## LASER FLASH PHOTOLYSIS STUDIES OF ELEMENTARY REACTIONS OF SIGNIFICANCE IN COMBUSTION J W DAVIES, M A HANNING-LEE, M J PILLING AND P W SEAKINS

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Abstract Recent measurements of radical-radical and radical-atom rate coefficients and of the heats of formation of ethyl and t-butyl radicals are discussed, in the context of the provision of rate data for elementary reactions of importance in combustion and pyrolysis.

## 1. Introduction

Increasingly, complex chemical kinetic systems, such as combustion processes and hydrocarbon cracking, are being modelled using numerical integration of detailed schemes of elementary reactions. In hydrocarbon cracking such models are used to optimise cracker conditions as feedstocks are modified. In combustion numerical integration is employed in studies of engine knock, ignition and extinction, flames and pollutant formation. Such models are only of value if they incorporate rate coefficients for the elementary reactions which are reliable and fully validated under the conditions of interest. This paper describes recent studies of several reactions of interest in modelling applications of this type.

In section 2 we examine radical-radical reactions which show a complex dependence on temperature and pressure because of the requirement of collisional stabilisation of the initially formed, energised adduct. The problems involved with such reactions are exemplified by reference to the  $CH_3 + CH_3$  and  $CH_3 + O_2$  reactions. Data are also presented on the  $CH_3 + NO$  reaction and it is argued that analysis of the fall-off curves provides evidence for the involvement of the bound, excited triplet state of  $CH_3NO$ . Atom + radical reactions are discussed in section 3 and new data on  $C_3H_5 + O$  and  $C_3H_5 + H$  are presented.

Radical heats of formation are also of importance in constructing detailed reaction mechanisms. They are used to determine the heat release from an elementary reaction, to estimate rate coefficients and to calculate unknown reverse rate coefficients from known values for the forward reaction. There has, recently, been some controversy surrounding values for alkly radicals. These problems have recently been resolved for  $C_2H_5$  and their resolution is discussed in section 4. The t- $C_4H_9$  radical is less well characterised though and the problems deriving from recent measurements are also examined in section 4.

# 2. Radical - radical reactions

2.1 Radical-radical reactions of the type

С

A + B ----->

show a complex dependence on temperature and pressure. They generally occur on a Type II potential energy surface, i.e. one without a potential energy maximum. The radicals initially form an energised species, C<sup>\*</sup>, which must be collisionally deactivated, by a third body M, before it redissociates if a stable C molecule is to be formed. In consequence, the overall rate coefficient for recombination,  $k_r$ , shows a characteristic dependence on pressure, increasing towards a high pressure limit,  $k_r^{\infty}$ , when all the energised molecules are collisionally stabilised.

As the temperature increases, the average energies of A, B and, therefore C<sup>\*</sup> increases, causing the mean rate coefficient for dissociation also to increase. In consequence, as the temperature increases a higher concentration of the third body, M, is required in order to acheive a specified degree of stabilisation, and the fall-off curve for  $k_r$  moves to higher pressures. Thus, if rate coefficients are to be determined for high temperature modelling applications, e.g. in combustion, then experimental measurements must be made over a wide range of conditions and the rate coefficients then expressed in a concise yet precise parameterised form. For particularly high temperature applications it may not be possible to extend experimental measurements into the required range. Under these circumstances, a model of the reaction, based on the low temperature data, must be constructed and used to extrapolate to higher temperatures.

In this section we briefly describe the experimental technique used in this laboratory to study radical-radical reactions and refer to results on  $CH_3 + CH_3$ ,  $CH_3 + O_2$  and  $CH_3 + NO$  as examples of reactions studied over a wide range of temperatures.

### 2.2 Experimental

Fig. 1 shows a schematic diagram of the apparatus.<sup>1,2</sup> An excimer laser (Lumonics, TE-861S-4) operating at 193 nm was used to generate methyl radicals from acetone. The photolysis is very clean, with more than 95% proceeding via the process:

$$CH_3 CO CH_3 \dots > 2CH_3 + CO$$

The radicals were generated in a stainless steel multiport cell, capable of being heated to temperatures of 1000 K. The radicals were monitored at 216.36 nm, using light from a 450 W Xe lamp, which was passed through the cell and then to a 1 m Hilger Monospek monochromator. The path length was 5 cm. The time dependent signals were averaged over several hundred laser shots and the resultant decay data analysed on a microcomputer or on a Norsk Data ND-540 main frame computer. The gases were slowly flowed through the cell, so that the cell contents were replaced between laser shots (2-3 Hz).



Fig 1. Schematic diagram of the laser flash/photolysis/uv absorption spectroscopy apparatus for the study of radical-radical reactions. B, Baratron gauge; FS, flow sensor; I, iris; L, lens; NV, needle valve; PD, photodiode; PM, photomultiplier; V, solenoid valve; Zn, zinc lamp for calibration.

### 2.3 Results and Discussion

M

(i)  $CH_3 + O_2 - CH_3O_2$  R1 Fig. 2 shows typical fall-off curves for reaction R1 over the temperature range 298 - 582 K.<sup>4,5</sup> More recently, these measurements have been extended up to 850K.<sup>6</sup>



Fig. 2. Fall off curves for  $CH_3 + O_2$  over the temperature range 298 - 582 K. Global fits to the data with two energy transfer parameters (----  $<\Delta E>_{down} = 285$  cm<sup>-1</sup> and ----  $<\Delta E >_{down} = 40 \text{ cm}^{-1}$ ) are also shown.

Fig. 2 also shows fits to the data using the simplified parameterised expression proposed by Troe and co workers, ' which is based on a modified Lindemann model:<sup>8</sup>

 $k = \{(k^{O}[M] / k^{\infty}) / (1 + k^{O}[M] / k^{\infty})\} F$ 

F is a 'broadening' parameter which arises because of deficiencies in the simple Lindemann model which assumes that the rate coefficient for dissociation of C\* is independent of energy and which makes the strong collision assumption.<sup>8</sup> F is given by:- $\sqrt{1 + \ln (k^0 M / k^\infty)}$ **Ig**F

$$F \approx 19F_{cent}(1 + 19 (K^2 [M]/K))/N$$

where  $N = 0.75 - 1.27 \text{ lgF}_{cent}$ and  $F_{cent}$  is the broadening parameter in the centre of the fall-off curve, i.e. when  $k^{O}[M] / k^{\circ} = 1$ .  $F_{cent}$  can be calculated from assumed properties of the transition state and estimates of the efficiency of energy transfer. Alternatively, it can be employed as a variable parameter in fitting the experimental fall-off curves. Keiffer et al.<sup>5,6</sup> developed a global fitting routine in which the fall-off curves at different temperatures were fitted together, the rationale being that the required properties of the transition state may be derived from the temperature dependence of  $k^{\infty}$ . They thus determined

the following rate parameters over the temperature range 298 - 850 K:  $k_{1}^{\infty} = (1.2 \pm 0.2) \times 10^{-12} (T/300 \text{ K})^{1.2} \pm 0.4 \text{ cm}^{3} \text{ molecule}^{-1}\text{s}^{-1}$   $k_{1}^{0} = (1.0 \pm 0.3) \times 10^{-30} (T/300 \text{ K})^{-3.3} \pm 0.4 \text{ cm}^{6} \text{ molecule}^{-2}\text{s}^{-1}$ k<sup>∞</sup>1 k<sup>0</sup>1 F<sub>cent</sub> = 0.466 - 0.039 (T/300 K)

Above 850 K, the peroxy radical becomes unstable and the oxidation of CH<sub>2</sub> occurs via alternative routes, thus these parameters cover the whole range of interest, the only uncertainty lying in their extrapolation to high pressures.

(ii) 
$$\stackrel{\sim}{}$$
 CH<sub>3</sub> + CH<sub>3</sub> -----> C<sub>2</sub>H

**R2** 

A similar data set was determined for reaction R2 over the temperature range 298 - 906 K. This time, however, the pressure range was extended down to 0.5 Torr in a parallel study by Slagle and Gutman at the Illinois Institute of Technology, using laser flash photolysis coupled with photoionisation mass spectrometry.<sup>11</sup> A global fitting routine was again used to fit the data for reaction R2; this approach is inadequate. because rate parameters are required at least up to 2000 K for use, for example, in modelling of flames. This problem was overcome by collaboration with Wagner and Wardlaw, <sup>12</sup> who employed a realistic model recently developed by Wardlaw and Marcus,<sup>13</sup> for "loose" transition states, such as those found on Type II surfaces. They validated the approach, fixing two variable parameters, by comparison with the

experimental data and then used the model to define rate parameters for the

temperature range 200 - 2000 K:-  $k_{2}^{\infty} = 1.79 \times 10^{-10} (T/300 \text{ K})^{-1.18} \exp (-330 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$   $k_{2}^{0} = 3.38 \times 10^{-24} (T/300 \text{ K})^{-7.03} \exp (-1390 \text{ K/T}) \text{ cm}^6 \text{ molecule}^{-1}\text{s}^{-1}$  $k_{2}^{02}$  = 3.38 x 10<sup>-24</sup> (T/300 K)<sup>-7.03</sup> exp (-1390 K/T) cm F<sub>cent</sub> = 0.619 exp (- T/1180 K) + 0.381 exp (- T/73.2 K) Μ

(iii) CH<sub>3</sub> + NO ----> CH<sub>3</sub>NO **R**3

Reaction R3 has previously only been studied at room temperature by flash photolysis/absorption spectroscopy<sup>14,15</sup> or flash photolysis/end product analysis.<sup>16,17</sup> Absorption spectroscopy requires radical concentrations of 10<sup>13</sup> cm<sup>-3</sup>, so that recombination (reaction R2) competes with reaction R3 on the experimental timescale of 100 µs. A mixed first -, second - order analysis is therefore required; the techniques involved have been discussed previously.1,4

Fig. 3 shows the fall-off curves for  $CH_3 + NO$  over the temperature range 296-509 K. Difficulties were experienced in fitting the experimental data using a conventional analysis;<sup>2</sup> in particular, very high energy transfer parameters were needed. A possible reason for these difficulties lies in the electronic complexity of the CH3.....NO potential energy surfaces. There are two surfaces, a singlet and a triplet, correlating with ground state radicals for reaction R2 and the triplet surface is repulsive so that recombination occurs exclusively along the singlet surface. NO, on the other hand, has a  ${}^{2}\Pi$  ground state so that there are four electronic surfaces, two of which correlate with bound states, the ground state X<sup>1</sup>A' (binding energy 14130  $(cm^{-1})^{18}$  and the first excited state,  $a^3A^*$  (binding energy 4440 cm<sup>-1</sup>). Recombination, therefore, occurs along two surfaces and the true high pressure limiting rate coefficient refers to both of these processes. Three loss processes are possible for the energised vibrational states of  $CH_3NO$  a<sup>3</sup>A<sup>\*</sup>, stabilisation, dissociation and intersystem crossing to the X<sup>1</sup> A' state. If the last processes predominates, then collisional stabilisation occurs exclusively within the X<sup>1</sup>A' state.



Fall-off curves for CH3 Fig. 3 + NO including inverse Laplace transform/master equation fits.

The microcanonical rate coefficients, k(E), for dissociation of an energised molecule are related to the limiting high pressure rate coefficient for association through detailed balance.<sup>8</sup> Association along the singlet surface occurs with a limiting

high pressure rate coefficient which is approximately one quarter of the overall value. Thus if the assumption is made that association occurs *exclusively* along the singlet surface, which is the case in a conventional analysis,<sup>2</sup> then the k(E) values inferred from detailed balance will overestimate the true values by a factor of four and a high value will be required for the energy transfer parameter in order to fit the experimental data - exactly the situation found for CH<sub>3</sub> + NO. The results for CH<sub>3</sub> + NO are, therefore, compatible with association along both of the bound triplet and singlet surfaces, with intersystem crossing occuring from <sup>3</sup>A" faster than either dissociation or collisional stabilisation at pressures up to 1 atm.

The data were analysed using a master equation description of the collisional and spontaneous process occuring in CH<sub>3</sub>NO X<sup>1</sup>A' and a<sup>3</sup>A". A new approach was adopted which relates k(E) to k<sup>∞</sup><sub>3</sub> using inverse Laplace transformation.<sup>20,21</sup> k<sup>∞</sup><sub>3</sub> (T) was parameterised in the form A<sup>∞</sup><sub>3</sub> exp (- E<sup>∞</sup><sub>3</sub>/k<sub>B</sub>T) and the whole set of (P,T) data fitted using a non-linear least squares technique with A<sup>∞</sup>, E<sup>∞</sup> and < $\Delta$ E><sub>down</sub>, the average energy transferred per collision in a downward direction, as variable parameters. The resulting best fit parameters were:-A<sub>2</sub><sup>∞</sup> = 1.5 x 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup>s<sup>-1</sup>

 $A_3^{\infty} = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$   $E_3^{\infty}/k_B = 60 \text{ K}$  $<\Delta E >_{down} = 235 \text{ cm}^{-1}$ , for an argon diluent.

The energy transfer parameter is now more compatible with values derived in other systems. These data correspond to

 $k_{3}^{0} = 6.9 \times 10^{-32} \exp(1430 \text{ K/T}) \text{ cm}^{6} \text{ molecule}^{-2} \text{s}^{-1}$ 

3. Atom - radical reactions

Novel procedures are required for atom + radical reactions, because it is necessary to determine the concentrations of both species. We recently developed a technique based on laser flash photolysis coupled with absorption spectroscopy (radical) and resonance fluorescence (atom), which we applied to the  $CH_3 + H$  reaction.<sup>22,23</sup> This section describes results on the allyl radical which is generated in high temperature pyrolysis and combustion. It is remoted primarily by atoms and radicals because of its slow reaction with molecules such as  $O_2$ .<sup>24,25</sup>

(i)  $C_3H_5 + H - C_3H_6$ 

**R4** 

Both  $C_3H_5$  and H were generated from the photolysis of hexadiene at 193 nm in the ratio  $[C_3H_5]$ : [H] ~ 100:1. No other radicals were generated in sufficient concentrations to interfere with the method of analysis. The reaction was studied at 298 K and at pressures of 100 - 400 Torr.  $k_4$  was found to be independent of pressure with a mean value of  $(3 \pm 1) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup>s<sup>-1</sup>.

(ii) 
$$C_2H_5 + O ----->$$
 products

**R5** 

 $C_3H_5$  was generated from hexadiene and O from the 193 nm photolysis of  $N_2O/N_2/H_2^{-26}$  and the reaction studied over the temperature range 300 - 600 K and at pressures of 50 - 400 Torr (N<sub>2</sub>). Within experimental error the rate coefficient was found to show no dependence on T and P. Parallel experiments at lower pressures were conducted using photoionisation mass spectrometry by Slagle et al.<sup>26</sup> and the mean value for the combined investigation over the temperature range 300 - 600 K is (2.7 ± 0.7) x 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup>s<sup>-1</sup>. Slagle et al.<sup>26</sup> also searched for products, finding only acrolein and suggesting that the channel

$$C_{3}H_{5} + O \dots > C_{3}H_{4}O + H$$

predominates.

Work is in progress on the  $C_3H_5 + HO_2$  reaction.

# 4. Alkyl radical heats of formation

#### 4.1 Introduction

Alkyl radical heats of formation have been based primarily on the measurement of

McMillen and Golden<sup>27</sup> rate coefficients for forward and reverse reactions. summarised measurements up to 1982, recommending the values shown in Table1, basing their recommendations primarily on the halogenation reactions

with X = I or Br. Tsang,<sup>28,29</sup> on the other hand, estimated  $\Delta H^{0}_{f}$  (R) from measurements of alkane dissociation/alkyl combination. His recommendations, which are also given in Table 1 are significantly higher than those of McMillen and Golden, with the discrepancy increasing with radical size. In sections 4.2 and 4.3 we examine recent results for  $C_2H_5$  and t- $C_4H_0$ , including measurements made in this laboratory.

### Table 1. Heats of formation for alkyl radicals

∆H°, 200/kJ mol<sup>-1</sup>

**R**6

**R7** 

R

	<b>,</b> ,		
	McMillen &	Golden <sup>27</sup> Tsang <sup>28,29</sup>	
C <sub>2</sub> H <sub>5</sub>	108.4 ± 4	119.5 ± 2.5	
i - C <sub>3</sub> H <sub>7</sub>	76.1 ± 4	93.3 ± 2.5	
$t - C_4 H_9$	36.4 ± 4	51.7 ± 2.2	

### 4.2

 $C_2H_5$ Brouard et al.<sup>30</sup> observed directly the approach to equilibrium following the 193 nm photolysis of  $C_2H_4$  to generate H. H reacts with  $C_2H_4$  to form  $C_2H_5$  which dissociates on the experimental timescale at temperatures > 775 K at 200 Torr total pressure (helium diluent):

 $H + C_{2}H_{4}$  $C_{2}H_{5}$ 

The H atom resonance fluorescence signal shows a characteristic relaxation to a non-zero value, as equilibrium is established. Analysis of the decay profile enables both the forward and reverse rate coefficients,  $k_6$  and  $k_{-6}$ , and hence the equilibrium constant,  $K_6$ , to be determined. Such an approach has clear advantages over the measurement of k<sub>6</sub> and k<sub>-6</sub> in separate experiments, especially given the pressure dependence of the rate coefficients. The system was examined over the temperature range 775 - 825 K.  $\Delta S^{0}_{6}(298)$  and  $\Delta C_{p,6}(T)$  were then calculated from spectroscopic parameters (vibrational frequencies, rotational constants) to allow  $\Delta H^{0}_{6}(298)$  and hence  $\Delta H^{0}_{f,298}(C_{2}H_{5})$  to be determined. The value of 118.7 ± 1.5 kJ mol<sup>-1</sup> is in good agreement with that proposed by Tsang<sup>28,29</sup>. Recently the measurements have been extended to a range of pressures (50 - 400 Torr) at 850 K, giving a similar value for ΔH<sup>o</sup><sub>f,298</sub>(C<sub>2</sub>H<sub>5</sub>).

Russell et al.<sup>31</sup> determined the temperature dependence of  $k_7$ 

C<sub>2</sub>H<sub>5</sub> + HBr -----> C<sub>2</sub>H<sub>6</sub> + Br They obtained

riev obtained  $k_7 = (1.0 \pm 0.1) \times 10^{-12} \exp \{(410 \pm 100) \text{ K/T}\} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$ with, surprisingly, a *negative* activation energy.  $k_7$  was estimated from previous relative measurements of Br + alkane reaction rates<sup>32,33</sup>, coupled with absolute measurements for Br + isobutane by Russell et al.<sup>34</sup>  $k_7 = (7 \pm 7) \times 10^{-10} \exp \{-(6400 \pm 300) \text{ K/T}\} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$ .

We have now made absolute measurements of k\_7 over the temperature range 423 -623 K using laser flash photolysis of CF2Br2 coupled with time resolved detection of  $Br^2P_{3/2}$  by resonance fluorescence: k<sub>7</sub> = (2.2 ± 1.2) x 10<sup>-10</sup> exp { - (6370 ± 180) K/T} cm<sup>3</sup> molecule<sup>-1</sup>s<sup>-1</sup>

in good agreement with the relative rate measurements. A second law analysis of  $K_7$  $(=k_7/k_{-7})$  gives  $\Delta H^0_{f,298}(C_2H_5) = 120 \pm 3 \text{ kJ mol}^{-1}$ . The most recent measurement of the ethyl radical heat of formation has been

made by Parmar and Benson<sup>35</sup> who studied the equilibrium

CI + C<sub>2</sub>D<sub>6</sub> -----> C<sub>2</sub>D<sub>5</sub> + DCI R8 in a very low pressure reactor, monitoring CI and C<sub>2</sub>D<sub>6</sub> by mass spectrometry. After correcting for zero point energy differences they obtained  $\Delta H^{0}_{f,298}(C_{2}H_{5}) = 118 \pm 1.7$ kJ mol<sup>-1</sup>

There is, therefore, good agreement between the recent determinations of the heat of formation of the ethyl radical and Tsang's estimate; a value of 119  $\pm$  2 kJ mol<sup>-1</sup> can be recommended with some confidence. Experimental uncertainties were probably underestimated in the early halogenation experiments. In addition, it was assumed that the activation energies for the R + HI and R + HBr reactions were  $(4 \pm 4)$  and  $(8 \pm 4)$  kJ mol<sup>-1</sup> respectively, whereas Russell et al.<sup>31</sup> determined a value of -3.4 kJ mol<sup>-1</sup> for  $C_2H_5 + HBr.$ 

4.3

 $t-C_{\mathcal{A}}H_{\mathcal{G}}$ Russell et al.<sup>34</sup> measured k<sub>9</sub>

 $t-C_4H_9 + HBr -----> i-C_4H_{10} + Br R9$ by laser flash photolysis/photoionisation mass spectrometry and k\_9 by the same

technique and also by monitoring Br by resonance fluorescence. The obtained  $k_g = (9.9 \pm 1.3) \times 10^{-13} \exp \{(700 \pm 100) \text{ K/T} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} + \frac{1}{29} = (1.83 \pm 0.18) \times 10^{-10} \exp \{-(3450 \pm 70) \text{ K/T} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} + \frac{1}{29} = (1.83 \pm 0.18) \times 10^{-10} \exp \{-(3450 \pm 70) \text{ K/T} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} + \frac{1}{29} + \frac{1}{29} \exp (-5.8 \text{ kJ} + 1) + \frac{1}{29} \exp (-5.8 \text{ kJ}$ mol<sup>-1</sup>) for reaction R9.

We have also measured k\_o by laser flash photolysis/resonance fluorescence (fig. obtaining

 $k_{-9} = (1.61 \pm 0.6) \times 10^{-10} \exp \{-(3460 \pm 180) \text{ K/T}\} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$  $k_{g} = (1.61 \pm 0.6) \times 10^{-5} \exp \{-(3460 \pm 160) \times 170^{-5} \exp \{-(3460 \pm 160) \times 170^{$  $mol^{-1}$ .





The crucial aspect of the work of Russell et al.<sup>34</sup> is the observation of a negative activation energy reaction for R9. This behaviour is unusual in a metathetical reaction and they argued that the mechanism probably invloves the initial formation of a weakly bound collision complex, promoted by the large polarisability of the bromine atom. This conclusion has been challenged by Muller-Markgraf et al.<sup>36</sup> who studied the reaction between t-C<sub>4</sub>H<sub>9</sub> + DBr using very low pressure photolysis and found the rate coefficient to *increase* significantly over the temperature range 295 - 385 K. Combining their measurements with the now well established reverse rate coefficient they obtained

 $\Delta H^{0}_{f,298}$  (t-C<sub>4</sub>H<sub>9</sub>) = 38.5 ± 2.0 kJ mol<sup>-1</sup>.

In contrast to the ethyl radical, there are clearly irreconcilable differences between the laser flash photolysis and very low pressure photolysis results. Attempts in this laboratory to resolve these difficulties by direct observation of the approach to equilibrium in Br, i- $C_4H_{10}$ , HBr mixtures have been produced inexpectedly complex behaviour. The heat of formation of i- $C_4H_{10}$  remains a controversial topic.

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