C{=}CH_2 + Pr^i$ | $13.8 \pm 0.5$ | $107 \pm 7$ | *d* |
| Bu$^t$CMe$_2$ | $i$-$C_4H_8 + Pr^i$ | $13.8 \pm 0.5$ | $114 \pm 7$ | *d* |
| MeO | $CH_2O + H$ | $14.2 \pm 0.5$ | $112.3 \pm 4.2$ | *e* |
| EtO | $CH_2O + Me$ | $15.0 \pm 0.5$ | $90.4 \pm 4.2$ | *e* |
| Pr$^n$O | $CH_2O + Et$ | $13.7$ | $65.3$ | *f* |
| Pr$^i$O | $Me + MeCHO$ | $14.6 \pm 0.5$ | $72.0 \pm 4.2$ | *e* |
| | | $13.8$ | $70.3$ | *f* |
| Bu$^i$O | $CH_2O + Pr^i$ | $13.7$ | $51.9$ | *f* |
| Bu$^t$O | $Me_2CO + Me$ | $15.5 \pm 0.5$ | $71.1 \pm 4.2$ | *e* |
| | | $14.1$ | $64.0$ | *f* |
| Bu$^s$O | $Et + MeCHO$ | $14.9 \pm 0.5$ | $64.0 \pm 4.2$ | *e* |
| | | $13.6$ | $56.5$ | *f* |
| $s$-$C_5H_{11}O$ | $Pr^i + MeCHO$ | $13.7$ | $43.1$ | *f* |
| $t$-$C_5H_{11}O$ | $Me_2CO + Et$ | $14.8 \pm 0.5$ | $57.7 \pm 4.2$ | *e* |
| | | $13.6$ | $51.9$ | *f* |
| | $MeEtCO + Me$ | $13.8$ | $67.4$ | *f* |
| $t$-$C_6H_{13}O$ | $Me_2CO + Pr^i$ | $13.6$ | $40.6$ | *f* |
| $C_2H_3Cl_2$ | $C_2H_3Cl + Cl$ | $14.3$ | $84.0$ | *g* |

*a* G. Pratt and D. Rogers, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 1089. Deduced from ethane pyrolysis in wall-less reactor 941—1073 K.  *b* G. McKay and J. M. C. Turner, *Int. J. Chem. Kinet.*, 1978, **10**, 89.  *c* C. E. Canosa and R. M. Marshall, *Int. J. Chem. Kinet.*, 1981, **13**, 303.  *d* R. R. Baldwin, R. W. Walker, and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 2157.  *e* Ref. 177. *f* Ref. 178; *A* factors estimated. Activation energies derived from *A* factors and experimental rate-constants from ref. *e* and other sources.  *g* Ref. 179.

ing a centrifugal effect are in good agreement with the experimental data of Ashmore and co-workers[180] and of Huybrechts and co-workers.[181]

**10 Radical Recombination and Addition Reactions (Table 12)**
The reverse of bond dissociation is the recombination of radicals to give molecules which is a process equally treated by unimolecular theory. The change in order for bond-dissociation from first to second at low pressures is paralleled by a change from second to third order for the corresponding radical recombination. If the process

$$A + B + M \rightarrow AB + M$$

[180] P. G. Ashmore, J. W. Gardner, A. J. Owen, B. Smith, and P. R. Sutton, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 657.
[181] G. Huybrechts, J. Katihabwa, G. Martens, M. Nejszaten, and J. Olbregts, *Bull. Soc. Chim. Belg.*, 1972, **81**, 65.

**Table 12** *Radical recombination and addition reactions*

| Reaction | T/K | Kinetic data* | Comments and Ref. |
|---|---|---|---|
| $CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2 + M$ | 298 | $k_{rec,0} = (4.32 \pm 0.22) \times 10^{11}$ (M = He)<br>$k_{rec,0} = (8.45 \pm 0.29) \times 10^{11}$ (M = N$_2$)<br>$k_{rec,0} = (1.85 \pm 0.05) \times 10^{12}$ (M = SF$_6$)<br>$k_{rec,\infty} = (4.82 \pm 0.60) \times 10^{9}$ | Rate constants extrapolated by approximate Troe method [a] |
| | 298 | $k_{rec} = (7.22 \pm 1.80) \times 10^{8}$ (50 Torr Ar/CH$_4$)<br>$k_{rec} = (9.60 \pm 1.80) \times 10^{8}$ (540 Torr N$_2$) | [b] |
| $2CF_3 + M \rightarrow C_2F_6 + M$ | 1250—1400 | $k_{rec,\infty} = (1.90 \pm 0.9) \times 10^{10}$ | Rate constants extrapolated by approximate Troe method [c] |
| | 930—1110 | $k_{rec,0} = 1.1 \times 10^{14}$ (M = Ar)<br>$k_{rec,\infty} = 5 \times 10^{9} - 5 \times 10^{10}$ | Extrapolated from fall-off data VLPP conditions [d] |
| $F + NO + M \rightarrow FNO + M$ | 195—288 | $k_{rec,0} = (2.99 \pm 0.18) \times 10^{10}$ (M = He)<br>$k_{rec,\infty} = (4.5 \pm 4) \times 10^{10} \exp(+0.88 \text{ kJ mol}^{-1} / RT)$ (M = NO) | [e] |
| $OH + NO_2 + N_2 \rightarrow HNO_3 + N_2$ | 225—389 | $k_{rec,0} = 8.34 \times 10^{11} (T/298)^{-2.9}$<br>$k_{rec,\infty} = 7.23 \times 10^{9} (T/298)^{-1.6}$ | Rate constants extrapolated by approximate Troe method [f] |

**Table 12**—*continued*

| Reaction | T/K | Kinetic data* | Comments and Ref. |
|---|---|---|---|
| $ClO + NO_2 + M \rightarrow ClONO_2 + M$ | 298 <br> 274—339 | $k_{rec} = 5.44 \times 10^{10}$ $(M = N_2)$ <br> $k_{rec} = (1.56 \pm 0.43) \times 10^9$ $(M = N_2)$ | Measured at 50 Torr [g] [h] |
| $O + NO + M \rightarrow NO_2 + M$ | 217—500 | $k_{rec,0} = 2.80 \times 10^{14} T^{-1.63}$ $(M = He)$ <br> $k_{rec,0} = 1.00 \times 10^{15} T^{-1.86}$ $(M = Ar)$ <br> $k_{rec,0} = 1.38 \times 10^{15} T^{-1.82}$ $(M = N_2)$ | Application of Troe Theory [i] |
| $Cl + NO + M \rightarrow NOCl + M$ | 200—400 <br> 298 | $k_{rec,0} = 1.39 \times 10^{15} T^{-1.91}$ $(M = N_2)$ <br> $k_{rec,0} = (1.49 \pm 0.07) \times 10^{10}$ $(M = He)$ <br> $k_{rec,0} = (1.59 \pm 0.10) \times 10^{10}$ $(M = Ar)$ | Application of Troe Theory [i] |
| $H + CO + M \rightarrow HCO + M$ | 298 | $k_{rec,0} = (3.6 \pm 0.9) \times 10^7$ $(M = CO)$ <br> $k_{rec,0} = (5.8 \pm 0.6) \times 10^7$ $(M = CH_4)$ <br> $k_{rec,0} = (3.8 \pm 0.4) \times 10^7$ $(M = H_2)$ | [j] |

* Units of $k_{rec,\infty}$ and $k_{rec}$ are $dm^3 \, mol^{-1} \, s^{-1}$. Units of $k_{rec,0}$ are $dm^6 \, mol^{-2} \, s^{-1}$. [a] S. P. Sanders and R. T. Watson, *J. Phys. Chem.*, 1980, **84**, 1664. [b] R. A. Cox and G. S. Tyndall, *Chem. Phys. Lett.*, 1979, **65**, 357. [c] K. Glänzer, M. Maier, and J. Troe, *J. Phys. Chem.*, 1980, **84**, 1681. [d] M. Rossi and D. M. Golden, *Int. J. Chem. Kinet.*, 1979, **11**, 775. [e] P. Kim, D. I. McLean, and W. G. Valance, *J. Phys. Chem.*, 1980, **84**, 1806. [f] L. G. Anderson, *J. Phys. Chem.*, 1980, **84**, 2152. [g] M. J. Molina, L. T. Molina, and T. Ishiwata, *J. Phys. Chem.*, 1980, **84**, 3100. [h] R. A. Cox and R. Lewis, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 2649. [i] Ref. 182. [j] C. J. Hochanadel, T. J. Sworski, and P. J. Ogren, *J. Phys. Chem.*, 1980, **84**, 231.

is described by the second-order rate constant $k_{rec}$ defined by

$$d[AB]/dt = k_{rec}[A][B]$$

then the limiting values of $k_{rec}$ are $k_{rec,\infty}$ at high pressures which is independent of [M], and $k_{rec,0}$ at low pressures which is given by

$$k_{rec,0} = k_{rec}[M]$$

At intermediate pressures (the fall-off region), $k_{rec}$ can be expressed in terms of $k_{rec,0}$, $k_{rec,\infty}$ and a broadening factor $F_c$ which expresses the deviation of the fall-off curve from the Lindemann-Hinshelwood expression. This convention which is due to Troe[36] has been adopted in a compilation of rate data prepared for the CODATA Task Group on chemical kinetics and which includes data on recombination reactions involved in atmospheric chemistry published up to December 1978.[37]

Table 12 contains some more recent data and comments on radical recombination and addition reactions, particularly those in which some unimolecular theory calculations have been applied. A particularly comprehensive study is that of Michael and Lee[182] for the addition reactions of O and Cl atoms with NO which is reported in the Table. Values of the collisional deactivation efficiency $\beta_c$ were derived by comparison of $k_{rec}$ with the theoretical strong-collision values calculated by the Troe theory. Some anomalies remain concerning the temperature dependence of $\beta_c$, but in general it was possible to reconcile both dissociation and recombination data on these reactions with the theoretical calculations.

[182] J. V. Michael and J. H. Lee, *J. Phys. Chem.*, 1979, **83**, 10.