The temperature-dependence of elementary reaction rates: beyond Arrhenius†

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The rates of chemical reactions and the dependence of their rate constants on temperature are of central importance in chemistry. Advances in the temperature-range and accuracy of kinetic measurements, principally inspired by the need to provide data for models of combustion, atmospheric, and astrophysical chemistry, show up the inadequacy of the venerable Arrhenius equation—at least, over wide ranges of temperature. This *critical review* will address the question of how to reach an understanding of the factors that control the rates of 'non-Arrhenius' reactions. It makes use of a number of recent kinetic measurements and shows how developments in advanced forms of transition state theory provide satisfactory explanations of complex kinetic behaviour (72 references).

1. Introduction

In their introduction to the subject of chemical kinetics, generations of students have become acquainted with the definition of the *rate constant* of a chemical reaction, $k(T)$,‡ and then rapidly learnt that it varies with temperature according to the equation (attributed to Arrhenius):

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† One of a collection of reviews on the theme of gas kinetics.
‡ Here, I follow the customary practice by using the term *rate constant*, rather than *rate coefficient*, when discussing the rates of reactions between thermally equilibrated reactants; that is, for reaction at a defined temperature. I shall use *rate coefficient* when considering experiments or theories dealing with reactions under non-thermal conditions; that is, involving some degree of energy- or state-selection.
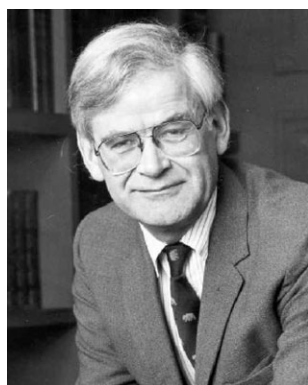
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Ian W. M. Smith

$$k(T) = A \exp(-E_{\text{act}}/RT) \qquad (1)$$

A is best called the *pre-exponential factor* and E_{act} is the *energy of activation*, and it is generally implied that both these quantities are sensibly independent of temperature. The main purpose of this article is to examine the current status of the Arrhenius description of how the rate constants for elementary reactions depend on temperature, given the recent progress in measuring reaction rate constants with high accuracy over wide ranges of temperature.

It is interesting to note that the most important early contributions to the development of the Arrhenius equation were actually made by van't Hoff.[1–3] He appreciated that, at equilibrium, the rates of forward and reverse reactions become equal so that the ratio of the rate constants, $k_f(T)$ and $k_r(T)$, for these reactions is equal to the equilibrium constant, $K_c(T)$, for the reaction: that is,

$$k_f(T)/k_r(T) = K_c(T) \qquad (2)$$

Moreover, the equation bearing van't Hoff's name

$$\text{d} \ln K_c(T)/\text{d}T = \Delta U_c^{\text{o}}/RT^2 \qquad (3)$$

expresses how $K_c(T)$ depends on temperature, so that combining eqns (2) and (3) one obtains:

$$\text{d} \ln k_f(T)/\text{d}T - \text{d} \ln k_r(T)/\text{d}T = \Delta U_c^{\text{o}}/RT^2 \qquad (4)$$

Van't Hoff then argued that the rate constants $k_f(T)$ and $k_r(T)$ are influenced by temperature by two different energies, E_f and E_r, whose difference corresponds to ΔU_c^{o}, so that:

$$\text{d} \ln k_f(T)/\text{d}T = E_f/RT^2 \text{ and } \text{d} \ln k_r(T)/\text{d}T = E_r/RT^2 \quad (5)$$

Van't Hoff further appreciated that ΔU_c^{o} is generally *not* independent of temperature and therefore realised that the energies E_f and E_r may also be temperature-dependent. Deriving the integrated form of eqn (5), he considered two possibilities; the first being that the energies (of activation) do not vary with temperature, which then recovers eqn (1).

(The second was that E_f and E_r varied as $B + DT^2$, which I shall not consider further.)

In 1889, five years after van't Hoff had published his work on the temperature-dependence of reaction rates,[3] Arrhenius, taking van't Hoff's treatment as his starting point, noted that the effect of temperature on chemical reaction rates was much too large to be the result of changes in the molecular translational energy and, in a hypothesis reminiscent of transition state theory, which of course came much later, suggested that an equilibrium is established between reactant molecules and 'active' ones that could react without further input of energy.[4] If this equilibrium obeys the van't Hoff equation for chemical equilibrium, then clearly one obtains eqn (5). Arrhenius did not consider the case where E_f and E_r are temperature-dependent and, as a result of his interpretation, eqn (1) has become known as the *Arrhenius equation*.

Finally in this brief historical survey, and in the light of later developments some of which are reviewed below, it is interesting to note that van't Hoff's student, D. M. Kooij, proposed[5] the following equation, now often referred to as the *modified Arrhenius equation*:§

$$k(T) = A'T^m \exp(-E'_{act}/RT) \qquad (6)$$

For many years after the earliest kinetics experiments, it was difficult to test the Arrhenius equation, especially the temperature independence of E_{act} and A, because only the rates of rather slow reactions could be measured. The rates of slow reactions are generally limited by large activation energies and this means that the rate constants are strongly temperature-dependent. Consequently, the range of temperatures over which measurements could be made was narrow; the lowest temperature being that at which the reaction rate became too slow for the patience of the experimenter and the highest temperature being that at which the rate was too fast for the time resolution of the measuring equipment.

Two unimolecular reactions provide examples. In 1962, the rate of isomerisation of CH_3NC to CH_3CN was measured[6] from 472.5–532.9 K and found to have an activation energy of 160.5 kJ mol^{-1}, and even earlier the dissociation of C_2H_5Cl to $C_2H_4 + HCl$ was studied[7] from 671–766 K and found to have an activation energy of 249 kJ mol^{-1}. The rate of the first of these reactions was followed by withdrawal of samples and analysis by gas chromatography. The measured rate constants varied from *ca.* 5×10^{-7} s^{-1} to 5×10^{-3} s^{-1}. The rate of the second reaction was observed by pressure rise and the experiments yielded rate constants varying from *ca.* 7×10^{-6} s^{-1} to 2×10^{-3} s^{-1}. Over these limited ranges of temperature, given the large variation in the rate constants, it is not surprising that no curvature was found in the Arrhenius plots of ln $k(T)$ *versus* $(1/RT)$.

Over the past three or four decades, there have been considerable advances in experimental technology allowing fast reactions to be followed over much wider temperature ranges than hitherto. These advances have, to a large extent,

been driven by the wish to provide kinetic data for elementary reactions that are important in combustion, in planetary atmospheres, especially that of Earth, and in the cold cores of dense interstellar clouds, where the temperatures are typically in the range 10–20 K. It is these measurements, mainly on bimolecular reactions, that form the backdrop to the matters that are discussed in this article.

Two reactions that have been studied over especially wide ranges of temperature, and which will be considered in greater detail later in this article, are those (a) between OH radicals and CO, for which rate constants have been measured from 80 to 2800 K, and (b) between CN radicals and O_2, for which rate constants have been measured from 13 to 3800 K. For kinetic measurements to be possible over such wide ranges of temperature, even using modern techniques, the temperature-dependence of the rate constants must be quite modest and generally the simple Arrhenius expression, eqn (1), does not provide an adequate description of $k(T)$, although it is frequently adequate over a small part of the whole temperature range—for example, that relevant in the Earth's atmosphere.

In general, the modified Arrhenius expression, eqn (6), can provide a satisfactory fit to experimental rate data, but the three parameters, A', m and E'_{act} have little physical meaning, in contrast to the situation with the activation energy from the simple Arrhenius equation which, when it has a significant positive value, is assumed to be related to, but not necessarily equal to, the height of a potential energy barrier on the minimum energy path leading from reactants to products (for further discussion, see the next section). Indeed many bimolecular reactions, for example those between free radicals such as $CN + O_2$, display a *negative* dependence on temperature; that is, $k(T)$ increases as the temperature is lowered. Again, over a limited temperature range, the values of $k(T)$ may be assigned a *negative* activation energy but its value then becomes even less clearly related to some property of the potential energy surface for the reaction.

Finally, I point out that when eqn (1) does not accurately fit the experimental rate constants its differential form:

$$E_{act}(T) = -d \ln k(T)/d(1/RT) \qquad (7)$$

can be used to define a temperature-dependent activation energy (and consequently imply a temperature-dependent pre-exponential factor), although this definition weakens the relationship between the measured activation energy and the potential barrier to reaction.

Acting on the expression for $k(T)$ given in eqn (6) according to eqn (7), we obtain

$$E_{act}(T) = E'_{act} + mRT \qquad (8a)$$

and

$$A(T) = A'(Te)^m \qquad (8b)$$

In the next two sections, we examine further the relationships between the activation energy, the potential energy barrier to reaction, and other energy quantities, in the light first of some simple models for reaction and then of *transition state theory*.

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§ In this article, I prefer to use the equivalent form, $k(T) = A'(T/298 \text{ K})^m \exp(-E'_{act}/RT)$, for the modified Arrhenius equation, so that A' and E'_{act} become equivalent to A and E_{act} in eqn (1) at 298 K.

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2. Definitions, nomenclature and simple models for bimolecular reactions

I have already introduced the notion that a *positive* activation energy is generally related to the theoretical concept of a potential energy barrier on the minimum energy path leading from the reactants to the products of an elementary reaction. In this section, I wish to explore this idea in greater detail, whilst also defining carefully the meanings of a number of energy quantities that are employed when discussing the kinetics and dynamics of elementary reactions—and which are occasionally used interchangeably, which can confuse a newcomer to the subject.

The term *activation energy* should, in the author's view, be restricted: either (a) to the quantity that is determined in kinetics experiments when rate constants are determined at different temperatures and analysed using eqn (1) or eqn (7),¶ or (b) when theoretically derived expressions for rate constants are similarly analysed. Examples of the latter procedure follow shortly.

The *potential energy barrier* to reaction can be estimated in two ways: (a) by performing *ab initio* quantum chemical calculations, that may be assisted by methods that track the evolution of the minimum energy path,[8] or (b) by connecting experimental measurements of rate constants, or other dynamical quantities for the reaction, to its barrier height, utilising theory to connect the measured quantity to the derived one. It is important to note that the term 'potential energy barrier', sometimes the 'classical potential energy barrier' is what is generated directly from the appropriate quantum chemical calculations without any correction for the quantisation of 'internal' modes of motion, either in the reactants or at any point along the path of minimum energy. If quantum corrections are made, one obtains the *zero-point corrected potential barrier*, usually denoted by $\Delta E_0^\dagger$ or $\Delta E_0^\ddagger$,‖ an important quantity in transition state theory (see below).

A final quantity that is important, both experimentally and conceptually, is the *threshold energy* for reaction. It is generally defined as the minimum energy associated with the relative translational motion of the reactants at which reaction takes place. The meaning of this quantity and its relation to the activation energy become clearer once one introduces the concept of a *reaction cross-section*. For my purposes here, a sufficient definition of the reaction cross-section, $\sigma(v)$, is that multiplied by the defined relative velocity (v) of the collisions between reactants (say, A and B), it defines a *rate coefficient* such that the rate of reaction in collisions between A and B at the relative velocity v is defined by:

$$-d[A]/dt = -d[B]/dt = \sigma(v)\, v\, [A]\, [B] \qquad (9)$$

The relationship between the thermal rate constant and this rate coefficient is clearly:

$$k(T) = \int \sigma(v)\, v\, f(v;\, T)\, dv \qquad (10)$$

where $f(v;\, T)$ is a normalised function describing the distribution of relative velocities in collisions between A and B at temperature T. The threshold energy, E^0_{trans}, is then the minimum value of $E_{trans} = \frac{1}{2}\mu v^2$, where μ is the reduced mass of A and B, at which $\sigma(v)$ is non-zero and it defines the lower limit of integration in eqn (10). Eqn (10) can be re-written in terms of E_{trans}, rather then v, yielding:

$$k(T) = (1/\pi\mu)^{1/2}(2/k_B T)^{3/2} \int_{E^0_{trans}}^{\infty} \sigma(E_{trans}) E_{trans} \exp(-E_{trans}/RT) dE_{trans}$$

$$(11)$$

Before continuing, it is worth making three points in respect of reaction cross-sections and threshold energies. Firstly, near threshold, the cross-section may approach zero only slowly—perhaps, but not only, because of tunnelling—making observation of the threshold very difficult. Secondly, the threshold energies for different combinations of reactant internal states may differ, causing uncertainty in the variation of the cross-section near threshold. Finally, although reaction cross-sections have now been measured at different collision energies for several reactions,[9,10] threshold energies can only be extracted from these results by somewhat uncertain extrapolations.

However, where the *excitation function*—that is, the variation of $\sigma(v)$ with v or $\sigma(E_{trans})$ with E_{trans}—has been measured for a reaction in molecular beam experiments, the temperature-dependence of the thermal rate constant can be inferred by applying eqn (10) or eqn (11) to the results.[10b] It is, however, necessary to enter two caveats to the use of this procedure. Firstly, the difficulty of measuring the *absolute* values of $\sigma(v)$ or $\sigma(E_{trans})$ means that one cannot compare the absolute values of the measured and inferred rate constants, only their dependence on temperature. Secondly, the use of eqn (10) or eqn (11) implies that the cross-sections and rate constants do not depend on the internal states of the reactants. In some cases, the agreement or lack of agreement between the actual and derived variation of $k(T)$ with temperature has been used to infer the absence or existence of such state-dependences.

Further insight into the meaning of the activation energy can be obtained by operating on eqn (11) according to eqn (7). This yields the Tolman expression for the activation energy:[11]

$$E_{act} = {<}E_{trans,\ reac}{>} - {<}E_{trans}{>} \qquad (12)$$

where ${<}E_{trans}{>} = {}^3/_2\, RT$ is the average translational energy in all collisions and ${<}E_{trans,\ reac}{>}$ is the average translational energy in all the collisions that lead to reaction. It is worth noting that, in principle, eqn (12) allows for the possibility of a small negative activation energy if the mean energy associated with the *reaction function*,[12] ${<}E_{trans,\ reac}{>}$, is less than ${<}E_{trans}{>}$.

It should also be noted that the treatment leading to eqns (11) and (12) makes no distinction in respect of different

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¶ In either case, the range of temperature over which the analysis is valid should be given.

‖ The superscript † is generally used to denote properties of the transition state prior to motion along the reaction coordinate being treated separately, ‡ denotes properties after such factorisation (see below in the next section). As the motion along the reaction coordinate is unbounded, there is no zero-point energy associated with it and $\Delta E_0^\dagger$ or $\Delta E_0^\ddagger$ are therefore numerically the same.

internal (rovibrational) states of the reactants. This is also a characteristic of the simplest theories of collisional reactions: the line-of-centres (LOC) collision theory and the angle-dependent line-of-centres (ADLOC) collision theory.[12]

The basic assumption in the LOC model is that the two reactants, treated as structureless hard-spheres, only interact when the separation of their centres reaches some critical value, conventionally set to the hard-sphere diameter (d) of A and B. At this point reaction occurs if the translational energy associated with motion *along the line-of-centres* exceeds the threshold energy E^0_{trans}. Simple geometric arguments then show that, according to this simple model, the *excitation function*, that is, the variation of the reaction cross-section with collision energy, is given by:

$$\sigma(E_{trans}) = \pi d^2 (1 - E^0_{trans}/E_{trans}) \qquad (13)$$

Substituting this expression into eqn (11) yields the familiar expression for the rate constant:

$$k(T) = \pi d^2 (8 k_B T/\pi\mu)^{1/2} \exp(-E^0_{trans}/RT) \qquad (14)$$

Using eqn (7) to define the activation energy, even for this simple model, we find a difference between the activation energy and the threshold energy:

$$E_{act}(T) = E^0_{trans} + {}^1/_2 RT \qquad (15)$$

A rather more realistic model for an elementary bimolecular reaction is obtained by assuming that the threshold energy depends on the orientation between some axis in one of the reactants and the line joining the line-of-centres of the two reactants, allowing for a *steric effect*. With certain reasonable assumptions, this model, generally now referred to as the angle-dependent line-of-centres (ADLOC) model,[12–14] gives rise to the following expression for the rate constant:

$$k(T) = (k_B T/2E'')\{\pi D^2 (8 k_B T/\pi\mu)^{1/2} \exp(-E^0_{trans}/RT)\}(16)$$

where D, replacing the hard-sphere collision radius d, is the distance between the centres of the two reactant species at the 'critical dividing surface',[12] and E'' is a measure of how steeply the threshold energy for reaction depends on orientation. For our present purposes, it is sufficient to note that the pre-exponential term on the right-hand side of eqn (16) depends on $T^{3/2}$, so that, in this case

$$E_{act}(T) = E^0_{trans} + {}^3/_2 RT \qquad (17)$$

The curvature in the Arrhenius plot predicted by this equation is connected to the increase in the *cone of acceptance* over which reaction can occur as T increases.[15]

It may also be instructive to use the expressions from this model to compare (i) the form of the '*reaction function*', which is the product of the *excitation function* and the Boltzmann distribution function for E_{trans}, with (ii) the Boltzmann distribution function itself. This comparison is made in Fig. 1 and it makes clear the Tolman definition of the activation energy, given in eqn (12). As the temperature is increased, the mean of the reaction function increases more rapidly than that of the Boltzmann distribution function, resulting in an increase in activation energy in accord with eqn (17).
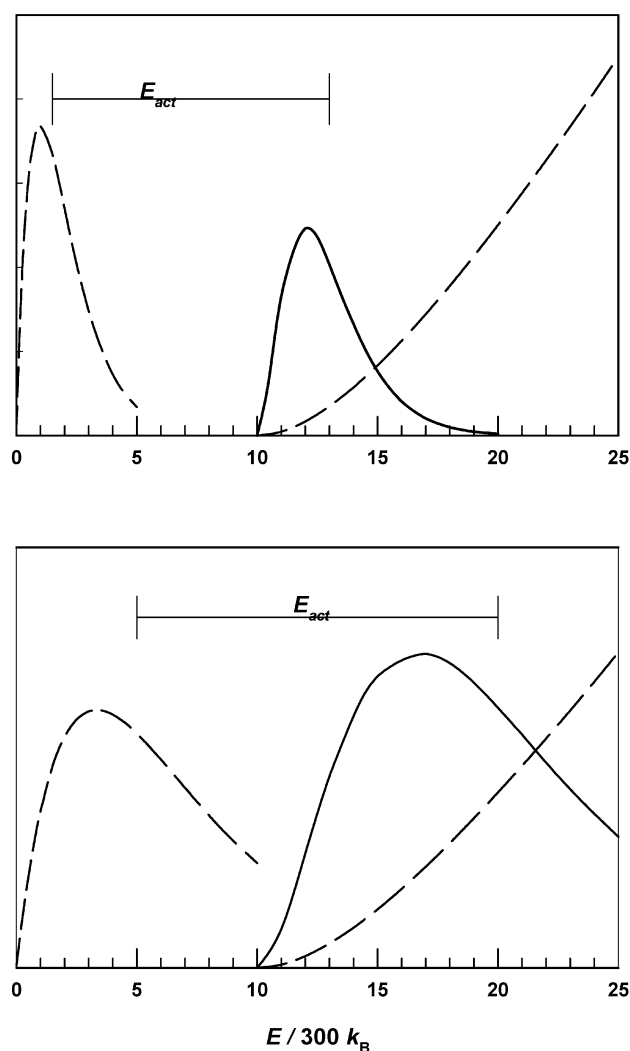
Fig. 1 Diagrams comparing: (a) on the left of each panel, the function $E_{trans} \exp(-E_{trans}/k_B T)$ describing the distribution of collision energies; (b) to the right, represented by the dashed line, an excitation function according to the ADLOC model, and (c) to the right, represented by a full line, the *reaction function*; that is, the product of (a) and (b). The threshold energy is taken to be (3000 K) k_B. The upper panel is for $T = 300$ K, the lower for $T = 1000$ K. The horizontal lines show the *activation energies* at these two temperatures according to the Tolman criterion (see eqn (12) in the text).

Finally in this section, and of particular relevance in this article, which places some emphasis on the kinetics of reactions where there is little or no barrier to reaction on the minimum energy path, I consider briefly simple models of 'capture' during collisions (of A and B), when there is a long-range attraction between the collision partners. The classic case is that between an ion and a spherically polarisable molecule, when the long-range potential is proportional to R_{AB}^{-4}. In this case, what is generally referred to as the Langevin model predicts that the capture cross-section will decrease as $E_{trans}^{-1/2}$ and the rate constant for capture in thermal collisions will be independent of temperature, as the decrease in the cross-section is exactly matched by the increase in the rate of collisions.

The rate constants for a number of ion–molecule reactions exhibit this behaviour.[16] In the presence of directional forces between an ion and a dipolar molecule, the rate constants for reaction increase as the temperature is lowered[17] and this temperature-dependence has been matched in both adiabatic capture[18] and statistical adiabatic channel[19] calculations.

The treatment that leads to the expressions for capture cross-sections and rate constants in the case of ions colliding with spherically polarisable molecules can be generalised[12] for any long-range potential that varies as R_{AB}^{-n}. Thus for $n = 6$—for example, in the presence of dispersion forces between neutral molecules—the cross-section for capture decreases with E_{trans} as $E_{trans}^{-1/3}$. However, because of the increase in the rate of collisions with temperature, the rate constant for capture in the presence of such a potential increases with temperature, as $T^{1/6}$.

3. Transition state theory

The simple classical models outlined in the previous section account for some of the important features of bimolecular reactions, at least those which either proceed over a significant potential energy barrier or proceed along a minimum energy path that falls monotonically from reactants to products. Of course, these models suffer from the major defect that there is no explicit recognition of the internal quantum states of the reacting system. This is a defect that is largely overcome in transition state theory (TST).

The conventional derivation[12,20] of TST imagines a dynamic equilibrium between the separated reactants (A and B) and the transition state species, sometimes referred to as activated complexes. The transient transition state species are viewed as being in the act of passing through a critical dividing surface, which separates approaching reactants from separating products, and are generally assumed to pass across a potential energy barrier on the potential energy surface. The constant for this equilibrium is expressed in terms of the 'per volume' partition functions of reactants and transition state species. Following separation of the partition function associated with the motion taking the system through the critical dividing surface, one multiplies the instantaneous concentration of transition state species by the frequency of passage through the transition state, to arrive at an expression for the rate constant for reaction between A and B:

$$k(T) = \left(\frac{k_B T}{h}\right)\left(\frac{Q^\ddagger}{Q_A Q_B}\right)\exp\left(-\Delta E_0^\ddagger / k_B T\right) \quad (18)$$

In this equation, Q_A, Q_B and $Q^\ddagger$ are the 'per volume' partition functions for A, B and the transition state species,** and $\Delta E_0^\ddagger$ is the difference in energy between the zero-point levels in the transition state and in the reactants. Separating translational and internal motions, this expression can be

** Of course, $Q^\ddagger$ represents the per volume partition function for the transition state species with the term associated with motion along the reaction co-ordinate factored out.

usefully recast as

$$k(T) = \left(\frac{k_B T}{h}\right)\left(\frac{1}{Q_{\text{reltrans}}}\right)\left(\frac{Q^\ddagger_{\text{int}}}{Q_{A,\text{int}} Q_{B,\text{int}}}\right)\exp\left(-\Delta E_0^\ddagger / k_B T\right)$$
$$(19)$$

and then further re-written as:

$$k(T) =$$
$$\left(\frac{k_B T}{h}\right)\left(\frac{1}{Q_{\text{reltrans}}}\right)\left(\frac{1}{Q_{A,\text{int}} Q_{B,\text{int}}}\right)\left\{Q^\ddagger_{\text{int}}\exp\left(-\Delta E_0^\ddagger / k_B T\right)\right\}$$
$$(20)$$

In order to calculate rate constants from this expression, spectroscopic data can be used to evaluate $Q_{A,\text{int}}$ and $Q_{B,\text{int}}$, so that the evaluation of the three terms in () brackets on the right-hand-side of eqn (20) is straightforward. However, the results of *ab initio* calculations are required to estimate $Q^\ddagger_{\text{int}}$ and $\Delta E_0^\ddagger$. Furthermore, even when the reaction is characterised by a pronounced barrier, it may be necessary to evaluate $Q^\ddagger_{\text{int}}$ accurately, not just within the rigid rotor harmonic oscillator approximation.[21]

Clearly, the pre-exponential factor in eqn (19) will depend on the complexity and structure of both the reactants and the transition state. In the context of the present article, it is valuable to examine the temperature-dependence of this factor. The first two bracketed terms result in a $T^{1/2}$-dependence; the third bracketed term may give rise to a variety of dependences. To take the example of two diatomic species reacting through a linear transition state (as in the CN + H_2 reaction considered below), the rotational partition functions in this term will give rise to an additional dependence of T^{-1}. A linear four-atom transition state will have six vibrational modes (remember that the contribution from the motion along the reaction path has been taken into account to arrive at eqn (18)): two of these modes in the transition state, those correlating with the vibrations in the two reactants, will be 'conserved modes', and four will be 'transitional modes'. At the linear transition state, the transitional modes will correspond to two doubly degenerate bending vibrations, but they will generally have frequencies that are much lower than those in similar stable linear molecules. In the low frequency classical limit, the partition function of a single oscillator is proportional to T, so four modes could contribute a T^4 dependence to $Q^\ddagger_{\text{int}}$ and cause the overall pre-exponential factor in eqn (19) to vary as $T^{2.5}$.

In principle, the accurate evaluation of the TST expression can overestimate the rate constant, since no allowance is made for what is generally called 're-crossing': that is, the possibility that some trajectories, which pass through the transition state in the direction from reactants to products, might then be reflected back through the transition state so that no reaction occurs. One response to this possibility, recognising that the 'true' transition state represents a dynamical bottleneck for the reaction, is to evaluate eqn (19) at various points along the reaction path. The minimum value of the calculated rate constants is then assumed to be the best TST estimate. This version of TST, *variational canonical transition state theory*

(VCTST),[21] rarely makes a large difference to the estimate of $k(T)$ for a reaction proceeding from the zeroth vibrational levels of the reactants over a significant potential energy barrier.

The statement made in the last sentence does not remain true, however, for reactions with low or zero potential energy barriers—typified, for example, by those between free radicals on the lowest potential energy surface correlating with reactants and products. In these cases, even the application of VCTST is unlikely to produce satisfactory results and a microcanonical version of theory must be applied. Probably the most familiar application of *microcanonical transition state theory* (μTST) is to unimolecular reactions, where it is applied to obtain rate coefficients for reaction either from states at a defined total internal energy or, more completely, from states of defined total internal energy (E) and total angular momentum (J). Semi-classical arguments can be used[12] to derive the expression:

$$k(E, J) = W^{\ddagger}(E, J)/h \, \rho(E, J) \qquad (21)$$

Here $W^{\ddagger}(E, J)$ is the number of internal states at the transition state accessible to species with total energy E and total angular momentum J, $\rho(E, J)$ is the density of states (number of states per unit energy interval) in the reactant at total energy E and total angular momentum J, and h is Planck's constant. On a potential where there is no well-defined barrier to reaction, as in the dissociation of a molecule to two radicals, values of $k(E, J)$ should be calculated variationally, since the position of the transition state varies with E, J. Having found values of $k(E, J)$, thermal rate constants can be calculated by integration of E and summation over J:

$$k(T) = \sum_{J=0}^{\infty} (2J + 1) \int_{0}^{\infty} k(E,J) f(E, J; T) \mathrm{d}E \qquad (22)$$

where $f(E, J; T)$ is the normalised internal energy distribution function for species with total angular momentum J at temperature T. In the light of what follows in this article, it is also useful to note that if there is competition between two dissociation channels (1 and 2), then the relative rates of these two reactions for species of defined E and J will simply depend on the ratio of the accessible internal states at the two transition states (TS1 and TS2); that is

$$k_1(E, J)/k_2(E, J) = W^{\ddagger}(E, J)_{TS1}/W^{\ddagger}(E, J)_{TS2} \qquad (23)$$

Georgievskii and Klippenstein[22] have implemented an (E, J) resolved version of variational transition state theory (μJ-VTST) to calculate the rate constants for a number of reactions believed to take place across potential energy surfaces with no potential energy barrier along the minimum energy path. The long-range potential was estimated by including dipole–dipole, dipole–quadrupole, dipole-induced dipole, and dispersion forces. For seven of the reactions on which calculations were carried out, the rate constants were found to be approximately equal to the observed value of the rate constant, $k(T)_{\mathrm{calc}}/k(T)_{\mathrm{obs}} < 1.5$ at the lowest temperature for which experimental results were available. For the remaining 19 reactions, the difference was greater but always in the same sense; that is, $k(T)_{\mathrm{calc}} > k(T)_{\mathrm{obs}}$. This difference strongly

suggests that generally a further 'bottleneck' to reaction exists at shorter inter-reactant separations, where chemical forces start to act.

A similar, and earlier, theoretical method of treating reactions that occur over potential energy surfaces with no significant barriers is the statistical adiabatic channel model (SACM) originally postulated in the 1970s by Quack and Troe,[23] and subsequently developed by Troe for unimolecular bond fissions (and the reverse radical associations) in order to estimate both thermal rate constants in the limit of high pressure[24] and specific rate constants, $k(E, J)$.[25] In the context of the present article, it is the first of these developments of the SACM which is more relevant, and I shall briefly consider its application to association reactions.

The SACM assumes reaction to occur along individual channels that correlate with specific combinations of quantum states in the separated (radical) reactants. The energy in each channel varies along the reaction path (x) and is expressed as the sum of three terms, representing the electronic potential energy, a centrifugal term and a term that represents how the specific channel energy evolves along x as the reactants approach:

$$V_{\mathrm{ad\ ch}}(x) = V_{\mathrm{el}}(x) + l(l + 1) \, \hbar^2/2\mu x^2 + E_{\mathrm{ch}}(x) \qquad (24)$$

In practice, the channel energies are evaluated using interpolation formulae and to estimate rate constants for processes proceeding through loose transition states, such as bond fission and radical association, the central problem becomes "the determination of the energy pattern of the channel threshold energies."[24] If that can be done, then the internal partition function of the transition state species expressed relative to the zero-point energies of the reactants, that is, the term in {} brackets in eqn (20), can be written as:

$$\left\{ Q_{\mathrm{int}}^{\ddagger} \exp\left(-\Delta E_0^{\ddagger} \big/ k_{\mathrm{B}} T\right) \right\} =$$
$$\sum_{J=0}^{\infty} (2J + 1) \int_{0}^{\infty} W^{\ddagger}(E, J) \exp\left(-\frac{E - E_0}{k_{\mathrm{B}} T}\right) \frac{\mathrm{d}E}{k_{\mathrm{B}} T} \qquad (25)$$

where $W^{\ddagger}(E, J)$ is the number of open channel states—that is, channels for which E exceeds the maximum on $V_{\mathrm{ad\ ch}}(x)$, and E_0 is the threshold energy of the lowest channel state. It is important to appreciate that the channel maxima will not be found at the same value of x just as is the case for the transition states in the μJ-VTST version of transition state theory.

I make two final points in respect of the application of the μJ-VTST and SACM treatments of rate constants. Firstly, in order to make accurate predictions of the rate constants for reactions proceeding across surfaces with zero or no barrier, it is necessary to have accurate calculations of the potential energy along the minimum energy path, usually in a region of the potential energy surface where *ab initio* calculations are difficult. Secondly, it is not easy to predict, for example from eqn (18), how the effective value of the internal partition function for the transition state species will vary with temperature. It is, however, useful to note that, at lower temperatures, reaction will increasingly occur from low energy states of the reactants. If these have higher values of $k(E, J)$ or lower

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Chem. Soc. Rev., 2008, **37**, 812–826 | 817

Table 1 Rate data for the reaction: CN + H$_2$ → HCN + H fitted to the parameters in the modified Arrhenius equation: $k(T) = A'\,(T/298)^m \exp(-E'_{\mathrm{act}}/RT)$

Ref.	Method[a]	Range of T/K	$A'/10^{-12}$ cm^3 molecule^{-1} s^{-1}	m	(E'_{act}/R)/K
Wagner and Bair[32]	TST calculation with *ab initio* barrier adjusted to 17.2 kJ mol^{-1}	250–3500	0.56[b]	2.45	1126
Szekely *et al.*[34]	ST/thermolysis of C$_2$N$_2$/ spectroscopic absorption of CN	2700–3500	within this limited high temperature range, $k(T) = (1.25 \pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}		
Wooldridge *et al.*[35]	ST/PLP of C$_2$N$_2$ at 193 nm; LA detection of CN	940–1860	data from this work and refs. 24, 25 and 28 were compared with the result of Wagner and Bair[b]		
Sims and Smith[29]	PLP of NCNO at 532 nm; LIF detection of CN	295–768	2.4 ± 0.7	1.6 ± 0.3	1340 ± 90
Atakan *et al.*[31]	PLP of C$_2$N$_2$ at 193 nm; LIF detection of CN	294–1000	0.56	2.45	1120
Sun *et al.*[30]	PLP of ICN at 248 nm; LIF detection of CN	209–740	0.35	3.31	756

[a] Abbreviations: TST: transition state theory; ST: shock tube; PLP: pulsed laser photolysis; LA: laser absorption; LIF: laser-induced fluorescence. [b] Following Wooldridge *et al.*[35] and Atakan *et al.*,[31] the value of A' has been reduced by a factor of ten from that reported in the text of Wagner and Bair's paper to be consistent with their Fig. 2.

channel maxima, then this can make a significant negative contribution to the overall temperature-dependence of the thermal rate constants.

4. Comparisons between experimental and theoretical results

In this section, I review the experimental information available for four individual bimolecular reactions each representing a different category in respect of the form of the minimum energy path. These examples have been chosen partly because they have been studied over particularly wide ranges of temperatures.

The whole range of temperature over which kinetic measurements have been performed can be divided into three overlapping regions, according to the method employed to achieve the temperature. The range from *ca.* 80 to 1500 K can be covered by relatively conventional methods: by heating or cryogenically cooling the reaction vessel in which the experiments are carried out. In this range, the method of choice for measuring $k(T)$ has become that based on pulsed laser photolysis (PLP) of a suitable precursor to produce the required free radicals. The rate of removal of these radicals, in the presence of a known concentration of the molecular co-reagent, is then generally determined by using a pulsed or continuous-wave dye laser that is tuned to excite laser-induced fluorescence (LIF) from the radicals. The LIF signals reflect the relative concentrations of radicals at different times after their formation and analysis of the decays of these signals yield pseudo-first-order rate constants that depend on the concentration of the co-reagent included in the gas mixture.

To achieve temperatures above 1500 K, shock tubes must be employed: the high temperature is achieved by adiabatic compression of the sample gas by inert gas from a driver section, when a diaphragm separating the two sections of the shock tube is ruptured.[26] After some years of doubt about the ability of shock tube experiments to deliver reliable kinetic data, the combination of shock tubes with photolytic and spectroscopic methods, frequently involving lasers, as well as the resolution of what had been seen as the boundary layer

problem, it is now clear that such experiments can be used to measure rate constants for both unimolecular and bimolecular reactions at temperatures up to several thousand K, with an accuracy that rivals that achievable at lower temperatures using the PLP-LIF technique.

The provision of kinetic data below 80 K has been revolutionised by the development of the CRESU[27] technique, which was originally devised by Rowe and his co-workers to study ion–molecule reactions. Isoentropic expansion of a gas mixture through an axially symmetric, convergent–divergent, Laval nozzle produces a jet of fairly dense gas (typically, 10^{16}–2×10^{17} molecule cm^{-3}) at a temperature determined by the design of the nozzle, by the nature of the carrier gas, and by the backing pressure upstream of the nozzle. Since the mid-1990s, the method has been adapted in order to study the kinetics of neutral–neutral reactions. These experiments usually employ photolytic methods to generate radicals in the gas jet and either LIF or chemiluminescence to follow the removal of the radical species.[28] Neutral–neutral reactions have been studied at temperatures as low as 13 K in some cases.

(a) The 'direct' reaction:

$$\mathrm{CN} + \mathrm{H_2} \rightarrow \mathrm{HCN} + \mathrm{H} \qquad \textbf{(R1)}$$

This reaction is chosen as one that has been the subject of kinetic experiments over a wide range of temperatures, for which there is clearly a potential energy barrier and no significant minimum along the path of minimum energy, and for which the conventional Arrhenius plot of ln $k(T)$ *versus* $(1/RT)$ exhibits clear curvature.

Experimentally measured values of the rate constants for this reaction are summarised in Table 1 and Fig. 2. There have been three studies covering the temperature range from 209 K to 1000 K, all using basically the same technique of pulsed laser photolysis to produce CN radicals (albeit using different precursors and laser wavelengths) and laser-induced fluorescence observations of relative CN concentrations using pulsed, tuneable dye lasers. As Fig. 2 shows, the results of these studies are in good agreement, especially those of Sims and Smith[29]
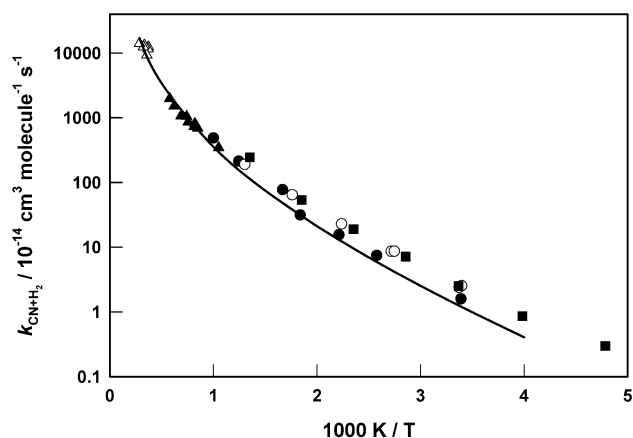
Fig. 2 Kinetic data for the CN + H$_2$ reaction. The points represent experimental values of the rate constants from: Sims and Smith[29] (○); Sun *et al.*[30] (■); Atakan *et al.*[31] (●); Szekeley *et al.*[34] (△); and Wooldridge *et al.*[35] (▲). The line shows the results of the transition state calculations of Wagner and Bair.[32]

and of Sun *et al.*,[30] with the rate constants derived by Atakan *et al.*[31] falling slightly lower. The fact that the parameters in the modified Arrhenius expressions derived by Sims and Smith and by Sun *et al.* differ markedly illustrates the difficulty in deriving these parameters accurately, even when the temperature ranges covered by the experiments are similar and the actual measured rate constants are very close.

Before any of these three experimental studies, Wagner and Bair[32] had carried out transition state theory calculations based on *ab initio* calculations of the properties at the potential energy barrier. The calculated barrier height was 25.1 kJ mol^{-1} and corrections for zero-point energies yielded a value of 26.8 kJ mol^{-1} for $\Delta E_0^{\ddagger}$. In their TST calculations, which included a Wigner tunnelling correction,[12] they lowered the barrier height to 17.1 kJ mol^{-1}, in order to obtain agreement with the limited experimental data then available. Later calculations by ter Horst *et al.*[33] confirm the lower value of the barrier height.

In the context of the present article, it is interesting to note that the value of the parameter m in the modified Arrhenius expression derived by Wagner and Bair was $m = 2.45$. This leads to the curvature of the line on the Arrhenius plot shown in Fig. 2. Wagner and Bair attributed this dependence of the pre-exponential factor to the partition functions associated with the low frequency bending modes in the transition state for the reaction.

The difficulty of reliably fitting experimental rate constants to the three parameters in the modified Arrhenius form has led other authors, notably Atakan *et al.*,[31] to adopt the value of m from Wagner and Bair's calculations and then to perform a two-parameter (A' and E'_{act}) fit to the experimental data. The results of this procedure are shown in Table 1.

Finally, I note that the experimental data for the CN + H$_2$ reaction covers an unusually wide range of temperature due to the shock tube experiments of Hanson and co-workers.[34,35] As Fig. 2 shows, the data over the full range of 209 K to 3500 K is internally consistent and can be well fitted by a single modified Arrhenius expression.

(b) The 'radical–radical' reaction:

$$CN + O_2 \rightarrow NCO + O \text{ (and NO + CO)} \quad \text{(R2)}$$
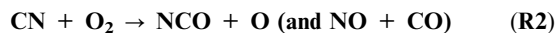
This reaction is chosen, in part, to exemplify bimolecular reactions between two free radicals. Such reactions are characterised by (a) the existence of multiple potential energy surfaces that correlate with the reactants, and (b) the existence of a deep minimum on (at least) the lowest surface with no barrier on the path leading from the separated reactants to this potential energy 'well'.[36,37] Reactions between free radicals frequently lead to pressure-dependent association but when, as in the case of CN + O$_2$, the initially formed adduct can dissociate by a pathway lower in energy than that for re-dissociation, two product species can result. In the case of CN + O$_2$, the principal products, formed by rupture of the O–O bond in the doublet NCOO complex that is initially formed, are NCO + O. However, there is experimental evidence that the more exothermic products CO + NO are formed in a minor pathway.[38,39] *Ab initio* calculations[38,40] demonstrate that the four-centre transition state leading to these products is too high in energy for reaction to occur in this way, and it seems more likely that CO + NO are either formed in a secondary collision that occurs before NCO and O part,[38] or following intramolecular rearrangements of the initially formed NCOO complex.[40] Whichever of these mechanisms occurs, the kinetics, almost invariably observed by following the loss of CN radicals in an excess of O$_2$, will reflect the kinetics of formation of the transient NCOO complex from CN + O$_2$.

The kinetics of this reaction have been followed over an extremely wide range of temperatures. The most recent experiments—all of which have measured $k(T)$ over a range of temperatures—are summarised in Table 2. These studies can be put into three categories identified earlier. Those by Sims and Smith,[41,42] Atakan *et al.*,[31] Durant and Tully[43] and Castleton and Balla[44] all use pulsed laser photolysis to generate CN radicals and follow their kinetic decay in the presence of O$_2$ by observing LIF from CN, excited by appropriately tuned radiation from either pulsed or cw dye lasers. As Fig. 3 shows, the results of these studies are in good agreement with one another and demonstrate that the rate constant exhibits a negative dependence on temperature between *ca.* 100 and 800 K with an apparent flattening out at the upper end of this range.

Shock tube experiments have been performed[45] at still higher temperatures, yielding the same rate constant at temperatures between *ca.* 1500 and 4500 K. The third category of experiments are those carried out in a CRESU apparatus by Sims *et al.*[46] In these CRESU experiments, the expanded gas mixtures contained a radical precursor (NCNO), the co-reactant (O$_2$), and a diluent gas (He, Ar or N$_2$) in large excess. The CN + O$_2$ reaction was the first reaction between neutral species that was studied in CRESU experiments and the lowest temperature reached in those experiments (13 K) remains the lowest achieved in kinetic experiments on neutral–neutral reactions in the gas-phase.

Table 2 Summary of the experiments carried out and the results obtained for the reaction between CN radicals and O_2

Ref.	Method	Range of T/K	Notes on values of $k(T)$ and temperature-dependence
Sims and Smith[41,42]	PLP of NCNO at 532 nm; LIF detection of CN	99–761	$k(T)$ fitted to $(2.49 \pm 0.02) (T/298)^{0.50 \pm 0.015} \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}
Atakan et al.[31]	PLP of C_2N_2 at 193 nm; LIF detection of CN	294–1000	$k(T)$ fitted to $(1.44 \pm 0.17) \times 10^{-11} \exp[+ (216 \pm 40)/T]$ cm^3 molecule^{-1} s^{-1}
Durant and Tully[43]	PLP of C_2N_2 or ClCN at 193 nm; cwLIF detection of CN	295–710	$k(T)$ fitted to $(1.24 \pm 0.04) \times 10^{-11} \exp[+ (196 \pm 12)/T]$ cm^3 molecule^{-1} s^{-1}
Castleton and Balla[44]	PLP of C_2N_2 at 193 nm; LIF detection of CN	292–1565	$k(T)$ fitted to $(1.02 \pm 0.12) \times 10^{-11} \exp[+ (220 \pm 25)/T]$ cm^3 molecule^{-1} s^{-1}
Davidson et al.[45]	ST/thermolysis and photolysis at 193 nm of C_2N_2; cwLA detection of CN	1500–4500	within this high temperature range, $k(T) = (1.67 \pm 0.33) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}
Sims et al.[46]	PLP of NCNO at 582 nm; LIF detection of CN	13–295	$k(T)$ fitted to $(2.49 \pm 0.17) (T/298)^{0.63 \pm 0.04} \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}
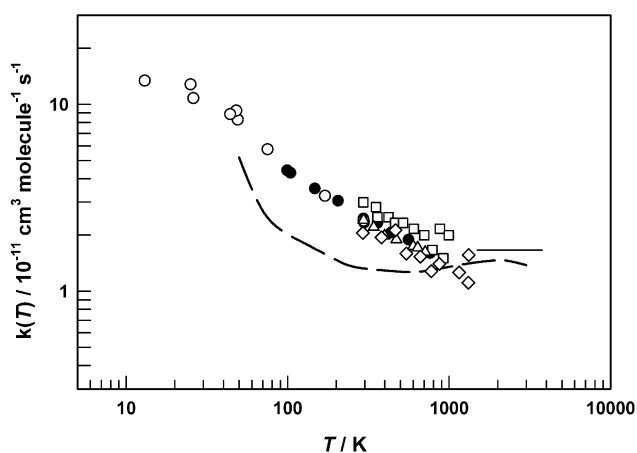
Fig. 3 Kinetic data for the CN + O_2 reaction. The points represent experimental values of the rate constants from: Sims and Smith[41,42] (●); Sims et al.[46] (○); Atakan et al.[31] (□); Durant and Tully[43] (△); Balla and Castleton[44] (◇); and ——, Davidson et al.[45] The dashed line shows the results of the variational statistical calculations of Klippenstein and Kim.[47]

The huge range of temperature (and particularly of reciprocal temperature) covered by these experiments makes it inappropriate to display the temperature-dependence of $k(T)$ on an Arrhenius plot—if one did the data would be very strongly curved. Fig. 3 shows the experimental data referenced in Table 2 on a log–log plot.†† As the notes in Table 2 make clear, Arrhenius expressions with negative activation energies can be used to represent $k(T)$ over a limited temperature range but, at the lowest temperatures, $k(T)$ varies approximately as $T^{-0.6}$.

Klippenstein and Kim[47] have examined the CN + O_2 reaction using a variational version of statistical RRKM theory designed to treat barrierless association reactions. They base these calculations on a model potential developed to match the results of ab initio electronic structure calculations of the energy at NC–OO separations ranging from 1.7 to 3.0 Å. Their approach involves separate treatment of the conserved modes, such as the CN and OO vibrations, and the transitional modes, such as those that correlate with CN and OO rotational motions. The partition functions of the

former modes are evaluated using the standard formulae for harmonic oscillators, whereas those for the transitional modes are estimated via determination of the corresponding phase space integrals. The reaction is assumed to occur only on the lower singlet potential energy surface that correlates with $CN(^2\Sigma^+) + O_2(^3\Sigma_g^-)$, not on the excited quartet surface.

The results of Klippenstein and Kim's calculations are shown by the dashed line in Fig. 3. They clearly reproduce the strong negative temperature-dependence of $k(T)$ at low temperatures and the essentially constant value at higher temperatures. Their analysis also makes it quite clear that the dynamics of this reaction are determined by behaviour at distances where directional chemical forces are important. Earlier 'adiabatic capture' calculations[48] based on the long-range dipole–quadrupole interaction between CN and O_2 strongly overestimate the rate constant and predict the wrong temperature-dependence, and variational transition state theory calculations based on a more complete description of the long-range asymptotic potential also overestimate the rate constant for CN + O_2,[22] confirming that the main 'bottleneck' for this system, even at the lowest temperatures, occurs at reactant separations where chemical forces contribute to the intermolecular potential. The observed variation of $k(T)$ is attributed by Klippenstein and Kim to an interplay between (a) the increase in bonding between NC and OO and (b) the increase in the repulsive bending forces, as R_{C-O} decreases. The influence of these directional bonding forces on $k(T)$ is reminiscent of those in reactions between ions and dipolar molecules,[16–18] when the rate constants are also quite constant at higher temperatures but increase rapidly at lower temperatures.
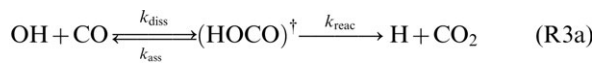
(c)   A reaction proceeding via a deep potential minimum:

$$OH + CO \rightarrow CO_2 + H \qquad (R3)$$

This reaction is chosen to exemplify those that proceed along a minimum energy path via a deep potential minimum, and whose kinetics are determined by passage through two transition states, one either side of the deep potential well. The reaction has been widely studied—at temperatures as low as 80 K[49] and as high as 2800 K.[50] Its Arrhenius plot is strongly curved and its rate constant, defined by $k_{2nd} = -\{d[OH]/dt\}/[OH][CO]$, is dependent on the total pressure. It has been widely studied because of both its interesting dynamical and

†† For fast low temperature reactions studied in a CRESU apparatus, this way of displaying the temperature-dependence of the rate constants is quite usual. Arrhenius plots would give undue weight to the low temperature data.

kinetic behaviour and its great importance in both combustion and atmospheric chemistry.

The explanation of the curious kinetic behaviour of the reaction between OH + CO was first suggested in 1977.[51] The hypothesis, that reaction proceeds *via* a rather strongly bound HOCO species, which can then dissociate at competitive rates either 'forward' to CO_2 + H or 'back' to OH + CO, or be stabilised by a collision, leads to the mechanism:

$$OH + CO \underset{k_{ass}}{\overset{k_{diss}}{\rightleftharpoons}} (HOCO)^{\dagger} \xrightarrow{k_{reac}} H + CO_2 \qquad (R3a)$$

$$\downarrow k_M[M] \qquad (R3b)$$

$$HOCO$$

This proposal has since been confirmed by quantum chemical calculations,[52] by thorough experimental studies over wide ranges of both temperature (82–2800 K)[49,50,53,54] and total pressure (up to 700 bar),[54] and by calculations that model the temperature- and pressure-dependences of the kinetic data.[54–56] The earliest comprehensive treatment of the extensive kinetic data obtained for this reaction, by themselves and others, was made by Fulle *et al.*[54b] and it is their analysis which is largely followed here.

The rather unique feature of the potential energy surface for the HOCO system is that the zero-point corrected barriers that separate (i) OH + CO and HOCO, and (ii) HOCO and CO_2 + H are very close in energy and are both only slightly higher than the energy of the separated OH + CO reactants. Based on their detailed theoretical modelling of the experimental results, Fulle *et al.*[54b] estimated the energy of the first barrier relative to OH + CO to be 1.2–1.8 kJ mol^{-1}, with the energy of the second barrier lying within ±0.7 kJ mol^{-1} of the first.

Fig. 4 shows some of the extensive kinetic data that have been obtained for this reaction. The experimental studies used to prepare this diagram are summarised in Table 3. Fuller listings of the investigations of this reaction can be found in ref. 54 and in the IUPAC evaluation of data for atmospheric chemistry.[57] The lower set of data shown in Fig. 4 has been obtained at total pressures low enough to ensure that collisional stabilisation of the energised HOCO complex, $(HOCO)^{\dagger}$, does not compete with the sum of the dissociations to OH + CO and CO_2 + H; that is, $k_M[M] \ll (k_{diss} + k_{reac})$. At 300 K, this condition is satisfied at total pressures below *ca.* 100 Torr.[54] Under these conditions, the complete expression for k_{2nd} in terms of the rate constants for the individual steps in the mechanism:

$$k_{2nd} = k_{ass} \left\{ \frac{k_{reac} + k_M[M]}{k_{diss} + k_{reac} + k_M[M]} \right\} \qquad (26)$$

reduces to

$$k_{2nd}^{o} = k_{ass} \left\{ \frac{k_{reac}}{k_{diss} + k_{reac}} \right\} \qquad (26a)$$

The higher set of data in Fig. 4 has been derived from two sources. The rate constants below room temperature are
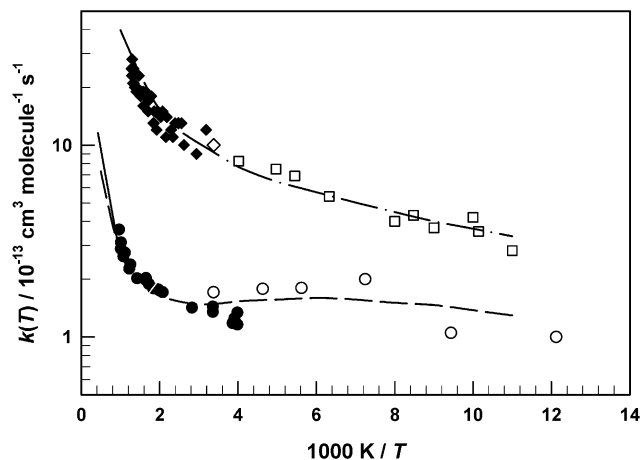
Fig. 4 Kinetic data for the OH + CO reaction. The upper set of points represent values of the high pressure limiting rate constants (a) from the high pressure measurements of Fulle *et al.*[54b] (□) and from vibrational relaxation measurements (◇, Brunning *et al.*;[58] and ◆, Fulle *et al.*[54b]). The lower set of points are low pressure rate constants (○, Frost *et al.*;[49] ●, Ravishankara and Thompson;[53] and ——, Wooldridge *et al.*[50] The lines are the results of the theoretical modelling of Fulle *et al.*[54b] with the zero-point corrected barrier at TS1 1.8 kJ mol^{-1} higher than the energy of OH + CO, and with the zero-point corrected barrier at TS2 0.6 kJ mol^{-1} lower than that at TS1.

derived from measurements at very high pressures (up to 700 bar).[54] In the limit of high pressure, eqn (26) reduces to

$$k_{2nd}^{\infty} = k_{ass} \qquad (26b)$$

Values of k_{ass} at and above room temperature have also been derived from measurements on the rate of vibrational relaxation of OH($v = 1$) by CO,[54,58] on the bases that (a) the rate of formation of $(HOCO)^{\dagger}$ will remain essentially unaffected by the vibrational state of OH, and (b) once an energised HOCO species is formed from OH($v = 1$) by CO, the excitation in the OH vibration will be lost to other degrees of freedom before the complex dissociates.[59]

Fulle *et al.*[54] have undertaken a comprehensive theoretical modelling of the complex temperature- and pressure-dependence of the rate constants for the reaction between OH radicals and CO. Their fits to the experimental data at the high and low pressure limits are reproduced in Fig. 4. The values of the rate constant k_{2nd}^{∞} and that for vibrational relaxation of OH($v = 1$) are governed by the rate of passage through the transition state (TS1) between separated OH + CO and the HOCO complex. They model this using a form of microcanonical transition state theory in which the internal partition function for the transition state is evaluated (*cf.* eqn. (25), above) using:

$$Q_{int,TS1}^{\ddagger} = \sum_{J=0}^{\infty} (2J + 1) \int_{0}^{\infty} W_{TS1}^{\ddagger}(E, J) \exp\left(-\frac{E}{kT}\right) \frac{dE}{kT} \qquad (27a)$$

where $W_{TS1}^{\ddagger}(E, J)$ is the number of internal states accessible at TS1 to a system with energy E and total angular momentum J,

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Chem. Soc. Rev., 2008, **37**, 812–826 | 821

Table 3 Summary of the experiments carried out and the results obtained for the reaction between OH radicals and CO

Ref.	Method[a]	Range of T/K	Notes on values of $k(T)$ and temperature-dependence
Ravishankara and Thompson[53]	FP of H_2O at $\lambda > 165$ nm; RF detection of OH	250–1040	$k(T)$ fitted to $\exp(-30.03 + 0.00122T)$ cm^3 molecule^{-1} s^{-1}
Frost et al.[49]	PLP of HNO_3 at 266 nm; LIF detection of OH	80–297	no analytical expression given for $k(T)$; at lowest T, $k(T) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}
Wooldridge et al.[50]	ST/thermolysis of HNO_3; cw LA detection of OH and CO_2	1080–2500	data fitted to an Arrhenius expression: $k(T) = 3.5 \times 10^{-12} \exp(-2630/T)$ cm^3 molecule^{-1} s^{-1}
Fulle et al.[54b]	PLP of N_2O at 193 nm + reaction of $O(^1D)$ with H_2O or H_2; LIF detection of OH	90–830	$k(T)$ are fitted (see Fig. 4) to the results of microcanonical TST calculations as described in the text
Fulle et al.[54b]	PLP of N_2O at 193 nm + reaction of $O(^1D)$ with H_2; LIF detection of OH($v = 1$)	314–781	$k(T)$ are fitted (see Fig. 4) to the results of TST calculations as described in the text
Brunning et al.[58]	FP of H_2O at $\lambda > 165$ nm; LIF detection of OH($v = 1$)	296	$k(296$ K) for vibrational relaxation = 1.0×10^{-12} cm^3 molecule^{-1} s^{-1}

[a] Abbreviations: FP: flash photolysis; RF: resonance fluorescence; PLP: pulsed laser photolysis; LIF: laser-induced fluorescence; cwLA: cwlaser absorption; ST: shock tube.

so that

$$k_{2nd}^\infty = \frac{kT}{h} \left(\frac{Q_{HOCO}}{Q_{HO}Q_{CO}} \right)_{el,trans} \left(\frac{1}{Q_{HO}Q_{CO}} \right)_{rot,vib} Q_{int,TS1}^\ddagger \quad (27b)$$

Calculations with various values of the zero-point corrected barrier, i.e., $\Delta E_0^{\ddagger}$, TS1, indicated that the best fit to the experimental data was obtained (see Fig. 4) with $\Delta E_0^{\ddagger}$, TS1 = 1.8 kJ mol^{-1}.

In modelling the low pressure rate constants, k_{2nd}^o, account has to be taken (see eqn (26a)) of the competition between dissociation of the energised HOCO complex to CO_2 + H and 'back' to OH + CO. In the calculations of Fulle et al., this was done microcanonically; that is, the values of k_{reac} and k_{diss} were replaced by values depending on E and J and the resultant expression was included in the integration of total energy and summation over total angular momentum, so that

$$k_{2nd}^o = k_{2nd}^\infty \times \left(\frac{W_{TS2}^\ddagger(E,J)}{W_{TS1}^\ddagger(E,J) + W_{TS2}^\ddagger(E,J)} \right) \quad (28)$$

Fig. 4 shows the accuracy of the fits obtained by Fulle et al.[54b] when (a) the zero-point corrected barrier at the first transition state (TS1) is 1.8 kJ mol^{-1}, and (b) the zero-point corrected barrier at the second transition state (TS2) is within 0.7 kJ mol^{-1} of that at TS1. The agreement with both sets of experimental data is excellent. Kinetic data for the reaction at still lower temperatures would greatly assist in establishing the height of the zero-point corrected barrier at TS1, but the reaction is probably too slow to allow its kinetics to be investigated in a CRESU apparatus.

(d) Reactions proceeding via a shallow potential minimum:

$$O(^3P) \text{ atoms } + \text{ alkenes} \qquad (R4)$$

The reactions of atomic and small molecular free radicals with unsaturated hydrocarbons have been widely studied. They proceed via the initial formation of a strongly bound adduct which may then dissociate exothermically to two product species, as in the case of CN + C_2H_4 → C_2H_3CN + H,[60]

or, in the absence of an exothermic dissociation route, the adduct may undergo pressure-dependent association, as in the case of OH + C_2H_4 (+M) → C_2H_4OH (+M), at temperatures below ca. 450 K.[61] In certain cases, under certain conditions, such product channels may be competitive. It is now realised that the initial formation of the bound, energised, adducts may occur along minimum energy paths on which there are shallow minima.

As an example of this kind of reaction, and for reasons that will become clear, I have chosen to discuss the reactions of ground state oxygen atoms, $O(^3P)$, with alkenes. In general, the energised triplet di-radical that is formed initially can either fragment or undergo collisional stabilisation.[62] However, although the relative rates of these processes, and therefore the branching ratio into the two product channels, may depend on a number of factors: (i) the total pressure, (ii) the temperature, and (iii) the number of atoms in the energised complex, the overall rate of reaction, as determined by observing the rate of loss of $O(^3P)$ atoms, will depend on the rate of formation of the initially formed adduct and be independent of the total pressure.

Rate constants for the reactions between $O(^3P)$ atoms and many unsaturated hydrocarbons were determined in a series of experimental studies carried out, mainly by Cvetanovic and his co-workers,[63] in the 1960s and 1970s using the technique of molecular modulation spectroscopy. These results and those obtained by flash photolysis methods[64] were summarised and evaluated by Cvetanovic in 1987.[62] Partly because of the quality and range of these data, and also because the reactions of $O(^3P)$ atoms with hydrocarbons play very little role in atmospheric chemistry,‡‡ there have been only a few recent experimental studies of these reactions at and around 298 K.

The reaction with ethene is the slowest of those between $O(^3P)$ atoms and alkenes. This finding is consistent with the notion (for further discussion, see below) that the kinetic data for the reactions of radicals with unsaturated hydrocarbons can be correlated with the differences between the ionisation energies (I.E.) of the molecular reagent and the electron

‡‡ In the troposphere, where unsaturated hydrocarbons are predominantly found, the concentration of $O(^3P)$ atoms is extremely low due to their rapid association with O_2 to form ozone.
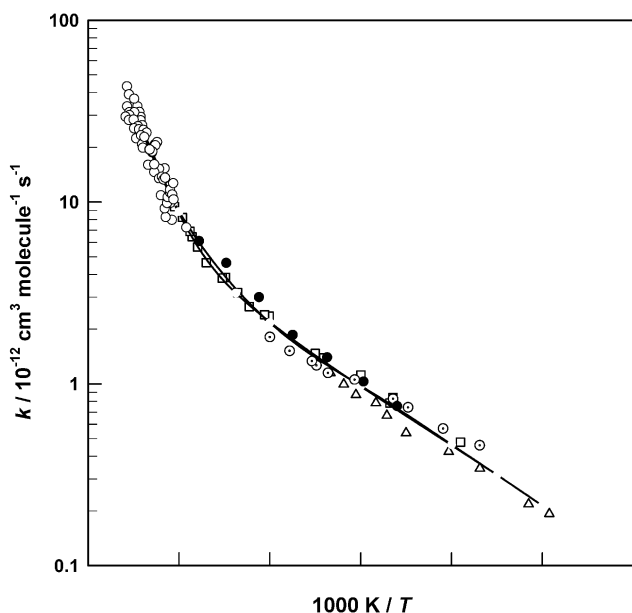
Fig. 5 Arrhenius plot of the rate constants for the reaction between O(^{3}P) atoms and C_2H_4 adapted from Fig. 5 in the paper by Klemm *et al.*[66] They measured the high temperature data (○). The other data shown in this diagram are from (△) Browarzik and Stuhl (*J. Phys. Chem.*, 1984, **88**, 6004), (□) Nichovich and Ravishankara (*Proc. 19th Int. Symp. Combust.*, 1983, 23), (⊙) Davis *et al.* (*J. Chem. Phys.*, 1972, **56**, 4868) and (●) Perry (*J. Chem. Phys.*, 1984, **80**, 153). Klemm *et al.*[66] are responsible for the fit represented by the line in the diagram. More sources of kinetic data for this reaction can be traced by reference to their paper.

affinity (E.A.) of the radicals, since ethene has the highest I.E. of the alkenes: 10.51 eV. Rate constants have been measured for this reaction at temperatures up to 1052 K, using high temperature photochemical techniques,[65] and between 1052 and 2284 K in experiments[66] that combined a shock tube to create high temperatures with flash photolysis of NO in the vacuum ultraviolet to generate O(^{3}P) atoms. The decays in concentration of atomic oxygen were followed by observing chemiluminescence from electronically excited NO_2, formed in the association of the atoms with undissociated NO. This method, apparently first employed by Perry,[64b] has been quite widely adopted (see below).

Within the temperature range covered in their experiment, Klemm *et al.*[66] could fit their rate constants to an Arrhenius expression, $k(T) = (1.3 \pm 0.1) \times 10^{-10} \exp[-(2770 \pm 130)/T]$ cm^3 molecule^{-1} s^{-1}, but combining their data with results obtained at temperatures down to *ca.* 200 K shows the Arrhenius plot over the full temperature range to be strongly curved, as Fig. 5 demonstrates. They chose to fit all the data to a sum of two Arrhenius expressions, though they expressed doubts as to whether this form for $k(T)$ indicated the existence of two independent reaction channels. What is clear from the strong positive temperature-dependence of $k(T)$ for O(^{3}P) + C_2H_4 is that there must be a significant potential energy barrier for this reaction, and this conclusion is confirmed by *ab initio* calculations,[67] which estimate the height of the barrier on the lowest triplet surface to be *ca.* 5–6 kJ mol^{-1}.

Fontijn and co-workers[68] have studied the temperature-dependence of the reactions of O(^{3}P) with the four butenes in the range 284–1110 K using high temperature photochemical techniques, with relative concentrations of the atoms observed by resonance fluorescence. Rate constants for the reactions with *iso*-butene (I.E. = 9.22 eV), *cis*-butene (I.E. = 9.11 eV), and *trans*-butene (I.E. = 9.10 eV) depend only slightly on temperature within this range, apparently showing a shallow minimum in the values of $k(T)$ at *ca.* 400 K with small increases to both higher and lower temperatures. The rate constants for O(^{3}P) + 1-butene (I.E. = 9.55 eV) do, however, show a monotonic increase with temperature through the range 335–1110 K, covered in the experiments of Ko, Adusei and Fontijn.[68a] These data are fitted quite well with a modified Arrhenius expression with *m* = 2.5 and (E'_{act}/R) = −518 K.

As mentioned above, the values of the rate constants for the reactions between radicals and unsaturated hydrocarbons, and their dependence on temperature, have been correlated for many years with differences between the ionisation energies (I.E.) of the molecular reagent and the electron affinity (E.A.) of the radical. Building on this foundation, Smith *et al.*[69] have recently examined low temperature kinetic data obtained in CRESU experiments.[28] They came to the tentative conclusion that when (I.E. − E.A.) is less than *ca.* 8.75 eV, then it is likely that any reaction between a radical and an unsaturated molecule would remain rapid at the low temperatures (10–20 K) found in interstellar clouds. Furthermore, they proposed that studies in a CRESU apparatus of the kinetics of the
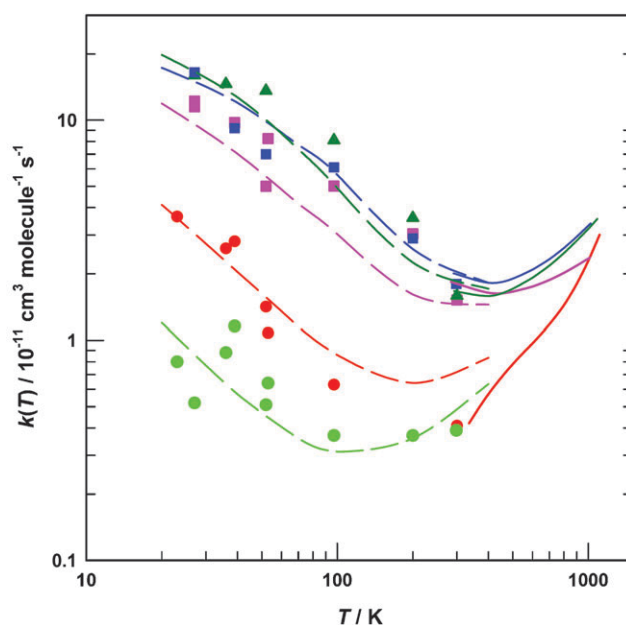
Fig. 6 Kinetic data for the reactions between: O(^{3}P) atoms and propene, and the four butenes. The points show the results of CRESU experiments by Sabbah *et al.*;[70] the solid lines fit the high temperature experimental data of Fontijn and co-workers,[68] and the dashed lines the results of μJ-VTST calculations reported by Sabbah *et al.*[70] The results for different alkenes are given in different colours: **green**, propene; **red**, 1-butene; **magenta**, *iso*-butene; **blue**, *trans*-butene; and **dark green**, *cis*-butene.

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Chem. Soc. Rev., 2008, **37**, 812–826 | 823

reactions between O(^{3}P) atoms and a series of alkenes would provide a valuable test of this prediction, since the I.E.s for simple alkenes mean that the values of (I.E. − E.A.) span the value of 8.75 eV.

Sabbah *et al.*[70] have very recently reported rate constants, at temperatures down to 23 K, for the reactions of O(^{3}P) atoms (E.A. = 1.46 eV) with propene (I.E. = 9.73 eV) and the four butenes: 1-butene, *iso*-butene, *cis*-butene and *trans*-butene. Their data, along with the rate constants measured at high temperatures by Fontijn and co-workers for the reactions of the four butenes, are displayed in Fig. 6. As expected, the reaction of oxygen atoms with ethene, for which (I.E. − E.A.) = 9.05 eV, was too slow to measure in CRESU experiments at temperatures below 298 K. What the results in Fig. 6 show is that the rate constants for reactions between O(^{3}P) and all the butenes, and also for O(^{3}P) + propene, pass through minima between 400 and 100 K and then increase to lower temperatures, although those for reactions with the alkenes with higher I.E.'s, *i.e.* 1-butene and propene, do not reach such high values at the lowest temperatures achieved in the CRESU experiments, as those for the reactions of *iso*-butene, *cis*-butene, and *trans*-butene, which have lower I.E.'s. These results confirm the prediction[69] that reactions for which (I.E. − E.A.) < 8.75 eV will remain rapid down to very low temperatures.

Building on previous work by Georgievskii and Klippenstein,[71] Sabbah *et al.*[70] explain the temperature-dependence of $k(T)$ for these reactions in terms of a model involving two transition states, not unlike that which has been proposed for OH + CO (see the previous section in this article). *Ab initio* calculations show that there are two transition states for the O(^{3}P) + alkene reactions: an outer one (TS1) at long-range, and an inner one (TS2) at or close to a maximum on the minimum energy path, at smaller inter-reactant separations than a shallow minimum arising from van der Waals forces. For O(^{3}P) + ethene, the zero-point energy of the inner transition state lies higher in energy than the separated reactants and this inner transition state controls the kinetics of reaction. For the other reactions in this series, the inner barrier is 'submerged'; that is, it lies lower in energy than the separated reactants, but the internal states at the inner transition state are more widely spaced than those at the outer transition state.

The calculations reported in the paper by Sabbah *et al.*[70] employ the μJ-VTST version of transition state theory described earlier. To calculate a partition function for the transition state species, they use eqn (22) but employ an effective value of $W^\ddagger(E, J)$ given by:

$$W_{\text{eff}}^\ddagger(E, J) = W_{\text{TS1}}^\ddagger(E, J)\, W_{\text{TS2}}^\ddagger(E, J)/\{W_{\text{TS1}}^\ddagger(E, J) + W_{\text{TS2}}^\ddagger(E, J)\} \quad (29)$$

This form arises because $W_{\text{TS1}}^\ddagger(E, J)$ determines the rate of passage through the outer transition state, whereas the term $W_{\text{TS2}}^\ddagger(E, J)/\{W_{\text{TS1}}^\ddagger(E, J) + W_{\text{TS2}}^\ddagger(E, J)\}$ determines the fraction of systems with (E, J) that, having reaching the shallow minimum, continue through the inner transition state to form the strongly bound adduct.

With only a slight adjustment to the inner barrier heights from those given by the *ab initio* calculations, the μJ-VTST

calculations yield the curves given in Fig. 6, which are in excellent agreement with the experimental data. These calculations demonstrate that the rate of the reaction of O(^{3}P) + ethene is determined by passage through the inner transition state, the rates for O(^{3}P) with the three butenes, *iso*-butene, *cis*-butene, and *trans*-butene, at least at the lowest temperatures, are determined very largely by passage through the outer transition state, whilst the rates of the reactions of O(^{3}P) + propene and 1-butene depend on passage through both transition states with the balance changing with temperature.

Summary and conclusions

The main focus of this article has been to examine the validity of the simple Arrhenius equation in the light of modern information about the temperature-dependence of elementary reaction rates. It is clear that, when rate constants can be measured over wide ranges of temperature, the values of $k(T)$ rarely, if ever, match the dependence on temperature predicted by eqn (1); that is, the simple Arrhenius 'law'. To illustrate this point, I have examined four bimolecular reactions (in one case a set of reactions) chosen partly because of the wide range of temperature over which their rate constants have been measured and partly because they serve as representatives of different categories of reaction: different in the way in which the potential energy varies along the minimum energy path. In all these cases, and by extrapolation in many other cases, the behaviour of the rate constants is 'non-Arrhenius'. Indeed, I would contend that non-Arrhenius behaviour is the norm, not the exception, if kinetic data are available or wanted, across a wide range of temperature.

Having made that point, it is important to enter two qualifications. First, it is often quite acceptable and sufficiently accurate to express the temperature-dependence of $k(T)$ in the Arrhenius form over a limited range of temperatures: for example, for use in models of atmospheric chemistry. Of course, whenever this is done—or even when the modified Arrhenius expression is used to represent $k(T)$—the range of temperature over which the relationship has been established should be reported. Second, for all the cases that have been examined in this article, the temperature-dependence of $k(T)$ is quite slight. It is this fact that makes it possible to determine rate constants across a wide range of temperature for many gas-phase reactions of free radicals. As I pointed out in the Introduction, unimolecular reactions generally have high activation energies: that is, their rate constants depend strongly on temperature. Consequently, they can frequently be studied over only a relatively narrow range of temperatures, making any non-Arrhenius dependence hard to uncover.

The second major point made in this article is that the observed variations of $k(T)$ can now frequently be well-matched employing the appropriate form of transition state theory based on *ab initio* calculations of the energies at important points on the potential energy surface for the reaction, even for reactions where there is no well-defined maximum, and therefore no well-defined transition state, on the path of minimum energy. Particularly for reactions with no barriers along the minimum energy path, it is necessary to employ microcanonical transition state theory, and, in these

cases, the rate of reaction may well depend on the initial quantum states of the reactants.[72]

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