

The kinetics and thermodynamics of free radical reactions

M J Pilling

School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K.

Abstract

Three experimental studies are described which emphasise the inter-relationship of kinetics and thermodynamics. The first involves $\Delta H_f^\ominus(t\text{-C}_4\text{H}_9)$, where discrepancies in experimental values have led to extensive kinetic studies of the reactions $t\text{-C}_4\text{H}_9 + \text{HX}$ ($X = \text{Br}, \text{I}$) which surprisingly have negative activation energies. The second study relates to forward and reverse reactions in the system $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$ where use of the equilibrium constant enables rate parameters for both reactions to be defined over a very wide temperature range. Finally, recent direct measurements are reported on the rate constant for the neopentyl peroxy \rightarrow hydroperoxy radical isomerisation. The results demonstrate an overestimate of the rate constant in previous indirect studies, which can be ascribed to the use of inaccurate thermodynamic data.

INTRODUCTION

The interdependence of thermodynamics and chemical kinetics has long been recognised. The relationship between forward and reverse rate coefficients and the equilibrium constant for an elementary reaction is widely used in modelling combustion processes where one of the rate coefficients is calculated from experimental measurements of the other together with a knowledge of the thermodynamic parameters, $\Delta_r H$ and $\Delta_r S$ [1]. Conversely, the measurement of forward and reverse rate coefficients is the primary source of heats of formation for free radicals [2].

The link between the rate coefficients of a series of mechanistically similar reactions and the thermodynamics of the reactions was recognised over fifty years ago and is embodied in the Evans-Polanyi relations [3]. The relations were originally primarily designed to examine the effects of pressure on reactions, but the wider correlations, e.g. between activation energy and reaction enthalpy, were also considered and rationalised. Such correlations are still widely employed in modelling combustion and hydrocarbon cracking processes.

In this paper we examine three recent examples of experimental studies which exploit or depend on the relationship between thermodynamics and chemical kinetics. The first concerns the measurement of the heat of formation of the $t\text{-C}_4\text{H}_9$ radical using reaction kinetics. The subject is controversial and the resolution of the problems has led to the surprising observation of a whole class of metathesis reactions for which the rate constant *decreases* with temperature. The implications of this observation are far-reaching and have not, as yet, been fully rationalised.

The second example concerns the classic reaction pair



which are central to the H_2/Br_2 chain reaction as the inhibition and slow propagation steps. The relationship between the available experimental data for the forward and reverse rate coefficients and the equilibrium constant was unsatisfactory and it was also difficult to rationalise the forward rate constant and available dynamical information. This reaction has now been re-examined and a coherent picture established which incorporates full compatible kinetics and thermodynamics.

The final example is drawn from combustion where a crucial reaction in the mechanism of hydrocarbon autoignition is the isomerisation of a peroxy radical to generate a hydroperoxy radical. Available estimates of the rate coefficients for such reactions depend on end product analysis, coupled with equilibrium constants. Recent direct determinations of the equilibrium constants require substantial revisions of the isomerisation rate coefficients, but these revisions have not been widely accepted. A new direct method for measuring the rate of isomerisation is reported.

1. HEAT OF FORMATION OF $t\text{-C}_4\text{H}_9$

The heats of formation of the saturated alkyl radicals have generated considerable recent controversy. The classical kinetic technique, based on the halogenation reactions



was developed by Benson and coworkers [4] and has been discussed in detail by McMillen and Golden [2]. This approach generally leads to lower values for $\Delta_f H^\circ(\text{R})$ than the analysis of Tsang [5], which is based on alkane dissociation/alkyl radical association reactions. The discrepancy is particularly marked for $t\text{-C}_4\text{H}_9$ with differences of $\approx 20 \text{ kJ mol}^{-1}$. The controversy was further fuelled by two recent determinations of the rate coefficient for the reverse reaction:



Muller-Markgraf *et al* [6] used very low pressure photolysis (VLP ϕ) to study $\text{DBr} + t\text{-C}_4\text{H}_9$ and, after correction for isotope effects obtained $k_{-1} = 2.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and an activation energy of 9.8 kJ mol^{-1} for the DBr reaction. Russell *et al* [7], using laser flash photolysis coupled with photoionisation mass spectrometry, obtained a room temperature rate coefficient of $1.04 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, a factor of 50 larger, and a *negative* activation energy (-5.8 kJ mol^{-1}) (Fig. 1). This higher room temperature value was supported by the laser flash photolysis/diode laser absorption experiments of Richards *et al* [8], who obtained $k_{-1} = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Combining identical values for $k_{-1}(298 \text{ K})$ with the Muller-Markgraf and the Russell values of $k_{-1}(298 \text{ K})$ in third law calculations gives, respectively, 38.5 kJ mol^{-1} and 48.5 kJ mol^{-1} for $\Delta_f H^\circ_{298}(t\text{-C}_4\text{H}_9)$.

In an attempt to provide additional independent information, we have carried out laser flash photolysis experiments in which Br is detected by time-resolved resonance fluorescence. The experiments were conducted on a 10^{-3} s timescale at total pressures between 50 and 300 Torr, so that any vibrationally excited radicals generated in the photolysis are fully relaxed on the experimental timescale and surface effects are unimportant because the transients are unable to reach the vessel wall.

In the first set of experiments, $t\text{-C}_4\text{H}_9$ was generated by the XeF laser photolysis of $(t\text{-C}_4\text{H}_9)_2\text{N}_2$ and k_{-1} determined at 298 K from the rate of appearance of Br . An average value of $(3.2 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained, higher even than the values of Russell *et al* and Richards *et al*. Combination of this rate coefficient with literature data for k_1 gives $\Delta_f H^\circ_{298}(t\text{-C}_4\text{H}_9) = 50.9 \pm 3.5 \text{ kJ mol}^{-1}$ via a third law treatment.

In the second series of experiments, Br was generated from the photolysis of CF_2Br_2 at 193 or 248 nm in the presence of $i\text{-C}_4\text{H}_{10}$ and HBr and at temperatures of 573 and 641 K. Under these experimental conditions, $k_1[i\text{-C}_4\text{H}_{10}] \approx k_{-1}[\text{HBr}]$ and the system relaxes exponentially to equilibrium with a reciprocal relaxation time equal to $(k_1[i\text{-C}_4\text{H}_{10}] + k_{-1}[\text{HBr}])$. Such experiments enable both the forward and reverse rate coefficients, and hence the equilibrium constant, to be obtained directly. The values obtained for k_{-1} are shown in Fig. 1; they support the negative activation energy obtained by Russell *et al* [7]. The third law values obtained for $\Delta_f H^\circ_{298}(t\text{-C}_4\text{H}_9)$ were $(44.2 \pm 4.0) \text{ kJ mol}^{-1}$ and $(48.1 \pm 4.0) \text{ kJ mol}^{-1}$ at 573 K and 641 K respectively, giving an average value from the three independent determinations of $(47.3 \pm 3.5) \text{ kJ mol}^{-1}$, in excellent agreement with the measurements of Russell *et al*.

Parallel to our own studies, Nicovich *et al* [9] have recently conducted a very thorough analysis of the kinetics of a range of alkyl radicals with HBr and DBr , again using laser flash photolysis coupled with observations of the rate of appearance of Br by resonance fluorescence.

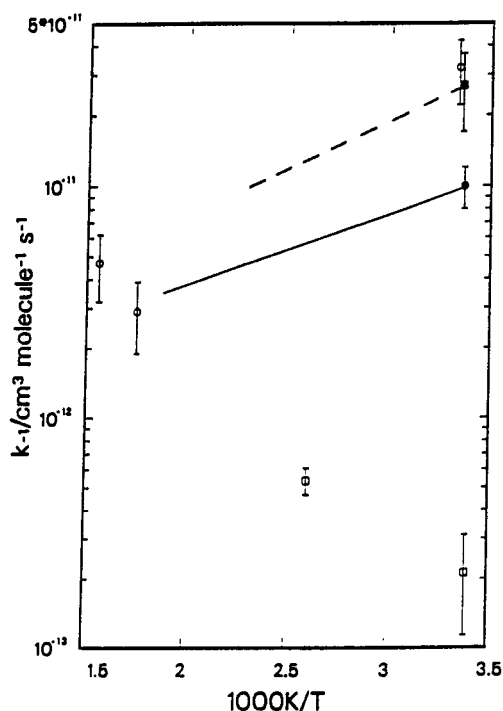


Fig. 1 Arrhenius plot for k_1 . O, this work; \bullet , Richards *et al* [8]; \square , Muller-Markgraf *et al* [6]; \blacksquare , - - -, Nicovich *et al* [9], —, Russell *et al* [7].

They obtained $k_1 = 2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297K, in good agreement with our own value, and an activation energy of -8.0 kJ mol^{-1} over the temperature range 297 - 429 K. (see Fig. 1). For $\Delta_f H_{298}$ ($t\text{-C}_4\text{H}_9$) they obtained $(51.5 \pm 2.9) \text{ kJ mol}^{-1}$.

Although the reasons for the discrepancy between the VLP ϕ experiments and the laser flash photolysis measurements is not clear, the weight of evidence clearly favours the higher value for $\Delta_f H$ ($t\text{-C}_4\text{H}_9$). The most striking result of these experiments, however, is the observation of a *negative* activation energy in a metathesis reaction. Russell *et al* [10] observed negative activation energies for a series of alkyl radicals reacting with HBr, with the absolute value increasing with the size of the radical in the series CH_3 to $t\text{-C}_4\text{H}_9$. These observations were confirmed by Nicovich *et al* [9] whilst Seetula *et al* [11] found similar behaviour for $\text{R} + \text{HI}$, with $E = -6.3 \text{ kJ mol}^{-1}$ for $\text{R} = t\text{-C}_4\text{H}_9$.

Clearly the mechanism of these reactions cannot involve a simple metathesis and a more complex mechanism must be invoked. McEwen and Golden [12] examined a mechanism in which R and IH first form a complex via a loose transition state, (TS1), (see Fig. 2.) which then forms the products via a tight triangular transition state, TS2. They were able to produce the broad features of the behaviour using an RRKM simulation at the low pressure limit.

Such a simulation does not fully illustrate the key determinants in a mechanism of this type and we present here a modified treatment based on a master equation. The energy states of the complex $\text{R} \cdots \text{I} \cdots \text{H}$ (C) are divided into bundles known as 'grains' (typical grain widths = $5 - 50 \text{ cm}^{-1}$) and the differential equations constructed to describe the time dependence of the grain populations, C_i

$$\frac{dC_i}{dt} = g_i - (k_{1i} + k_{2i})C_i$$

where g_i is the rate of formation of C_i and k_{1i} and k_{2i} are the microcanonical rate coefficients for dissociation of the complex via transition states TS1 and TS2. k_{1i} and k_{2i} can be calculated using standard procedures [13] from the parameters provided by McEwen and Golden [12]. Equation 1 applies at the low pressure limit when $(k_{1i} + k_{2i}) \gg \omega$, the collision frequency. Such a condition is

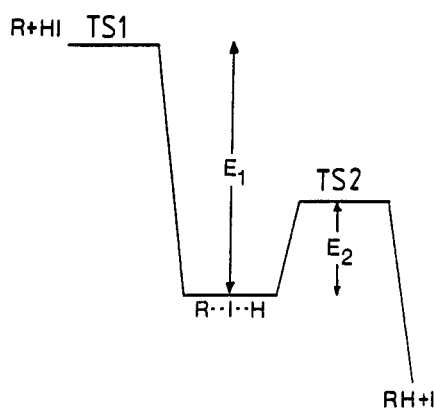


Fig. 2 Schematic diagram of the energy profile for the reaction $\text{R} + \text{HI} \rightarrow \text{RH} + \text{I}$ [12].

obeyed in the present system for the experimental conditions studied. g_i may be calculated from detailed balance [13]:

$$g_i = k_r^{\infty} f_i [A][B]$$

where k_r^{∞} is the limiting high pressure rate coefficient for forming R ... I ... H from R + IH. f_i is given by [13]:

$$f_i = W_{1i} \exp(-E_i / kT) / \sum_{i=m}^{\infty} W_{1i} \exp(-E_i / kT)$$

where W_{1i} is the sum of rovibrational states at energy E_i at TS1 and $i=m$ is the first grain above the dissociation limit of C to form A + B (i.e. $E_1 = m\delta$ where δ is the grain width). The microcanonical rate coefficients are given by [13]:

$$k_{1i} = W_{1i} / (h\rho_i) ; k_{2i} = W_{2i} / (h\rho_i)$$

where ρ_i is the density of states of the complex C at energy E_i . By applying the steady-state approximation to C, and determining the overall rate of forming products by summing over all grains, the bimolecular rate coefficient k_b for H atom transfer is readily shown to be given by:

$$k_b = k_r^{\infty} \sum_{i=m}^{\infty} (W_{1i}W_{2i} / (W_{1i} + W_{2i})) \exp(-E_i / kT) / S_1$$

$$\text{where } S_1 = \sum_{i=m}^{\infty} W_{1i} \exp(-E_i / kT)$$

k_r^{∞} is an association rate coefficient and so is likely to show only a weak dependence on temperature. The primary contributions to the negative temperature coefficient in k_b must, therefore, derive from the sums of states terms. At energies only just above threshold, provided E_1 is significantly greater than E_2 , $W_{2i} \gg W_{1i}$, despite the looser nature of TS1, because of the greater internal energy available in TS2. (Fig. 2). Thus, at very low temperatures, where the threshold states dominate, k_b tends to k_r^{∞} , so that all the complexes formed from A + B generate products. At high energies, $W_{1i} \gg W_{2i}$, because TS1 is so much looser than TS2, and the high temperature asymptotic form for k_b is:

$$k_b = k_r^{\infty} S_2 / S_1$$

$$\text{where } S_2 = \sum_{i=m}^{\infty} W_{2i} \exp(-E_i / kT)$$

Since W_{2i} increases more rapidly with energy than W_{1i} , S_2/S_1 is a decreasing function of temperature. Thus k_b shows the complex dependence on T symptomatic of a reaction involving competing channels whose relative importance depends on energy. Note that provided collisional stabilisation is unimportant k_b depends only on E_2 , the energy of the tight transition state and on the structures of TS1 and TS2. It is independent of E_1 , the bond energy of the RIH complex. Finally, it should be emphasised that this simple model has made no attempt to incorporate angular momentum effects which could be significant in a reaction proceeding through loose and tight transition states at the low pressure limit.

2. FORWARD AND REVERSE RATE COEFFICIENTS

The procedure of calculating a reverse rate coefficient from that for the forward reaction coupled with the equilibrium constant is frequently employed in combustion chemistry. Problems can arise, however, even when the thermodynamic parameters are well-established if the reactions show non-Arrhenius behaviour and the reverse rate coefficient is required in a temperature range over which the forward rate coefficient is not well-defined. Such a situation frequently arises for a reaction with a large value for $\Delta_r H$. The discrepancies that can arise are clearly illustrated by the reaction:



for which k_1 and k_2 had previously been studied over non-overlapping temperature ranges.

The reverse rate coefficient was determined in a range of classic studies of the H_2/Br_2 chain reaction for which it constitutes the rate determining chain propagation step. An evaluation of these data by Baulch *et al* [14] gave

$$k_2 = 2.82 \times 10^{-10} \exp(-9640 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

which they employed, together with K_2 , to calculate k_2 . They restricted their recommended temperature range to 500 - 1700 K but extrapolation outside this range, to 300 K, clearly underestimates the room temperature measurements of Husain and Slater [15] and Jourdain *et al* [16] who used flash photolysis/resonance fluorescence and discharge flow/epr respectively. There is better agreement with the data of Endo and Glass [17], who also used discharge flow, especially with the temperature dependence.

Discrepancies between rate coefficient ratios and the corresponding equilibrium constant can arise if the exothermic reaction channels products preferentially into excited states, provided relaxation is slow. Such an explanation of the present discrepancies is eliminated by the infra-red chemiluminescence studies of Bly *et al* [18] who set an upper limit of 1.3% on the yield of $\text{Br}(^2\text{P}_{3/2})$, by the crossed-molecular beam results of Hepburn *et al* [19] who set an upper limit on this yield of 2% and by the CARS results of Aker *et al* [20] who, even at a collision energy of 1.6 eV, found only 9% of the available energy was channelled into vibration. An analysis of the molecular beam results of Hepburn *et al* [19] by Sudhakaran and Raff [21] using a model LEPS surface were most closely compatible with an energy barrier of 0.8 kJ mol⁻¹, over a factor of 10 less than the activation energy derived from the evaluation of Baulch *et al* [14] and the measurements of Endo and Glass [17]. This incompatibility between the extrapolated values of k_2 and the room temperature measurements of k_2 by Husain and Slater [15] and Jourdain *et al* [16], coupled with the dynamical behaviour of the forward reaction, was further emphasised by the low temperature measurements of k_2 by Umemoto *et al* [22] using pulse radiolysis coupled with resonance absorption.

In order to try to resolve the disagreement, we undertook higher temperature measurements which provide some overlap with the measurements of k_1 . Fig. 3 shows an Arrhenius plot for all the experimental data except for the data of Endo and Glass, together with values for k_1 calculated from the higher temperature measurements of k_2 and K_2 . All the data are satisfactorily fitted with the non-Arrhenius expression:

$$k_2 = 2.1 \times 10^{-14} (T/\text{K})^{1.05} \exp(-82\text{K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

over the range $200 \leq T/\text{K} \leq 1700$. Although the plot is strongly curved, the temperature exponent is physically reasonable for a reaction of this sort. Fig. 4 shows the same data employed in an

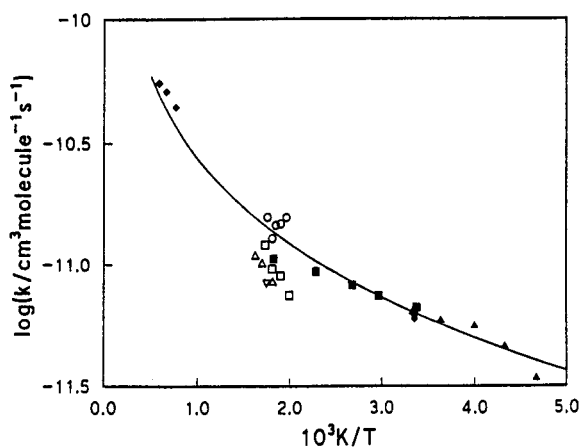


Fig. 3 Non-linear Arrhenius plot for k_2 . This work (■); Umemoto *et al* [22] (▲); Husain and Slater [15] (▼); Jourdain *et al* [16] (◆). Values for k_2 calculated from $k_2 K_2$; Britton and Cole [22] (◆); Vidal [23] (O); Bodenstein and Lind [24] (□); Bach *et al* [25] (Δ); Kistiakowsky and Van Artsladen [26] (▽).

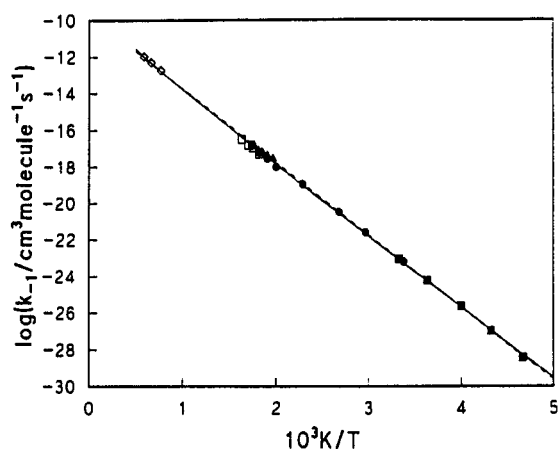


Fig. 4 Non-linear Arrhenius plot for k_2 . The data points are as for Fig. 3. —, non-linear least squares fit;, k_2/K_2 .

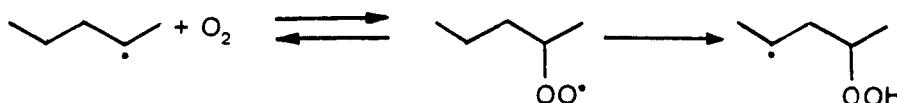
Arrhenius plot for k_2 ; the high activation energy substantially masks the curvature in this case. The best-fit expression for the rate coefficient is:

$$k_2 = 6.9 \times 10^{-12} (T/K)^{0.43} \exp(-8970K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the same temperature range. There is a considerable covariance between the parameters in these two expressions and a simple statement of their individual uncertainties is unwarranted. The overall uncertainty in the rate coefficients is $\approx \pm 15\%$ at temperatures below 500 K, rising to a factor of 2 at 1700 K. It would be of interest to reanalyse the molecular beam data of Hepburn *et al* [19] together with these rate measurements in order to define the individual parameters more precisely. A literal interpretation of the exponential term for k_2 gives an energy barrier of 0.7 kJ mol^{-1} , in good agreement with the analysis of Sudhakaran and Raff [21].

3. PEROXY RADICAL ISOMERISATION

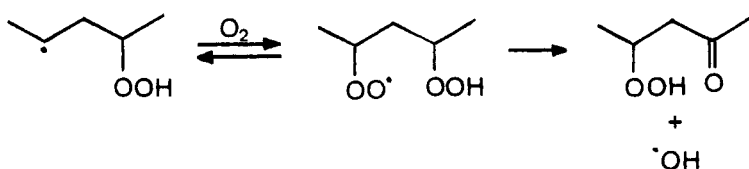
The phenomenon of knock in a petrol engine is closely related to autoignition which occurs in the comparatively low temperature combustion of hydrocarbons at around 600 K [27]. Under these conditions, peroxy radicals are of central importance; they are generated by the addition of O_2 alkyl radicals and they isomerise to form hydroperoxy radicals, e.g. :



The hydroperoxy radical then regenerates OH in a variety of ways e.g.



Alternatively, the hydroperoxy radical adds a further oxygen molecule which can decompose to form a hydroperoxide, ROOH

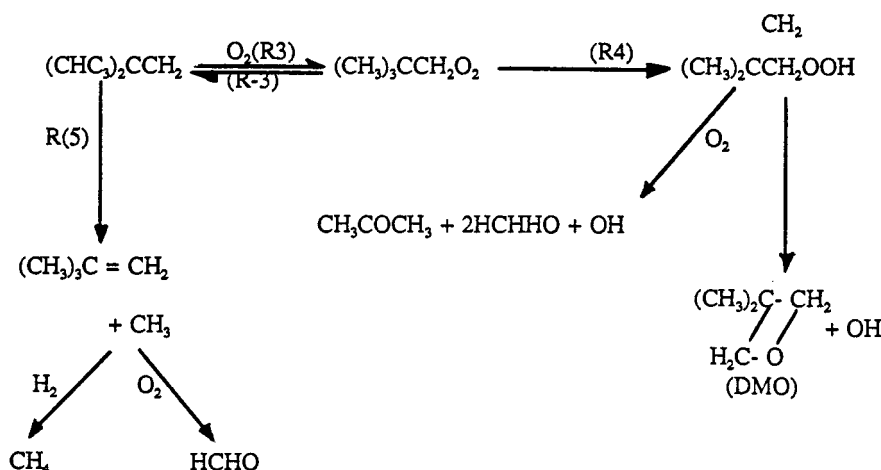


The hydroperoxide acts as a degenerate branching agent, decomposing to generate $\text{RO} + \text{OH}$. Branching leads to an acceleration of the reaction rate and to a rise in temperature of $\sim 100 \text{ K}$. The incipient ignition is then quenched partly because the peroxy radical becomes unstable and dissociates to regenerate the alkyl radical, and partly because this radical decomposes more rapidly at higher temperature [28]. As well as being implicated in autoignition, this low temperature process leads to a variety of thermokinetic processes such as oscillatory ignitions and oscillatory cool flames in continuously stirred flowing tank reactors.

A crucial step in this overall process is the internal H abstraction in which the peroxy radical is converted into the hydroperoxy radical. The most direct studies of this reaction have been made by Baldwin, Walker and coworkers [29] who added small amounts ($\sim 1\%$) of an alkane to slowly reacting mixtures of hydrogen and oxygen at temperatures of $\sim 750 \text{ K}$. For example, if neopentane is added, then neopentyl radicals are formed and react according to the scheme at the top of p. 1479.

$$\text{Thus } \frac{d\{[\text{CH}_3\text{COCH}_3] + [\text{DMO}]\}}{d[(\text{CH}_3)_2\text{C}=\text{CH}_2]} = \frac{K_3 k_4 [\text{O}_2]}{k_5}$$

provided $k_4 \ll k_3$, a justifiable assumption under the conditions used. Thus end product analysis permits k_4 to be determined provided K_3 and k_5 are known. Baldwin *et al* used Benson's bond



additivity data [30] to estimate K_3 , whilst k_5 was estimated by thermochemical means, coupled with comparisons with other alkyl radicals. The resulting Arrhenius form for k_4 is:

$$k_4 = 1.2 \times 10^{13} \exp(-14400\text{K}/T) \text{s}^{-1}$$

Baldwin *et al* [29] similarly examined a variety of alkyl radicals and proposed a set of generic Arrhenius parameters for the possible types of internal hydrogen atom transfer (e.g. 1,4 primary, 1,5 secondary, etc.) which are of considerable value in modelling low temperature combustion systems.

Considerable uncertainty in these values has, however, been generated by the recent direct measurement of K_3 for several radicals by Gutman and coworkers (see, for example, ref. 31). They measured equilibrium constants which were higher than those determined from Benson's bond additivity arguments, the discrepancy increasing with the complexity of the alkyl radical. Thus, for $t\text{-C}_4\text{H}_9$, for example, the measured equilibrium constant at 600 K is a factor of 50 higher than that estimated from bond additivity. This reduces k_4 by a similar factor.

We have recently developed a time-resolved technique for measuring k_4 directly for the neopentyl radical system. The C_5H_{11} radical was generated by the laser photolysis (248 nm) of neopentyl iodide in the presence of 50 Torr O_2 and at a total pressure of 700 Torr in a helium diluent. Simulations based on the rate data of Baldwin *et al* [29] demonstrated that, at temperatures of ≈ 700 K, OH is generated from $\text{C}_5\text{H}_{10}\text{OOH}$ following direct dissociation or reaction with O_2 followed by dissociation; furthermore, the rate determining step in the generation of OH is the isomerisation (reaction 4).

Fig. 5 shows a typical profile for OH, detected by laser induced fluorescence. The profile responded satisfactorily to a biexponential analysis given a first-order rate constant for the rise of $(1.2 \pm 0.2) \times 10^3 \text{ s}^{-1}$. The rate constant was independent of $[\text{C}_5\text{H}_{11}\text{I}]$ over the range $7 \times 10^{11} - 7 \times 10^{12}$ molecule cm^{-3} and of $[\text{O}_2]$ over the range 30 - 100 Torr. It may be ascribed to the isomerisation reaction (4) on the basis that this is the rate determining step for OH generation.

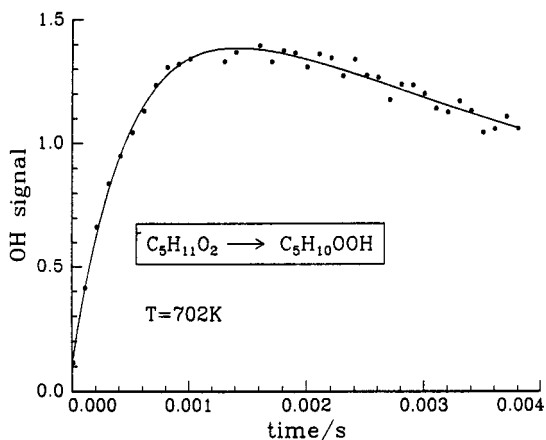


Fig. 5 OH fluorescence signal obtained at 702K following the photolysis of $7.2 \times 10^{12} \text{ cm}^{-3}$ $\text{C}_5\text{H}_{11}\text{I}$ in the presence of 50 Torr O_2 and 578 Torr He.

This value of k_4 is a factor of 10 lower than the value determined by Baldwin *et al.* Their results can be brought into line with the present direct results if the equilibrium constant, K_3 , employed to interpret their experimental data, is increased by a factor of 10. Such an increase is in qualitative agreement with the conclusions of Slagle *et al* [31] but the increase required in K_3 is much smaller than the increase they proposed. It should be emphasised that these results are of a preliminary nature and further experiments are planned over a range of temperatures. The techniques should enable the extensive rate data set of Baldwin *et al* to be placed on an absolute basis.

Acknowledgements

I am grateful to the experimental skill and chemical insight of Kevin Hughes, Phil Lightfoot, Richard Pereira and Paul Seakins without whom none of this article would have been possible.

REFERENCES

1. S.W. Benson, *Thermochemical Kinetics*, Wiley, 2nd Ed. (New York) 1976.
2. D.F. McMillen and D.M. Golden, *Ann. Rev. Phys. Chem.* 1982, **33**, 493.
3. M.G. Evans and M. Polányi, *Trans. Faraday Soc.*, 1936, **32**, 1333.
4. D.M. Golden and S.W. Benson, *Chem. Rev.* 1969, **69**, 125.
5. W. Tsang, *J. Am. Chem. Soc.* 1985, **107**, 2872.
6. W. Muller-Markgraf, M.J. Rossi and D.M. Golden, *J. Am. Chem. Soc.*, 1989, **111**, 956.
7. J.J. Russell, J.A. Seetula, R.S. Timonen, D. Gutman and D.F. Nava, *J. Am. Chem. Soc.*, 1988, **110**, 3084.
8. P.D. Richards, R.J. Ryther and E. Weitz, *J. Phys. Chem.*, 1990, **94**, 3663.
9. J.M. Nicovich, C.A. van Dijk, K.D. Kreutter and P.H. Wine, *J. Phys. Chem.* (in press).
10. J.J. Russell, J.A. Seetula and D. Gutman, *J. Am. Chem. Soc.*, 1988, **110**, 3092.
11. J.A. Seetula, J.J. Russell and D. Gutman, *J. Am. Chem. Soc.*, 1990, **112**, 1347.
12. A.B. McEwen and D.M. Golden, *J. Mol. Struct.*, 1990, **224**, 357.
13. P.J. Robinson and K.A. Holbrook, *Unimolecular Reactions*, Wiley (London) 1970.
14. D.L. Baulch, J. Duxbury, S.J. Grant and D.C. Montague, *J. Phys. Chem. Ref. Data*, 1981, **10**, Supplement No. 1.
15. D. Husain and J. Slater, *J. Chem. Soc. Faraday Trans. 2*, 1980, **76**, 276.
16. J.L. Jourdain, G. Le Bras and J. Combourieu, *Chem. Phys. Letters*, 1981, **78**, 483.
17. H. Endo and G.P. Glass, *J. Phys. Chem.*, 1976, **80**, 1519.
18. S.H.P. Bly, D. Brand and J.C. Polanyi, *Chem. Phys. Letters*, 1979, **65**, 399.
19. J.W. Hepburn, D. Klimek, K. Liu, R.G. McDonald, F.J. Northrup and J.C. Polanyi, *Chem. Phys.*, 1981, **74**, 6226.
20. P.M. Aker, G.J. Germann and J.J. Valentini, *J. Chem. Phys.*, 1989, **90**, 4795.
21. M.P. Sudhakaran and L.M. Raff, *Chem. Phys.*, 1985, **95**, 165.
22. H. Umemoto, Y. Wada, S. Tsunashima, T. Takayanagi and S. Sato, *Chem. Phys.*, 1990, **143**, 333.
22. D. Britton and R.M. Cole, *J. Phys. Chem.*, 1961, **65**, 1302.
23. C. Vidal, *J. Chem. Phys.*, 1971, **68**, 1360.
24. M. Bodenstein and S.C. Lind, *Z. Phys. Chem.*, 1906, **57**, 168.
25. F. Bach, K.F. Bonhoeffer and E.A. Moelwyn-Hughes, *Z. Phys. Chem.*, 1935, **B27**, 71.
26. G.B. Kistiakowsky and E.R. Van Artsladen, *J. Chem. Phys.*, 1944, **12**, 469.
27. R.A. Cox in 'Modern Gas Kinetics', ed. M.J. Pilling and I.W.M. Smith Blackwell's Scientific Publications, Oxford, 1987, p. 262.
28. V.K. Proudler, P. Cederbalk, A. Horowitz, K.J. Hughes and M.J. Pilling, *Phil. Trans. Roy. Soc.*, in press.
29. R.R. Baldwin, M.W.M. Hisham and R.W. Walker, *J. Chem. Soc. Faraday Trans. 1*, 1982, **78**, 1615.
30. S.W. Benson and R. Shaw in 'Organic Peroxides' ed D. Swern, Wiley, New York, Vol. 1, 1970, p. 105.
31. I.R. Slagle, E. Rataczak and D. Gutman, *J. Phys. Chem.* 1986, **90**, 402.