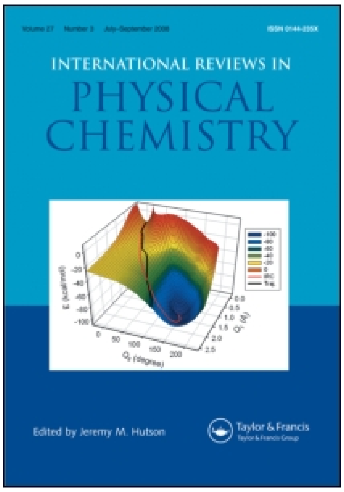

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Reactions of alkyl radicals

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Recent investigations into the reactions of alkyl radicals are reviewed. Reactions discussed are: heats of formation, association, addition, dissociation, hydrogen atom transfer and oxidation. A trend towards the greater use of direct time-resolved methods for measuring rate coefficients is noted and future developments, based on the availability of high-quality *ab initio* potential energy surfaces, are anticipated.

1. Introduction

The reactions of alkyl radicals are of central importance in many industrial processes based on pyrolysis or combustion. Experimental investigations have spanned several decades; they were based initially on competitive (Kerr and Parsonage 1976) or rotating sector techniques (Shepp 1956) and, more recently, on discharge flow (Kaufman 1984) or flash photolysis (Macpherson *et al.* 1985) with a wide range of detection methods including u.v. absorption (Macpherson *et al.* 1983), i.r. diode laser (Caldwell *et al.* 1989) and photo-ionisation (Slagle and Gutman 1985) spectroscopy.

Heats of formation of alkyl radicals are of importance, *inter alia*, in establishing rates of heat release in combustion, in estimating rate coefficients, in relating unknown 'reverse' rate coefficients to known or estimated 'forward' values and in rectifying or adjusting *ab initio* potential energy surfaces. Entropies are of similar importance but are more easily estimated from spectroscopic data, from group additivity (Benson 1976) or from *ab initio* surfaces. Free radical heats of formation, by contrast, are based primarily on rate coefficient measurements, although spectroscopic data, such as appearance potentials or dissociation limits, are sometimes employed, especially for small free radicals. The dependence on kinetic data has led to significant uncertainties and disagreements in values quoted in the literature (McMillen and Golden 1982). Some difficulties have recently been resolved but problems and controversy remain, especially for the larger alkyl radicals. Section 2 briefly reviews the current situation for the methyl, ethyl, *i*-propyl and *t*-butyl radicals.

Section 3 examines the status of association reactions. Recent years have seen a considerable concentration of effort on the measurement of radical–radical recombination reactions, especially for CH_3, and on the development of theoretical models. Less progress has been made on radical dissociation reactions and on radical addition which are discussed in section 4. Dissociation and their complementary association/addition rate coefficients are, of course, linked via equilibrium constants. Comparisons of the rate of coefficient quotients with equilibrium constants has proved remarkably disappointing, even for the C_2H_6/CH_3 reaction, where the thermochemistry is comparatively well established (Troe 1988).

A further area discussed in section 4 relates to radical dissociation reactions where different product channels compete. For example the *i*-propyl radical can dissociate via loss of CH_3 or H and the respective rate coefficients show a complex (T, P) dependence. Related problems include (i) the addition of H to propene at the 2-position where fragmentation to give $CH_3+C_2H_4$ competes with stabilisation and (ii) the combination of methyl radicals which, at high temperatures, can generate $H+C_2H_5$ in competition with the usual stabilisation channel. Experimental data on the various channels are usually very limited and it is not always easy to extrapolate these data to the regions of interest. A recently proposed approach, based on inverse Laplace transformation of association rate coefficients and a master equation analysis, is briefly described.

Rate coefficients for H atom transfer reactions are very well characterised at low temperatures (~600 K), based primarily on competitive measurements made in the 1960s. More recently the reactions have been studied at higher temperatures, revealing highly non-Arrhenius behaviour. Section 5 gives a brief account of the CH_3+H_2 reaction and of a recent analysis by Furue and Pacey (1986) which implicates a significant tunnelling contribution to the reaction.

Finally, in section 6, the reactions of alkyl radicals with O_2 are examined. At low temperatures the reaction proceeds via the peroxy radical, which begins to decompose at higher temperatures, when alternative reaction channels become important. Section 6 discusses the pressure dependence and thermodynamics of the peroxy radical formation reactions, the mechanism of the high temperature reactions for CH_3 and C_2H_5 and the reactions of the peroxy radical.

2. Heats of formation of alkyl radicals

2.1. *Introduction*

The standard heats of formation ΔH_f° of simple alkyl radicals are still uncertain despite numerous experimental determinations. Recently, McMillen and Golden (1982) reviewed the available experimental data and recommended values for ΔH_f° based primarily on halogenation experiments, which rely on the determination of forward and reverse rate coefficients for reactions of the types

$$R+HX \rightleftarrows X+RH, \qquad R+X_2 \rightleftarrows X+RX.$$

Tsang (1978, 1985), on the other hand, derived values from alkyl radical and alkane dissociation rate coefficients together with the reverse association values, obtaining significantly higher values, especially for *t*-butyl (table 1).

Some progress has recently been made in resolving these difficulties, although ΔH_f° (*t*-butyl) is still not well defined. The following sections give an account of these measurements. They should be prefaced by an appreciation of one important aspect of

Table 1. Recommended heats of formation for alkyl radicals.

	$\Delta H_{f,298}^\circ$ (kJ mol^{-1})	
Radical	McMillen and Golden (1982)	Tsang (1978, 1985)
CH_3	$146{\cdot}9\pm0{\cdot}6$	
C_2H_5	$108{\cdot}4\pm4$	$119{\cdot}5\pm2{\cdot}5$
i-C_3H_7	$76{\cdot}1\pm4$	$93{\cdot}3\pm2{\cdot}5$
t-C_4H_9	$36{\cdot}4\pm4$	$46{\cdot}2\pm2{\cdot}5$–$51{\cdot}7\pm2{\cdot}2$†

† The lower heat of formation refers to S_{298}° (t-C_4H_9) calculated with a 10 kJ mol^{-1} barrier to internal rotation, the higher value to an entropy based on free internal rotors.

much of the halogenation work. Experimental measurements were made of the I + RH, I + RI or Br + RH rate coefficients as a function of temperature. Activation energies were then *assumed* for the reverse reactions:

$E(\mathrm{R}+\mathrm{X_2}) \simeq 0 \pm 4\,\mathrm{kJ\,mol^{-1}}$, $E(\mathrm{R}+\mathrm{HI}) \simeq 4 \pm 4\,\mathrm{kJ\,mol^{-1}}$, $E(\mathrm{R}+\mathrm{HBr}) \simeq 8 \pm 4\,\mathrm{kJ\,mol^{-1}}$.

The heats of formation were then determined from the temperature dependences of the forward and reverse rate coefficients, that is the values of $\Delta H_f^\circ(\mathrm{R})$ depend sensitively on the assumed activation energies for the reverse reactions. Golden and Benson (1969) have discussed in detail the experimental evidence on which these assumptions were based.

2.2. *CH*$_3$

(*i*) Russell *et al.* (1988b) studied reaction R1 between 295 K and 532 K in a coated tubular reactor,

$$\mathrm{CH_3} + \mathrm{HBr} \rightarrow \mathrm{CH_4} + \mathrm{Br}. \qquad \text{(R1)}$$

The reactions and products were monitored in time-resolved experiments by a photo-ionisation mass spectrometer (PIMS). Methyl radicals were produced from the excimer laser photolysis of acetone at 193 nm. Conditions were maintained such that secondary reactions were too slow to be of any importance.

Combining the Arrhenius expression for k_1 with an expression for k_{-1} from other studies (Russell *et al.* 1988b, Fettis *et al.* 1960, Coomber and Whittle 1966), Russell *et al.* calculated a standard heat of formation for $\mathrm{CH_3}$ of $148 \pm 3\,\mathrm{kJ\,mol^{-1}}$ using a second-law treatment.

They also found that reaction R1 has a negative activation energy ($-1{\cdot}3\,\mathrm{kJ\,mol^{-1}}$), from which they deduced a value for $\mathrm{CH_3} + \mathrm{I_2}$ of $-5{\cdot}4\,\mathrm{kJ\,mol^{-1}}$, somewhat lower than the low limit inferred by Golden and Benson. Russell *et al.* (1988b) then recalculated $\Delta H_{f,298}^\circ$ ($\mathrm{CH_3}$) from the iodination rate data and their newly estimated activation energy for $\mathrm{CH_3} + \mathrm{I_2}$, obtaining a value of $148\,\mathrm{kJ\,mol^{-1}}$.

Dobis and Benson (1987) measured the equilibrium constant for reaction R2,

$$\mathrm{Cl} + \mathrm{CH_4} \rightarrow \mathrm{HCl} + \mathrm{CH_3} \qquad \text{(R2)}$$

at 298 K using a modified very-low-pressure reactor coupled with a quadrupole mass spectrometer. No secondary reactions were observed. The major alteration from previous VLPR studies was that two side chambers, and not one, were used for differential pumping on the reaction mixture, producing a better collimated molecular beam and thus greater sensitivity. Using known entropies and heats of formation (i.e. a third-law analysis), a value of $146{\cdot}7 \pm 0{\cdot}42\,\mathrm{kJ\,mol^{-1}}$ was obtained for the methyl radical heat of formation at 298 K.

Russell *et al.* (1988c) have also studied reaction R2 over the temperature range of 296–495 K using the same apparatus as in the study of reaction R1. Combining their value for k_{-2} with literature data for k_2, a second-law treatment of the data gave a standard heat of formation for the radical of $145{\cdot}2 \pm 2{\cdot}5\,\mathrm{kJ\,mol^{-1}}$. Since the structure and hence the entropy of the methyl radical is well known, a third-law analysis was then undertaken giving a more accurate value for $\Delta H_{f,298}^\circ$ ($\mathrm{CH_3}$) of $145{\cdot}6 \pm 1{\cdot}3\,\mathrm{kJ\,mol^{-1}}$.

2.3. *C*$_2$*H*$_5$

The most direct determination to date of the ethyl radical heat of formation was undertaken by Brouard *et al.* (1986). They directly monitored the approach to equilibrium in the $\mathrm{H} + \mathrm{C_2H_4} \rightleftarrows \mathrm{C_2H_5}$ system using the technique of laser flash photolysis/resonance fluorescence over the temperature range of 775–825 K and at 200 Torr. The hydrogen atom resonance fluorescence signal was analysed to yield the forward and reverse rate coefficients, and hence the equilibrium constant, at each temperature. Using a third-law treatment, the standard heat of formation of the ethyl radical was calculated to be 118·7 ± 1·5 kJ mol^{-1}.

Russell *et al.* (1988b) studied reaction R3 between 295 K and 532 K using laser flash photolysis/PIMS:

$$C_2H_5 \rightarrow C_2H_6 + Br. \qquad (R3)$$

The ethyl radical precursor was diethyl ketone. Using the same method as for the methyl radical, a second-law analysis of the data yielded a heat of formation for the ethyl radical of 120 ± 3 kJ mol^{-1}. As in the methyl radical study, reaction R3 was found to have a negative activation energy ($-3{\cdot}4$ kJ mol^{-1}). Reassessing the $C_2H_5 + I_2$ data in the light of this negative activation energy, they obtained excellent agreement between the recalculated and their measured ethyl radical heat of formation

Parmar and Benson (1989) have recently studied the reaction

$$Cl + C_2D_6 \rightarrow C_2D_5 + DCl, \qquad (R4)$$

in a very low pressure reactor, detecting Cl and C_2D_6 by mass spectrometry and measuring k_4 and K_4. After correction for zero-point energy differences they obtained $\Delta H^\circ_{f,298}$ $(C_2H_5) = 118 \pm 1{\cdot}7$ kJ mol^{-1}.

2.4. i-C_3H_7

Using the same technique, and based on the reaction

$$i\text{-}C_3H_7 + HBr \rightarrow C_3H_8 + Br, \qquad (R5)$$

Russell *et al.* (1988b) found $E_5 = -4{\cdot}5$ kJ mol^{-1} and $\Delta H^\circ_{f,298}$ $(i\text{-}C_3H_7) = 88{\cdot}0 \pm 2{\cdot}5$ kJ mol^{-1}. A re-analysis of the iodination data based on an activation energy for $i\text{-}C_3H_7 + I_2$ in the range 12–17 kJ mol^{-1} gave $\Delta H^\circ_{f,298}$ $(i\text{-}C_3H_7) = 88$–93 kJ mol^{-1}.

2.5. t-C_4H_9

Russell *et al.* (1988a) studied reaction R5 over the temperature range 296–532 K and R6,

$$t\text{-}C_4H_9 + HBr \rightarrow i\text{-}C_4H_{10} + Br, \qquad (R6)$$

over the range 533–710 K. Experiments on R6 were also conducted over the range 298–478 K using flash photolysis-resonance fluorescence. Analysis gave

$$k_6 = (9{\cdot}9 \pm 1{\cdot}3) \times 10^{-13} \exp[(5{\cdot}8 \pm 0{\cdot}9)\,\text{kJ mol}^{-1}/RT]\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

$$k_{-6} = (1{\cdot}83 \pm 0{\cdot}18) \times 10^{-10} \exp[-(28{\cdot}7 \pm 0{\cdot}8)\,\text{kJ mol}^{-1}/RT]\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

$$\Delta H^\circ_{f,298}(t\text{-}C_4H_9) = 48{\cdot}6 \pm 1{\cdot}7\ \text{kJ mol}^{-1}.$$

Re-analysis of the iodination data gave

$$\Delta H^\circ_{f,298}(t\text{-}C_4H_9) = 44\text{–}49\ \text{kJ mol}^{-1}.$$

An interesting aspect of the results of Russell *et al.* (1988a, b) is the observation of a negative activation energy for the R + HBr reactions whose magnitude increases with the size of R. They argued that the mechanism involves the formation of a complex, rather than a simple, direct abstraction. Conflicting results, however, have been obtained by Muller-Markgraf *et al.* (1980) who studied the $t\text{-}C_4H_9 + DX$ (where

X = Br, I) reaction using very-low-pressure photolysis. They found that k_6 *increases* with temperature, obtaining values a factor of 60 less than did Russell *et al.* at 295 K and a factor of 16 less at 384 K. When they combined their measurements with the k_{-6} expression reported by Russell *et al.* (1988b), they obtained $\Delta H^\circ_{f,298}$ (t-C_4H_9) = 38·5 ± 2·0 kJ mol^{-1}. Further experimental work on reaction R6 and its analogues would be of great value.

3. Alkyl radical association reactions

3.1 *Introduction*

Significant advances, both experimental and theoretical, have been made in recent years in the study of radical association reactions. Several significant problems face the experimentalist. The reactions are second order in radical, so that the absolute radical concentration must be established. For the smaller radicals, the reactions are in the fall-off region. Comparison with theory is most easily effected through the high pressure limit k^∞, which can, in general, only be determined by a nonlinear extrapolation. Finally much interest has centred on the weak dependence of k^∞ on temperature; precise determinations of the pressure dependent rate coefficients are, therefore, needed if the dependence of k^∞ on temperature is to be accurately determined.

The subtle dependence on temperature arises because such reactions occur on a type II potential energy surface, namely one without a potential maximum. In consequence, the transition state is not constrained to a specific geometry. It is located at the position of the minimum sum of rovibronic states; this minimum is generated by the opposing effects of decreasing potential energy and increasing spacing in the energy levels of the newly formed molecule as the bond length decreases. Figure 1 shows the correlation diagram for the reaction R7,

$$CH_3 + CH_3 \rightarrow C_2H_6. \qquad \text{(R7)}$$

The modes which change most dramatically in energy spacing are the (x, y) rotations, which correlate with the rocking vibrations in C_2H_6, and the opposite sense rotations about the z axis which correlate with the torsional mode. In addition, the (x, y) figure axis rotations of C_2H_6 are formed from fragment translations, generating the characteristic centrifugal barrier for association in a specific J state.

3.2 *Theory*

The major problem presented to theoreticians is that of describing the energy levels or, equivalently, of calculating the sum of states. Several approaches have been used.

The simple Gorin model (Gorin 1938, Benson 1976) locates the activated complex at the centrifugal barrier, thereby neglecting the correlation of fragment rotations and complex rocking and torsional modes. A modified Gorin model has been developed (Smith and Golden 1978) in which the rocking modes are replaced by two two-dimensional methyl rotors whose effective moments of inertia are decreased using an empirical hindrance parameter χ. A canonical approach is adopted and k^∞ (T) calculated. As the temperature increases, the average rotational quantum number increases and the positions of the centrifugal barrier and of the activated complex move to smaller inter-nuclear separations. Consequently χ increases with the temperature and k^∞ (T) does not rise as quickly as the simple Gorin model would predict; it may even decrease with T, depending on the degree of tightening. Smith and Golden (1978), for example, modelled ethane dissociation/methyl radical recombination using

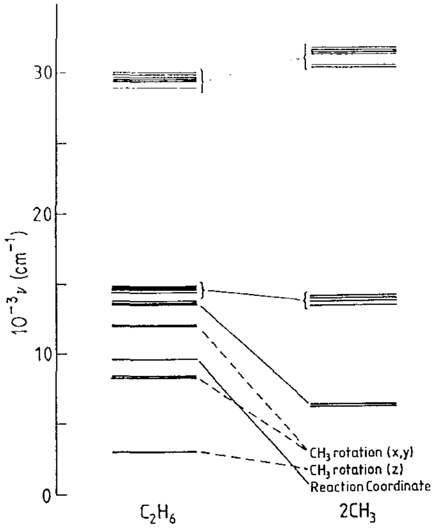


Figure 1. Correlation diagram for $2CH_3 \rightarrow C_2H_6$. The correlations of the transitional modes are shown as dashed lines.

$\chi = 152{\cdot}4\text{–}224{\cdot}3\,(T/K)^{-1/6}$ where the functional dependence on T is based on an r^{-6} interaction potential in the region of the centrifugal barrier.

A more detailed microcanonical approach has been developed by Quack and Troe (1974). It is based on the correlation of individual eigenstates and is termed the statistical adiabatic channel model (SACM). Channel energies for each eigenstate are calculated as a function of fragment separation and the number of 'open' channels determined by summation for a particular total energy, E, and rotational quantum number, J. $k_d^{\infty}(T)$, the dissociation rate coefficient, is then found by summing over a Boltzmann distribution, and $k_a^{\infty}(T)$ the association rate coefficient, from $k_d^{\infty}(T)$ and the equilibrium constant. In the early applications, a global experimental parameter, α, was used to correlate fragment and product molecule frequencies, while the radial potential was represented by a Morse function with the parameter β determined spectroscopically or varied. A great many reactions conformed to the ratio $\alpha/\beta = 0{\cdot}5$, permitting some degree of *a priori* modelling. Recently, a more realistic approach has been adopted with the specific incorporation of the angular fragment–fragment potential, which determines the dependence of the rocking modes on bond length. Troe has described the modelling of HO_2 dissociation using such an approach (Troe 1988).

A major problem arises, however, in describing the eigenstates in the region of the activated complex. There is significant interaction between the rocking and torsional modes which cannot, therefore, be treated as separable. Wardlaw and Marcus (1986) have developed a technique which can be applied in this situation. The J-specific sum of states, $N(E, J)$ is calculated as a convolution of the sum of the transitional states, $N_t(E, J)$ with the density of the conserved states,

$$N(E,J) = \int_0^E \rho_c(E-X, J) N_t(X, J)\, dX.$$

The conserved degrees of freedom are those whose general form of motion changes little between the fragments and the product molecule (e.g. the C–H stretching vibrations), and which can be treated as separable degrees of freedom, so that conventional direct state counting techniques can be employed to calculate $\rho_c(E-X, J)$ (Stein and Rabinovitch 1973). The transitional degrees of freedom are those, such as the rocking vibrations, whose character changes dramatically and which cannot be considered separable. A full angular potential is required to calculate N_t and for C_2H_6 this was generated using a simple directional Morse potential for the C–C interaction and Lennard-Jones potentials for the non-bonded interactions. N_t was then calculated using a Monte Carlo method assuming classical behaviour, although Klippenstein and Marcus (1987) have demonstrated that this approximation introduces little error. One adjustable parameter, α, was employed; α describes the generally weak dependence of the conserved degrees of freedom on bond distance. An exception is the $-CH_3$ out of the plane bending vibration (umbrella motion) where the change in frequency is quite marked.

3.3. *Experiment*

3.3.1. CH_3+CH_3

Baulch and Duxbury (1980) recently reviewed experimental results on the $CH_3 + CH_3$ reaction. Most experimental data were generated using flash photolysis coupled with absorption spectroscopy or molecular modulation spectroscopy. The energised association product, $C_2H_6^*$, needs to be stabilised by collision with a third body M, so that the rate coefficient for association, k_7, is pressure dependent (Robinson and Holbrook 1972), approaching a high-pressure limit, k_7^∞. No fall-off was observed in k at room temperature, suggesting that the reaction was at the high pressure limit, although shock tube measurements revealed a pressure dependence at 1350 K (Glanzer *et al.* 1976): association reactions move further into the fall-off region as the temperature increases (Pilling 1989). The room temperature measurements showed good agreement, with $k_7^\infty = (4{\cdot}3 \pm 0{\cdot}5) \times 10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.

There have been three recent determinations of the methyl radical association rate coefficient, all employing excimer laser flash photolysis of azomethane or acetone. Hippler *et al.* (1984) studied the reaction at room temperature and at pressures up to 200 bar in order to establish unequivocally the high pressure limit, which they determined as $5{\cdot}8 \times 10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$. Interestingly, they found that, at pressures greater than 30 bar, the rate coefficient begins to decrease; they ascribed this effect to the onset of diffusion-control with increasing medium viscosity.

The temperature dependence of k_7 has been studied over the range 300–900 K and at pressures of 0·5–600 Torr in a combined study, using absorption spectroscopy to monitor CH_3 at higher pressures and photo-ionisation mass spectrometry at lower pressures (Macpherson *et al.* 1983, 1985, Slagle *et al.* 1988). The reaction was shown to be in the fall-off region at all temperatures, although the high-pressure limit was approached quite closely at room temperature (figure 2).

Macpherson *et al.* (1985) fitted the experimental data obtained by absorption spectroscopy at $300 \leqslant T/K \leqslant 600$ using a simple parameterised fall-off model devised by Troe and co-workers (Gilbert *et al.* 1983). Their analysis suggested that k^∞ decreases slightly with increasing temperature:

$$k_7^\infty(T) = 4{\cdot}12 \times 10^{-11} \exp(136\,K/T)\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}.$$

Wagner and Wardlaw (1988) fitted the full set of data (300–900 K) using the Wardlaw–Marcus (1986) model, coupled with a simplified fall-off analysis. They then used the model to extend the parameterised representation up to 2000 K, the upper limit of interest for the reaction in atmospheric pressure flames.

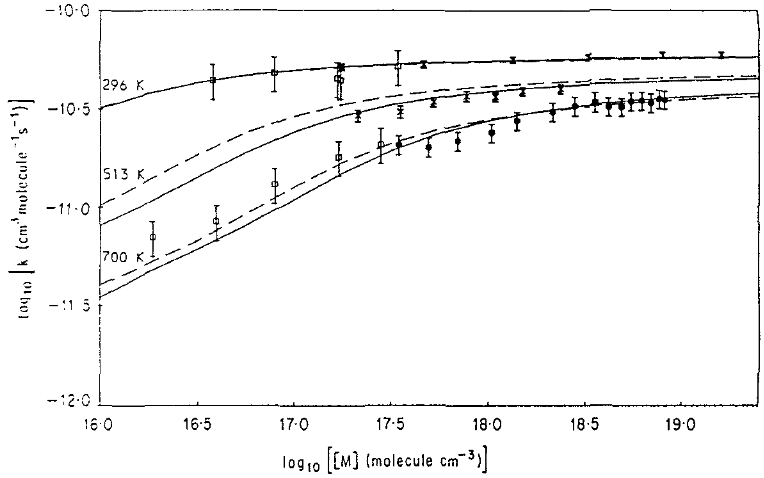


Figure 2. Fall-off plots for $CH_3 + CH_3 \rightarrow C_2H_6$. □, photo-ionisation mass spectrometry (Slagle *et al.* 1988); ●, absorption spectroscopy (Slagle *et al.* 1988); ×, absorption spectroscopy (Macpherson *et al.* 1985). (---), Troe fits; (—), Wagner and Wardlaw (1988).

They gave

$$k_7^\infty = 1{\cdot}5 \times 10^{-7}(T/K)^{-1{\cdot}18} \exp(-329K/T)\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$$

which predicts a decrease in k_7^∞ of a factor of 3·6 over the temperature range 300–2000 K. This conclusion has been questioned by Troe (1988) on the basis of SACM calculations, which suggest that k_7^∞ is independent of temperature.

3.3.2. *Other reactions*

Reaction R8 is the simplest combination reaction involving an alkyl radical:

$$CH_3 + H \rightarrow CH_4. \tag{R8}$$

Brouard *et al.* (1989), using laser flash photolysis coupled with absorption spectroscopy to detect CH_3 and resonance fluorescence to detect H, showed that this reaction is well into the fall-off region at 300 K; in consequence extrapolation to k_8^∞ is extremely uncertain. They then studied the reaction between CH_3 and D (Brouard *et al.* 1989).

$$\begin{array}{c} CH_3 + D \rightleftharpoons CH_3D^* \rightarrow CH_2D + H \\ \downarrow M \\ CH_3D \end{array}$$

Zero-point energy differences ensure that loss of H from CH_3D^* is much faster than loss of D, so that a D atom reacts each time the adduct is formed (i.e. the rate coefficient determined from the D atom decay corresponds to the high-pressure limit, k_8^∞). They obtained a temperature-independent value of $1{\cdot}7 \times 10^{-10}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$ over the range 300–400 K. A theoretical analysis by Aubanel and Wardlaw (1989) confirms this result and suggests that k_7^∞ increases slightly over a wider temperature range.

By contrast, high-pressure limiting rate coefficients for the recombination of large radicals show strong negative temperature dependences. Parkes and Quinn (1976) obtained $k_9^\infty = 4{\cdot}0 \times 10^{-11}(T/300\,K)^{-1{\cdot}5}$ for the reaction

$$t\text{-}C_4H_9 + t\text{-}C_4H_9 \rightarrow C_8H_{18}, \tag{R9}$$

and Danis *et al.* (1989) found $k_{10} = 3{\cdot}3 \times 10^{-12}(T/298)^{-1{\cdot}0}$ cm^3 molecule^{-1} s^{-1} for the reaction

$$CCl_3 + CCl_3 \rightarrow C_2Cl_6. \qquad (R10)$$

These results are at least qualitively compatible with the models discussed above. As the temperature increases, the mean energy of the energised adduct also increases and the transition state moves to smaller internuclear separations. This tightening reduces $\Delta S^{\neq}(T)$ the entropy of activation, but the reduction depends on the degree of interaction of the fragments. For $CH_3 + H$, this interaction is limited, so that the reduction in $\Delta S^{\neq}(T)$ is small. For t-C_4H_9, however, there is a strong interaction leading to severe hindrance of the angular modes and a significant reduction in $\Delta S^{\neq}(T)$ and $k^{\infty}(T)$ as T increases.

This interpretation has been questioned because of the difficulty in establishing the high-pressure limit, especially as the temperature increases (Troe 1988). Thus at 1 bar reaction R7 is close to the high-pressure limit at 300 K, but far from it at 900 K. Extrapolation to k_7^{∞} is therefore more uncertain at higher temperatures, casting some doubt, it is argued, on the inferred T dependence. This argument is less convincing, though, for reactions R9 and R10 where the densities of states for the energised adducts are much higher, leading to smaller microcanonical rate coefficients for redissociation and a more facile approach to the high-pressure limit. Confirmatory experimental measurements are needed, as are applications of detailed models with realistic potentials.

4. Addition, radical dissociation reactions

Addition reactions of H, such as

$$H + C_2H_4 \rightarrow C_2H_5 \qquad (R11)$$

have been widely studied using resonance fluorescence coupled with discharge flow or flash photolysis techniques (Pilling 1989). Addition reactions of alkyl radicals, such as

$$CH_3 + C_2H_4 \rightarrow 1\text{-}C_3H_7, \qquad (R12)$$

have been studied primarily by steady-state techniques and the data set is less extensive. The most recent analysis of k_{12} is by Holt and Kerr (1977) who employed competition between reaction R12 and abstraction from isobutane. Basing their analysis also on previous results, they gave $k_{12} = 3{\cdot}5 \times 10^{-13} \exp(-3700K/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 350–500 K; k_{12} presumably corresponds to the high-pressure limit.

Radical dissociation rate coefficients have been primarily determined by end-product analysis, such as mercury photosensitised decomposition (Loucks and Laider 1967) or pyrolysis (Trenwith 1985) of ethane, mercury photosensitised decomposition of propane (Back and Takamuku 1974) or pyrolysis of azo-n-propane (Kerr and Calvert 1961). The decomposition reactions of ethyl (Baulch *et al.* 1990) and propyl (Tsang 1988) are included in recent evaluations.

At low temperatures, the 1-propyl radical decomposes almost exclusively via reaction R12 and the channel

$$CH_3CH_2CH_2 \rightarrow H + CH_3CHCH_2$$

is unimportant. How important, though, does this reaction become at industrial cracker temperatures (≈ 1100 K)? A related question is the fractionation of the addition of H to propene between the two possible reaction channels which follow addition at the central carbon atom:

$$H + CH_3CHCH_2 \rightarrow 1-C_3H_7, \qquad (R13\,a)$$

$$\rightarrow CH_3 + C_2H_4. \qquad (R13\,b)$$

A possible means of providing answers to these questions, using experimental data obtained at lower temperatures, has been proposed by Clark *et al.* (1990).

The canonical high-pressure limiting rate coefficient for dissociation, $k_d^\infty(T)$, is related to the microcanonical rate coefficient for dissociation, $k(E)$, through a Laplace transformation:

$$k_d^\infty(T) = \int k(E)\rho_{v,r}(E)\exp(-E/kT)\,dE/q_{v,r}$$

where $q_{v,r}$ is the partition function and the subscripts v and r refer to vibration–rotation degrees of freedom. This relationship was recognised by Slater (1955) but has found limited application: it is often difficult to measure $k_d^\infty(T)$ *accurately* over a wide range of temperatures, because it varies so rapidly with T. Davies *et al.* (1986) proposed the simple alternative of using the association rate coefficient, $k_a^\infty(T)$, which generally varies only weakly with temperature, can be measured accurately and directly over a wide range of temperatures and is linked to $k_d^\infty(T)$ and, therefore to $k(E)$, via the equilibrium constant. Davies (1989) has demonstrated the validity of the method in reconstructing fall-off curves and in fitting fall-off data for $CH_3 + O_2$ and $CH_3 + NO$.

In general terms the two channel microcanonical rate coefficients for dissociation of the energised adduct, A*,

$$A^* \rightarrow B + C, \quad (b)$$

$$\rightarrow Y + Z, \quad (y)$$

are calculated from the respective association reactions, k_{-b}^∞, k_{-y}^∞ and then incorporated into an energy-grained master equation:

$$dn_i = g_i - k_{b,i}n_i - k_{y,i}n_i - \sum_j k_{j,i}n_i + \sum_j k_{i,j}n_j,$$

where n_i is the population of the ith grain, and each grain is a bundle of energy levels typically of grain width 50–200 cm^{-1}. $k_{b,i}$ and $k_{y,i}$ are the appropriately averaged microcanonical dissociation rate coefficients for grain i and $k_{j,i}$ and $k_{i,j}$ are the collisional rate coefficients for transfer from grain i to j and from j to i respectively. An exponential down model is usually assumed for the dependence of the collisional transfer probability on energy gap, which is parameterised in terms of $\langle \Delta E \rangle_{down}$, the average energy transferred in a downward direction. g_i is the source term which depends on the problem under consideration. For a two-channel dissociation reaction, for example

$$1-C_3H_7 \rightarrow H + CH_3CHCH_2,$$

$$\rightarrow CH_3 + C_2H_4,$$

g_i is set to zero, while for a two-channel association reaction, such as

$$CH_3 + CH_3 \rightarrow C_2H_6, \qquad (R7\,a)$$

$$\rightarrow H + C_2H_5, \qquad (R7\,b)$$

g_i is related to the overall association rate coefficient and the microcanonical rate coefficients for dissociation, via this channel, using detailed balance (Robinson and Holbrook 1972).

The master equation is solved in the steady state $(dn_i/dt = 0)$ using a matrix formulation. The required channel rate coefficients are calculated from the appropriate summations, for example, for the two-channel dissociation

$$A \rightarrow B + C, \quad (b)$$

$$A \rightarrow Y + Z, \quad (y)$$

then $k_b = \Sigma_i k_{b,i} n_i$ and $k_y = \Sigma_i k_{y,i} n_i$, while for the association reaction

$$B + C \rightarrow A, \qquad (-b)$$

$$B + C \rightarrow Y + Z, \quad (y')$$

then $k_{y'} = \Sigma_i k_{y,i} n_i$, as before, and $k_{-b} = \Sigma_i k_{c,i} n_i$, where $k_{c,i}$ is the rate coefficient for collisional energy transfer into a so-called 'cemetery' state, placed somewhat below the lower dissociation limit and from which collisional energisation to states above this limit is of negligible probability. The optimal position of the cemetery state is determined by trial and error; its use has been described by Green *et al.* (1990).

Figure 3 shows the temperature and pressure dependence of the rate coefficients for reactions R7*a* and R7*b*. At low temperatures, k_{7b} is small because this channel is endothermic, and the reaction proceeds via the C_2H_6 channel which is, of course, pressure-dependent. At temperatures around 2000 K and at normal pressures, the C_2H_6 channel is well into the fall-off regime while the rate coefficient for formation of $H + C_2H_5$ has increased significantly and now makes an important contribution. Both channels have been studied experimentally but never under the same conditions. The method developed by Clark *et al.* (1990) permits the available experimental rate data to be employed to calculate channel rate coefficiencts under any conditions. If necessary a simple parameterisation can then be used to express these rate coefficients in a concise form for modelling studies. An alternative approach has been developed by Stewart *et al.* (1989).

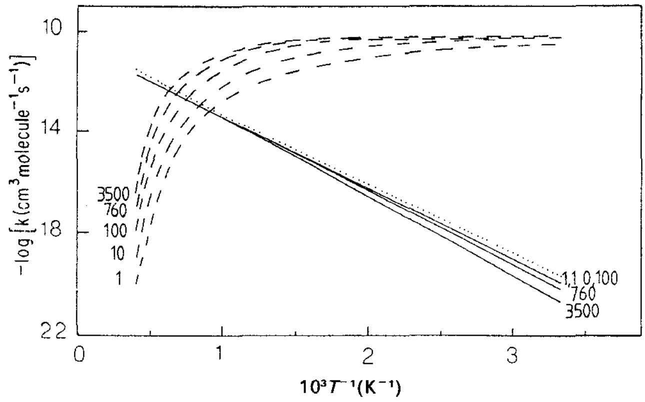


Figure 3. The temperature and pressure dependences of k_{7a} and k_{7b}, calculated using a two channel master equation model. The curves are labelled with the corresponding pressures (Torr). Key: k_{7a} (- - -); k_{7b} (—); (· · ·) k_{7b} calculated from k $(H + C_2H_5)$ via the equilibrium constant.

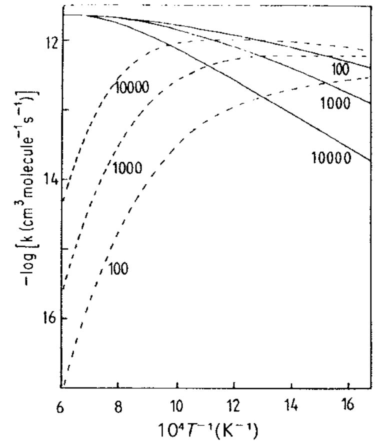


Figure 4. The temperature and pressure dependences of k_{13a} and k_{13b}, calculated using a two-channel master equation model. The curves are labelled with the corresponding pressures (Torr). Key: k_{13a} (- - -); and k_{13b}(—).

Figure 4 shows the calculated temperature and pressure dependence of k_{13a} and k_{13b}. The competition between stabilisation and dissociation now occurs at comparatively low temperatures and both channels show a pressure dependence, k_{13b} decreasing as the pressure is increased and the stabilisation channel R13 *a* is favoured. An increase in temperature, by contrast, favours R13 *a* because the population of states above the higher dissociation limit is increased.

5. H atom transfer reaction

Rate coefficients for H atom transfer reactions involving alkyl radicals have primarily been determined by competitive methods. Figure 5 summarises the results for the reaction

$$CH_3+H_2 \rightarrow CH_4+H, \qquad \text{(R14)}$$

while table 2 summarises the techniques used. Generally, the rate coefficient has been measured relative to the recombination rate coefficient, k_7, with the experimental parameter returned directly from the analysis being of the form $k_{14}/k_7^{0\cdot5}$. Uncertainties in k_7 are, therefore, reflected in the resulting values of k_{14}, although the contribution is small at low temperatures. At high temperatures it is necessary to correct for fall-off in k_7, a procedure that has not been followed universally.

Figure 5 shows distinct curvature in the Arrhenius plot. A recent evaluation (Baulch *et al.* 1990) proposes an expression of the form:

$$k=4\cdot8\times10^{-22}(T/K)^{3\cdot12}\exp(-4380K/T)\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$$

The curvature is even more marked for the reaction

$$CH_3+C_2H_6 \rightarrow CH_4+C_2H_5, \qquad \text{(R15)}$$

with $k_{15}=2\cdot45\times10^{-31}(T/K)^6\exp(-3040K/T)\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$.

The origin of this curvature has been discussed by Furue and Pacey (1986). If tunnelling is neglected, then the temperature exponent, *n*, corresponds to $\Delta C^{\neq}/R$, the change in heat capacity on forming the activated complex from the reactants. For reaction R14, $\Delta C^{\neq}/R$ is substantially larger than the value of 4 J K^{-1} mol^{-1} predicted

Table 2. Techniques used in the determination of the rate coefficients for $CH_3 + H_2$.

Method	Technique for determining k	T(K)	Reference
Decomposition $Hg(CH_3)_2/H_2$	Relative to k $(CH_3 + CH_3)$	825	Gowenlock *et al.* (1953)
Competitive photolysis CH_2CO	Relative to k $(CH_3 + CH_3)$	372–480	Gesser and Steacie (1956)
Pyrolysis CH_3COCH_3/H_2	Relative to $k(CH_3 + CH_3COCH_3$	780	Benson and Jain (1959)
Photolysis $CH_3COCH_3/H_2/D_2$	Relative to k $(CH_3 + D_2)$	398–645	Shapiro and Weston (1972)
Shock tube pyrolysis $CH_3N_2CH_3/H_2/He$	Computer fit to product spectrum	1340	Clark and Dove (1973)
Pyrolysis $C(CH_3)_4/H_2$ in flow system	Relative to k $(CH_3 + CH_3)$	829–929	Kobrinsky and Pacey (1974)
Flow pyrolysis $CH_3N_2CH_3/H_2$	From time dependence of CH_4, C_2H_6 yields	584–671	Marshall and Shahkar (1981)
Shock tube pyrolysis $CH_3N_2CH_3$, $Sn(CH_3)_4$ $Hg(CH_3)_2/H_2/Ar$	Time-resolved absorption spectroscopy of CH_3	1066–2169	Moller *et al.* (1986)

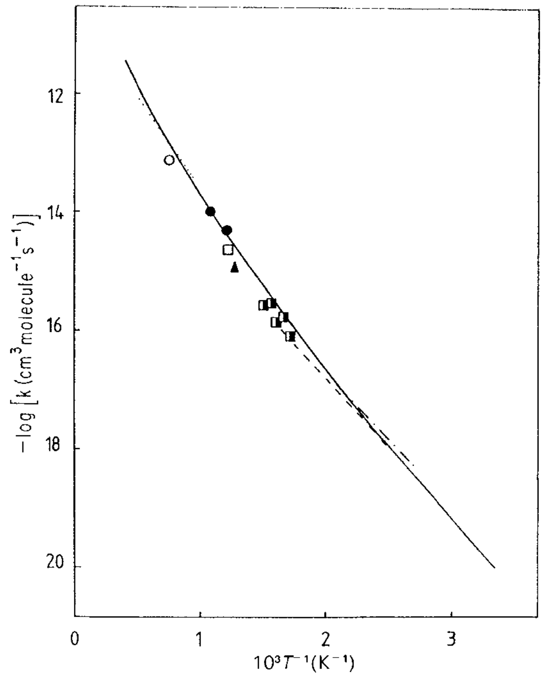


Figure 5. Arrhenius plot for $CH_3 + H_2 \rightarrow CH_4 + H$. □, Gowenlock *et al.* (1953); (-·-·-), Gesser and Steacie (1956); (▲), Benson and Jain (1959); (- - -), Shapiro and Weston (1972); (○), Clark and Dove (1973); (o), Kobrinsky and Pacey (1974); (◨), Marshall and Shahkar (1981); (····), Moller *et al.* (1986); and (—) recommendation of Baulch *et al.* (1990).

by simple collision theory from the $T^{0\cdot5}$ term and also larger than the value of $21\,\mathrm{J\,mol^{-1}\,K^{-1}}$ predicted by transition state theory with the bending modes in C_2H_5 treated classically.

Furue and Pacey proposed that tunnelling must be making a significant contribution. They employed a symmetrical one-dimensional Eckart barrier to represent the potential energy surface using the characteristic tunnelling temperature, T^* as a variable parameter. T^* is proportional to the square root of the (negative) curvature of the surface at the transition state. High values of T^* correspond to a narrow barrier and a high tunnelling contribution. The required barrier is much narrower than that corresponding to the minimum energy path calculated by Schatz *et al.* (1984) using an *ab initio* approach. Furue and Pacey pointed out that this may not be surprising since the potential corresponding to the minimum energy path is not appropriate to the tunnelling process (Marcus and Coltrin 1977).

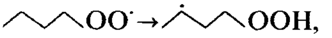
6. Alkyl radical oxidation

6.1. *Introduction*

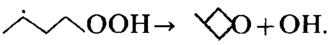
In low-temperature combustion systems, alkyl racidals are oxidised via the peroxy radical (Cox 1987):

$$R+O_2 \rightarrow RO_2. \qquad \text{(R16)}$$

The peroxy radical then isomerises to form an alkyl hydroperoxy radical, for instance


(R17)

which decomposes in a chain propagating step, for example


(R18)

Alternatively, and especially at lower temperatures, the hydroperoxy radical may be further oxidised,

$$\dot{R}'OOH+O_2 \rightarrow O_2R'OOH. \qquad \text{(R19)}$$

This hydroperoxy peroxy radical can decompose by loss of OH to form a hydroperoxide which acts as a degenerate branching agent, that is, it decomposes slowly in a branching step, leading to delayed ignition.

At higher temperatures, the peroxy radical becomes unstable and reaction R16 is reversed, producing a negative temperature dependence in and slowing down of the reaction rate, following the temperature rise accompanying ignition. This behaviour is implicated in auto-ignition (knocking) in petrol engines and in the oscillatory behaviour observed in hydrocarbon oxidation.

At higher temperatures, the alkyl radicals are oxidised via alternative routes. For CH_3, there are two possible channels:

$$CH_3+O_2 \rightarrow CH_3O+O, \qquad \text{(R20)}$$

$$\rightarrow CH_2O+OH. \qquad \text{(R21)}$$

For higher radicals, the formation of the conjugate olefin predominates, for example

$$C_2H_5+O_2 \rightarrow C_2H_4+HO_2.$$

The development of detailed mechanisms of hydrocarbon oxidation requires an understanding of these elementary reactions and of the equilibrium constant for reaction R16 (Cox 1987).

6.2. $R+O_2\xrightarrow{M}RO_2$

6.2.1. *Reaction 22*

$$CH_3+O_2\xrightarrow{M}CH_3O_2 \qquad (R22)$$

Reaction R22 has been studied over a wide range of temperatures (298–850 K) and pressures (20–600 Torr) (Keiffer *et al.* 1987, Keiffer and Pilling 1990). Under these conditions, the reaction is well into the fall-off region and the aim was to determine $k(T, P)$ accurately and to fit the fall-off data (figure 6), using parameterised expressions, under conditions appropriate to low-temperature combustion. Laser flash photolysis of acetone at 193 nm was employed, coupled with absorption spectroscopy of CH_3. They used Troe's semi-empirical model (Gilbert *et al.* 1983) to fit the fall-off data. They found that the fits were insensitive to the energy transfer parameter $\langle \Delta E\rangle_{down}$, and that the activation barrier to reaction was small. The optimal fits to the high- and low-pressure limiting rate coefficients were

$$k_{22}^{\infty}=(1{\cdot}2\pm0{\cdot}2)\times10^{-12}(T/300\,K)^{1{\cdot}2\pm0{\cdot}4}\,cm^3\,molecule^{-1}\,s^{-1},$$

$$k_{22}^{0}=(1{\cdot}0\pm0{\cdot}3)\times10^{-30}(T/300\,K)^{-3{\cdot}3\pm0{\cdot}4}\,cm^6\,molecule^{-2}\,s^{-1}.$$

At higher temperatures, CH_3 reacts via channels

$$CH_3+O_2\rightarrow CH_3O+O, \qquad (R20)$$

$$CH_3+O_2\rightarrow HCHO+OH. \qquad (R21)$$

There has been considerable discussion, over the years, on the channel efficiencies. The most recent measurements of k_{23} were made by Hsu *et al.* (1983) using shock tube measurements on azomethane/O_2 mixtures, and monitoring CO and by Saito *et al.* (1986) who monitored O, H and OH in a shock tube study of $C_2H_6/O_2/Ar$ and $CH_3I/O_2/Ar$. Both of these investigations relied on kinetic modelling to extract k_{20}. A recent evaluation (Baulch *et al.* 1990) proposes

$$k_{20}=2{\cdot}2\times10^{-10}\exp(-15800K/T)\,cm^3\,molecule^{-1}\,s^{-1}$$

based largely on these two studies.

Saito *et al.* also obtained an estimate for k_2 and a very similar value has recently been obtained by Fraak and Zellner (1990), who monitored CH_3 and OH in a shock tube study of azomethane/O_2/Ar mixtures. They obtained a good correlation between the rates of CH_3 decay and OH production. Baulch *et al.* (1990) recommended

$$k_{21}=5{\cdot}5\times10^{-13}\exp(-4500K/T)\,cm^3\,molecule^{-1}\,s^{-1}$$

based on the measurements of Fraak and Zellner and Saito *et al.*

Thus the CH_3+O_2 reaction shows a complex temperature dependence, with reaction R22 dominating at temperatures below ~900 K for pressures of ~1 atm, with R24 then taking over as the principal channel until ~1800 K when R23 begins to dominate. Even so, methane oxidation can be very sensitive to k_{23} at temperatures considerably below 1800 K, because of the branching nature of this reaction.

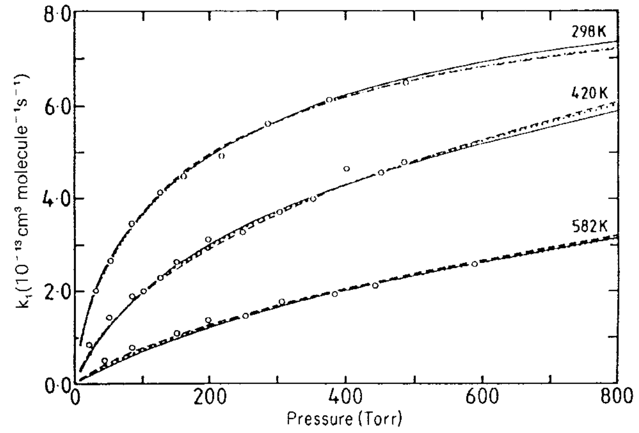


Figure 6. Fall-off plots for $CH_3+O_2 \rightarrow CH_3O_2$: (○) experimental points. Fitted fall-off curves obtained using the Troe model: (—), $\langle \Delta E \rangle_{down} = 285\,cm^{-1}$, activation energy, $E_a = 0$. (- - -), $\langle \Delta E \rangle_{down} = 40\,cm^{-1}$, $E_a = 0$. (· · ·), $\langle \Delta E \rangle_{down} = 80\,cm^{-1}$, $E_a = 1{\cdot}9\,kJ\,mol^{-1}$ (Keiffer *et al.* 1987).

6.2.2. *Reaction 23*

$$C_2H_5 + O_2 \xrightarrow{M} C_2H_5O_2, \qquad (R23\,a)$$

$$\longrightarrow C_2H_4 + HO_2. \qquad (R23\,b)$$

This reaction has been examined in detail (Wagner *et al.* 1989) using a combination of laser flash photolysis/photo-ionisation mass spectrometry and RRKM modelling. The experiments were conducted over the temperature range 300–900 K (i.e. up to conditions where $C_2H_5O_2$ is very unstable). Wagner *et al.* concluded that the direct abstraction channel is unimportant under the experimental conditions and that C_2H_4 is formed by an addition–elimination mechanism:

$$C_2H_5 + O_2 \rightarrow C_2H_5O_2 \rightarrow C_2H_4 + HO_2.$$

This conclusion contrasts with that of McAdam and Walker (1987) who argue that a direct abstraction mechanism operates.

6.2.3. *Reaction 16*

$$R + O_2 \rightarrow RO_2. \qquad (R16)$$

Ruiz and Bayes (1984) noted a strong correlation between the rate coefficient for $R+O_2$ and the ionisation energy of the alkyl radical. They used a modified version of the SACM theory (Quack and Troe 1974) and argued that the long range $R \cdots O_2$ potential was strongly influenced by charge-transfer interactions. Recent measurements by Xi *et al.* (1988) on neopentyl + O_2 show that the rate coefficient for this reaction lies significantly below the linear ln *k* against ionisation energy correlation; similar behaviour has been observed for *i*-butyl + O_2. They also found a negative temperature dependence for the rate coefficient

$$k\,(\text{neopentyl} + O_2) = 2{\cdot}1 \times 10^{-12}(T/300\,K)^{-2{\cdot}1}\,cm^3\,molecule^{-1}\,s^{-1}$$

suggesting that the low value is not associated with an activation barrier. Xi *et al.* (1988) proposed that there must be significant steric effects operating in the reaction of branched alkyl radicals with O_2.

6.3. *Heats of formation of RO_2 radicals*

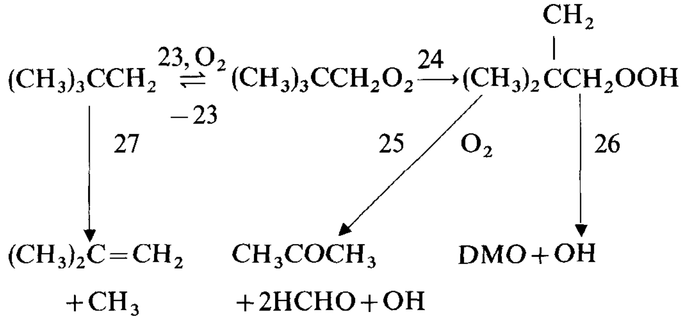
The heats of formation of the alkyl peroxy radicals are required to calculate ΔH° for reaction R16, which in turn is a primary determinant of the *ceiling temperature*, T_c, where $k_{16}(O_2) = k_{-16}$ for a particular oxygen pressure (usually 0·1 bar). Values for T_c were initially derived from estimates of ΔH_f° (RO_2) made by Benson (1965) and based group additivity principles.

ΔH_f° (RO_2) has also been determined experimentally in recent years, especially for $R = CH_3$. Khachatryan *et al.* (1982) studied the $CH_3 + O_2$ equilibrium over the temperature range 706–786 K using a radical freezing method on a CH_4/O_2 system. The peroxy radical concentration was determined by electron spin resonance (ESR) and the methyl radical concentration from the rate of production of ethane. Slagle and Gutman (1985) directly observed the approach to equilibrium, using photoionisation mass spectrometry following laser flash photolysis of CH_3I in the presence of O_2. Equilibration was also observed over the temperature range 775–850 K by Keiffer and Pilling (1990) using laser flash photolysis of acetone/O_2 mixtures. A third law analysis of the three sets of data gives $\Delta H_f^\circ(CH_3O_2) = 11{\cdot}7 \pm 4{\cdot}6\,\mathrm{kJ\,mol^{-1}}$.

Slagle *et al.* (1985, 1986) have also determined the heats of formation of the ethyl, *i*-propyl and *t*-butyl radicals, obtaining values of $-27{\cdot}2$, $-69{\cdot}9$ and $-105{\cdot}0\,\mathrm{kJ\,mol^{-1}}$. The measured heats of reaction (R16) differ significantly from those calculated using bond additivity methods if Benson's alkyl radical heats of formation are employed, with the disagreement increasing with radical complexity. This discrepancy is substantially removed if the higher alkyl radical heats of formation, discussed in section 2, are employed. Slagle *et al.* (1986) showed that good agreement is finally obtained if the heat of formation of the O–(C) (O) group is reduced by $8\,\mathrm{kJ\,mol^{-1}}$.

6.4. *Internal hydrogen abstraction in peroxy radicals*

The internal hydrogen abstraction reaction (*e.g.* R17) in peroxy radicals or in hydroperoxy peroxyradicals has a considerable bearing on the overall kinetics when alkane oxidation proceeds via the peroxy radical route. Alkyl peroxy radical heats of formation are of great significance in interpreting the available experimental data, which has been obtained by Baldwin *et al.* (1982). Their technique is to add an alkane to a slowly reacting H_2/O_2 mixture at 753 K. For example, adding neopentane leads to production of neopentyl and the sequences involving the neopentyl radical are



where DMO is 3,3-dimethyloxetan. A steady state treatment shows that, provided $k_{24} \ll k_{-23}$,

$$[(\mathrm{DMO})+(\mathrm{acetone})]/(i\text{-butene})=K_{23}k_{24}(\mathrm{O}_2)/k_{27}.$$

This analysis is somewhat complicated by a channel generating isobutene from the hydroperoxy radical, but this complication has been accommodated by measurements of the channel efficiencies. End-product analysis does therefore enable k_{24} to be determined, provided K_{23} and k_{27} are known. Baldwin *et al.* (1982) based their analysis on Benson's values for the equilibrium constant and applied their method of analysis to a wide range of alkyl radicals, obtaining best fit generic rate constants for the different H atom transfer reactions (e.g. 1,4 secondary etc.). If the equilibrium constants determined by Slagle *et al.* (1988) are employed instead, then k_{24} is decreased for the more highly hindered radicals by up to a factor of 50. Direct measurements of k_{24} would be of considerable value, both to place the large body of rate coefficients determined by Baldwin *et al.* (1982) on a firmer base and to provide a further insight into the controversy surrounding alkyl and alkyl peroxy radical heats of formation.

7. Conclusions

The last few years have seen an increasing use of direct time-resolved methods for measuring rate coefficients for alkyl radical reactions, over a widening range of conditions. There is, however, still a considerable reliance on less direct techniques, especially at high temperatures. The major problem with such approaches is their reliance on an assumed, sometimes complex reaction mechanism, with resulting ambiguities and dependence on rate parameters for contributing reactions. Alkyl radicals are also much more difficult to detect, at low concentrations, than are other species such as H, O and OH. Photo-ionisation mass spectrometry is sensitive, but restricted to low pressures. Absorption spectroscopy is applicable over a wide range of conditions, but is less sensitive and quite high radical concentrations are required, leading to possible complications from competing reactions. Resonance-enhanced multiple-photon ionisation and diode laser spectroscopy are now starting to be applied to alkyl radical kinetics and the next few years should see an increasing application of all these techniques to a wide range of reaction types.

Methods for modelling reactions of alkyl radicals, especially CH_3, whether proceeding directly or via a complex, are reasonably well developed. The major deficiency is the absence of high-quality *ab initio* potential energy surfaces. Such surfaces are now being developed for a wide range of often complex reactions (e.g. $O+C_2H_2$) so that we can look forward to considerable advances in the future development of our understanding of a wide range of alkyl radical reactions.

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