

Energy Barriers for the Addition of $\dot{\text{H}}$, $\dot{\text{C}}\text{H}_3$ and $\dot{\text{C}}_2\text{H}_5$ to $\text{CH}_2=\text{CHX}$ where $\text{X} = \text{H}, \text{CH}_3, \text{OH}$, and, H-atom addition to $\text{RCH}=\text{O}$ where $\text{R}=\text{H}, \text{CH}_3$ and $n\text{-C}_3\text{H}_7$; Some Implications for the Gas-Phase Chemistry of Enols

J. M. Simmie*, H. J. Curran

Combustion Chemistry Centre, National University of Ireland, Galway, Ireland

Abstract

Although enols have been identified in alcohol and other flames, in interstellar space and have been implicated in the formation of carboxylic acids in the urban troposphere in the past few years the reactions which give rise to them are virtually unknown. In order to address this deficit, particularly with regard to bio-butanol combustion, a number of high-level ab initio calculations determined the activation enthalpies for radical addition to $\text{CH}_2=\text{CHX}$ where $\text{X} = \text{H}, \text{OH}$ and CH_3 and of H-addition to $\text{RCH}=\text{O}$, where $\text{R}=\text{H}, \text{CH}_3$ and $n\text{-C}_3\text{H}_7$. We conclude that 1-buten-1-ol should be almost as abundant as its isomeric aldehyde 1-butanal during the combustion of 1-butanol and that this will also be the case for other alcohols provided that the appropriate structural features are present.

Introduction

The development of detailed chemical kinetic mechanisms [1] to both understand and predict the behaviour of existing and novel bio-fuels is of major current interest. The present-day market leader bio-ethanol, no matter how it is produced, suffers from some significant drawbacks as an automotive fuel in terms of both its physical and chemical properties.

The search is therefore on for novel, 'next-generation', bio-fuels [2] which do not impact adversely on the environment (atmosphere and hydrosphere), are not produced from animal or human foodstuffs and which have desirable performances in internal combustion engines or gas turbines.

One possible candidate is bio-butanol (normal or 1-butanol) for which new methods of production through the manipulation of biological systems [3] offers significant advantages over fermentation. Consequently a number of experimental studies have emerged very recently on the combustion of butanol [4–9]. It is probable that, in comparison to hydrocarbons, the burning of this oxygenated compound will lead to increases in the formation of aldehydes and lower rates of formation of particulate matter but our understanding of the combustion chemistry of this and other oxygenates is at an early stage of development.

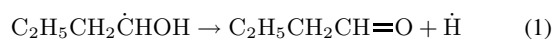
For example, it has only very recently been recognised that enols, strictly compounds with a hydroxyl group *adjacent* to a C–C double bond, $\text{R}_1\text{R}_2\text{C}=\text{CH}(\text{OH})$, are implicated in the combustion of oxygenated compounds as well as hydrocarbons following on from their observation in flames. In addition there is a growing recognition that enols may play a role in the chemistry of the interstellar medium with ethenol first detected by microwave emissions from Sagittarius B2N in 2001 [10] and a number of other enols in cold plasma discharges of alcohols very recently [11]. These latter experiments utilised tunable synchrotron radiation in the vacuum ultraviolet to selectively photo-ionise both stable and transient species and then detect these qualitatively, and quantitatively, via molecular-beam mass spectrometry [12–14]. Clearly this new technique, which has been recently incorporated into a flow reactor [15], has provided additional capabilities in reactive flows and will generate valuable data for the validation of reaction mechanisms.

Taatjes *et al.* [14] found that the reaction of $\dot{\text{O}}\text{H}$ with ethene is the dominant route to ethenol formation in ethene flames and speculated that addition–elimination reactions of $\dot{\text{O}}\text{H}$ with other alkenes is likely to be responsible for enol formation in flames.

However work by Wang *et al.* [11] seems to suggest fairly conclusively that other pathways to enols are more likely.

The possible impact of these species on the chemistry of the atmosphere has been investigated by Archibald *et al.* [16] and a novel mechanism (not based however on elementary reactions) proposed by which the reactions of enols contribute significantly towards gas-phase carboxylic acid concentrations which are underestimated by major atmospheric chemistry models. Their results indicate that the atmospheric transformation of enols may be an important missing secondary source term for carboxylic acids in the urban troposphere.

In elegant flame speciation experiments [5] on all four isomers of butanol Qi and co-workers have shown that both butanal and 1-buten-1-ol are formed in n-butanol flames in approximately a 20:1 ratio [17]. Almost certainly these intermediates are formed from $\text{C}_2\text{H}_5\text{CH}_2\dot{\text{C}}\text{HOH}$, the α or 1-hydroxybutyl radical, which we have shown [18] in high-level theoretical calculations, is one of the predominant species formed in H-atom abstraction reactions by $\dot{\text{O}}\text{H}$ and $\text{H}\dot{\text{O}}_2$, from the parent. The α -radical can eliminate a H-atom to form butanal, (1), or butenol, (2):



or break the $\text{C}_\beta\text{—C}_\gamma$ bond to form an ethyl radical + ethenol in a β -scission reaction (3):



Consequently estimates of the barrier heights for such reactions are desirable (since there is no data available in the literature to our knowledge) and can best be achieved by treating the reactions (1)–(3) in the *reverse* direction, that is H-atom addition to butenol and butanal and ethyl radical addition to ethenol.

Specific Objectives

The aims of this work were to explore the possible routes of formation for recently identified intermediates, enols, in the combustion of alkenes and alcohols. The further aim was to establish just how important such species are likely to be, specifically in the high-temperature oxidation of butanol, and in oxygenate combustion in general.

Computational Methodology

Estimates of the barrier heights for the addition of methyl and hydrogen atoms to $\text{H}_2\text{C}=\text{CHX}$ where $\text{X} = \text{H}, \text{OH}$ and

*Corresponding author: john.simmie@nuigalway.ie
Proceedings of the European Combustion Meeting 2009

CH₃ at both ends of the double bond were obtained through ab initio calculations. Reaction enthalpies for these strongly exothermic additions, in which a π -bond is being replaced by a σ -bond, were also computed. The complete basis set methodologies of Petersson *et al.*, namely CBS-QB3 [19] and CBS-APNO [20], were used, as implemented in Gaussian-03 [21]. In the QB3 method geometry optimisation and frequency calculations at the DFT level (B3LYP/CBSB7) are followed by single point calculations at CCSD(T)/6-31+G(d), MP4SDQ/CBSB4 and MP2/CBSB3 with CBS extrapolation.

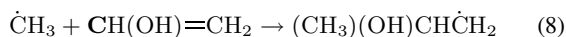
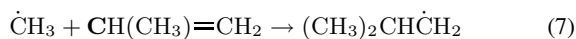
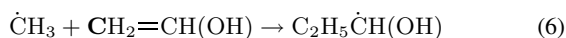
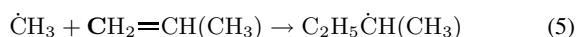
The APNO procedure is considerably more expensive involving an initial geometry optimisation and frequency calculations at HF/6-311G(d,p), followed by a geometry re-optimisation at QCISD/6-311G(d,p) and five single point calculations including QCISD(T)/6-311++G(2df,p), MP2(Full)/CBSB6, HF/CBS-B5A and MP2/CBSB5 with CBS extrapolation.

There are a very large number of methods available [22, 23] for the computation of reaction barriers and enthalpies ranging from general purpose ones to those specifically designed for thermochemistry and kinetics — Fischer and Radom [24] list 35 methodologies for evaluating the methyl + ethene reaction. However we have found that the combination of two differing approaches embodied by CBS-QB3 and CBS-APNO offer a reasonable compromise between high precision and inexpensive computing.

Unless otherwise stated the results reported here for ethenol refer to the *syn*-rotamer with a dihedral angle C–C–O–H of approximately 0° which is more stable than the *anti*-rotamer by 4.5 and 4.8 kJ mol⁻¹ at CBS-QB3 and CBS-APNO, respectively, in very good agreement with the microwave measurements of Rodler [25] of 4.5 ± 0.6 kJ mol⁻¹ and the recent calculations of da Silva and co-workers [26] of 4.6 kJ mol⁻¹.

Results and Discussions

Addition of methyl: In the case of methyl group addition:



both CBS-QB3 and CBS-APNO yielded consistent results, Table 1. Here and elsewhere a single imaginary frequency characterised the location of each transition state for which an optimised geometry could be found. The values obtained for methyl addition to ethene and propene at the CH₂ end, reactions (4) and (5), are in agreement with the vibrationless barriers previously reported by Gómez-Balderas *et al.* [27] at CBS-QB3. The CBS-RAD results of Fischer and Radom [24] for reactions (5) and (6) are within 0.5 kJ mol⁻¹ of the vibrationless barriers computed in *this work*.

Saeyns *et al.* [28] reported CBS-QB3 values (based however on geometrically constrained transition states) for methyl addition to ethene and to the tail of propene which are in broad agreement with those found here.

As regards addition to the CH₂ group the identity of X does not influence the enthalpy of activation to any significant extent; that is, there is at most a difference of 2 kJ mol⁻¹ predicted by CBS-QB3 for reactions (4)–(6) whilst the CBS-APNO results show an even smaller variation.

The activation enthalpy for ‘tail’ addition to CHX is, due to steric and reaction enthalpy effects, somewhat higher and

does show dependence on the nature of group X rising from 26.7 to 31.5 to 37.3 kJ mol⁻¹ for X = H, CH₃ and OH for the CBS-APNO calculations with a similar outcome for CBS-QB3. These findings for X = Me parallel those of Henry *et al.* [29] who found that $\Delta H^{\ddagger}(0\text{ K})$ increased from 36.7 — for addition to CH₂ — to 42.3 kJ mol⁻¹ for CH(CH₃) addition in G3X-RAD calculations performed on QCISD/6-31G(d) optimised geometries.

Comparison with experiment: The addition of a methyl radical to ethylene to form n-propyl radical has been studied experimentally by two groups. Hogg and Kebarle [30] determined a rate constant of $4.59 \times 10^{11} \exp(-3,940/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ over the temperature range 392–434 K in a static reactor by normalising the expression relative to the rate constant for methyl radical self-reaction producing ethane, $2\dot{\text{C}}\text{H}_3 \rightarrow \text{C}_2\text{H}_6$. Holt and Kerr [31] determined $k = 2.09 \times 10^{11} \exp(-3,670/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ over temperatures of 350–503 K and pressures of 548–652 Torr. Thus, activation energies of 32.7 and 30.6 kJ mol⁻¹ respectively, are indicated which are in excellent agreement with our calculated values of 31.4 and 32.8 kJ mol⁻¹ based on a mean temperature of 400 K and on the relationship $E_a = \Delta H^{\ddagger} + (1 - \Delta n^{\ddagger})RT$ where Δn^{\ddagger} is the change in the number of molecules in going from reactants to the transition state.

The rate constant for ‘head’ addition of a methyl radical to propene to form *sec*-butyl radical has been much studied [32–38]. Miyoshi and Brinton [32] and Cveticović and Irwin [33] reported on the overall rate of addition of a methyl radical to propene, both ‘head’ and ‘tail’ addition, without distinguishing between them. Knyazev *et al.* [35], using the terminal/internal branching ratio measured by Baldwin *et al.* [36] at temperatures of 403 K and 753 K, derived $k = 1.09 \times 10^{12} \exp(-4,240/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $E_a = 35.2 \text{ kJ mol}^{-1}$ attributable to both of these sets of data. The most recent review by Baulch *et al.* [37] recommends a rate constant of $2.11 \times 10^{11} \exp(-3,700/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in the temperature range 300–600 K with an activation energy of 30.8 kJ mol⁻¹.

The addition of a methyl radical to the propene ‘tail’ produces an *iso*-butyl radical. A rate constant of $5.79 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was measured by Baldwin *et al.* [36] at 753 K and they also recommended $k = 2.0 \times 10^{11} \exp(-4,390/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in the temperature range 353–753 K for this reaction with activation energy of 36.5 kJ mol⁻¹. Tsang [38], in his review of propane oxidation kinetics, recommended a rate constant of $9.64 \times 10^{10} \exp(-4,030/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ between 300 and 2,500 K corresponding to an activation energy of 33.5 kJ mol⁻¹.

Thus, the experimental evidence regarding the change in barrier heights in methyl addition to CH₂ *versus* CHCH₃ in propene seems to suggest an increase from 30.8 to 36.5 kJ mol⁻¹ which is in good agreement with our theoretical predictions of a modest increase of some 5 kJ mol⁻¹.

Reaction enthalpies: Enthalpy changes for reactions (4), (6) and (7) are in good agreement with values computed by Sabbe *et al.* [39] and with values calculated from enthalpies of formation taken from an authoritative source [40] in conjunction with ΔH_f for *syn*-ethenol of $-125.5 \text{ kJ mol}^{-1}$ from da Silva *et al.* [26] and $-62.6 \pm 11.7 \text{ kJ mol}^{-1}$ for the 2-hydroxypropyl radical, (CH₃)(OH)CH $\dot{\text{C}}\text{H}_2$, from Sun and Bozzelli [41]. The uncertainty associated with the latter is quite high so reaction enthalpies for an isodesmic reaction (using acetone, iso-propanol and acetylonyl) were computed of $-27.2 \pm 0.9 \text{ kJ mol}^{-1}$ which yields ΔH_f of $-62.6 \pm 2.2 \text{ kJ mol}^{-1}$ — in excellent agreement

Reaction	$\Delta H^{\circ,\ddagger} / \text{kJ mol}^{-1}$		$\Delta_r H / \text{kJ mol}^{-1}$		
	CBS-QB3	CBS-APNO	CBS-QB3	CBS-APNO	Lit. [40]
$\dot{\text{C}}\text{H}_3 + \text{CH}_2=\text{CH}_2$	25.7	26.7	- 97.1	-100.3	- 98.0 \pm 1.0
$\dot{\text{C}}\text{H}_3 + \text{CH}_2=\text{CH}(\text{CH}_3)$	24.7	26.1	- 98.0	-100.2	- 97.9 \pm 2.0
$\dot{\text{C}}\text{H}_3 + \text{CH}_2=\text{CH}(\text{OH})$	26.8	27.7	- 97.0	- 99.4	- 98.5 \pm 3.5
$\dot{\text{C}}\text{H}_3 + \text{CH}(\text{CH}_3)=\text{CH}_2$	30.6	31.5	- 92.9	- 95.2	- 93.1 \pm 1.1
$\dot{\text{C}}\text{H}_3 + \text{CH}(\text{OH})=\text{CH}_2$	36.4	37.3	- 86.4	- 84.3	- 86.1 \pm 11.9
$\dot{\text{H}} + \text{CH}_2=\text{CH}_2$	2.7	5.5	-148.4	-152.1	-150.9 \pm 0.7
$\dot{\text{H}} + \text{CH}_2=\text{CH}(\text{CH}_3)$	—	3.4	-148.6	-151.5	-148.0 \pm 2.0
$\dot{\text{H}} + \text{CH}_2=\text{CH}(\text{OH})$	—	3.0	-149.8	-152.5	-149.7 \pm 3.4
$\dot{\text{H}} + \text{CH}(\text{CH}_3)=\text{CH}_2$	8.2	9.8	-135.9	-138.9	-136.9 \pm 1.1
$\dot{\text{H}} + \text{CH}(\text{OH})=\text{CH}_2$	14.7	15.4	-119.3	-117.9	-118.5 \pm 2.6

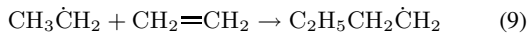
Table 1: Enthalpy of activation, $\Delta H^{\circ,\ddagger}$, and of reaction, $\Delta_r H$, at 298.15 K for methyl & H-atom addition.

Reaction	Dihedrals	Mean
$\text{CH}_2=\text{CH}(\text{OH})$	TG	26.4
$\text{CH}_2=\text{CH}(\text{OH})$	GG'	24.3
$\text{CH}_2=\text{CH}(\text{OH})$	G'G	24.3
$\text{CH}(\text{OH})=\text{CH}_2$	GT	32.7
$\text{CH}(\text{OH})=\text{CH}_2$	TG'	33.1
$\text{CH}(\text{OH})=\text{CH}_2$	G'G	31.6

Table 2: Ethyl + syn-ethenol: $\Delta H^{\circ,\ddagger} / \text{kJ mol}^{-1}$.

with the Sun and Bozzelli result but much less uncertain.

Addition of ethyl: The addition of ethyl radical to ethene leading to the formation of n-butyl:



takes place with barriers of 24.1 and 24.2 kJ mol^{-1} , slightly smaller than for methyl addition. The calculated exothermicities of ethyl addition of -93.5 and -96.9 kJ mol^{-1} compare well with the literature value of $-94.5 \pm 2.2 \text{ kJ mol}^{-1}$. Our standard CBS-QB3 result for $\Delta E(0 \text{ K}) = 28.1 \text{ kJ mol}^{-1}$ is within 0.8 kJ mol^{-1} of the non-standard CBS-QB3 calculation of 27.3 kJ mol^{-1} reported by Saeys *et al.* [28].

Of particular interest here is the addition of ethyl radical to the 'head' or methylene end of syn-ethenol; this situation is more complex than for methyl addition since three transition states can be postulated with differing CCCC and CCCO dihedral angles (classified as trans T or gauche G), see Table 2.

However the results are scarcely different and are very close to the methyl radical addition values; reinforcing the previous finding that the nature of group X (as defined here) has very little influence on barrier height.

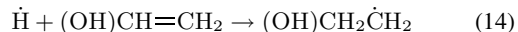
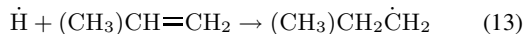
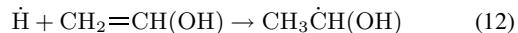
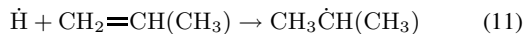
As before addition at the 'tail', or CH(OH), end results in a higher barrier height by about 7 kJ mol^{-1} and also as before effectively the same barrier as for methyl addition.

Comparison with experiment: The addition of ethyl radical to ethene has been studied by a number of groups [42–44]. In the temperature range 417–460 K, Kerr and Trotman-Dickenson [42] reported $k = 1.12 \times 10^{12} \exp(-4,330/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ with an activation energy, E_a , of 36.0 kJ mol^{-1} . Later, Kerr and Parsonage [43] carried out an extensive literature review and recommended $k = 1.58 \times 10^{11} \exp(-3,670/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from 348–482 K and a lower activation energy of 30.6 kJ mol^{-1} . Morganroth and Calvert [44] reported a rate constant of

$2.90 \times 10^{10} \exp(-3,270/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from 430–520 K with an even lower $E_a = 27.2 \text{ kJ mol}^{-1}$.

Our computed value for reaction (9) of $\Delta H^{\circ,\ddagger} = 24.2$ and $E_a = 30.9 \text{ kJ mol}^{-1}$ is thus in very good agreement with the Kerr and Parsonage [43] recommended activation energy.

Addition of H-atom A similar approach to that described above was adopted for H-atom addition for the following reactions:



but transition states for reactions (11) and (12) could not be located in direct CBS-QB3 computations. The geometrical optimiser which is employed by this model chemistry is the popular functional B3LYP with a CBSB7, effectively a 6-311G(2d,d,p) basis set — and this fails to converge to a transition state. It is possible to use a basis set with diffuse functions, 6-311+G(d,p), which does converge for reaction (11). Miller and Klippenstein [45] in their comprehensive paper on the kinetics of reaction (10) used B3LYP/6-311++G(d,p) and found a significantly longer H–C forming bond distance than QCISD(T) values. Hence it would be possible to employ a frozen geometry in a CBS-QB3 calculation but this is not an optimal solution since, *inter alia*, it does not work for reaction (12) for either expanded basis set.

Note that Saeys and co-workers [28] utilised a different approach, carrying out CBS-QB3 single-point energy calculations along a B3LYP/6-311G(d,p) intrinsic reaction path and locating the transition state by interpolation. Consequently their $\Delta E(0 \text{ K})$ of 10.1 kJ mol^{-1} for H-atom addition to ethene is substantially different to the standard CBS-QB3 result of 6.3 kJ mol^{-1} .

It is clear therefore that a DFT-based method such as CBS-QB3 struggles to compute the transition states for these hydrogen atom addition reactions. However no problems were encountered with CBS-APNO calculations and results are summarised in Table 1. Good agreement is obtained between computed reaction enthalpies and values from the literature.

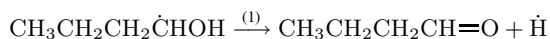
Comparison with experiment: The clearest experimental evidence for the increase in barrier height in going from 'head',

reaction (11), to ‘tail’, reaction (13), addition of $\dot{\text{H}}$ to propene:



comes from the work of Wagner and Zellner [46]; they indicate that E_a changes from 5.2 to 11.5 kJ mol⁻¹ in line with our results of $\Delta H^{\circ,\ddagger}$ going from 3.4 → 9.8 kJ mol⁻¹, Table 1.

Addition to butanal/ethanal/methanal Theoretical calculations of the energy barrier for H-atom addition to the aldehyde butanal at the O-centre did not present any difficulties; both CBS-QB3 and CBS-APNO methods yield transition states which lie 38.5 and 36.9 kJ mol⁻¹ above the reactants. In conjunction with computed reaction enthalpies of -108.0 and -110.5 kJ mol⁻¹ the enthalpies of activation are 146.5 and 147.5 kJ mol⁻¹ respectively, for the reverse reaction:



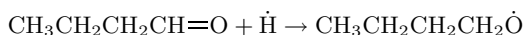
In the case of O-centred addition of a hydrogen atom to acetaldehyde/ethanal:



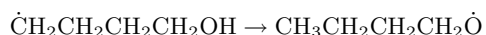
barriers heights of 38.5–38.9 kJ mol⁻¹ are found. This result shows that the nature of the alkyl group attached to the carbonyl carbon has little influence; indeed below we show that for methanal/formaldehyde a virtually identical barrier is computed.

H-atom addition at the C-centre of butanal is expected to be kinetically and thermodynamically favoured over O-centre addition as Henry and others [29] have shown in the case of methyl radical adding to formaldehyde by > 50 kJ mol⁻¹ and somewhat less, 46 kJ mol⁻¹ for methyl addition to ethanal (acetaldehyde).

Indeed this is the case since we calculate barriers of 17.2 and 19.5 kJ mol⁻¹ for the reaction:

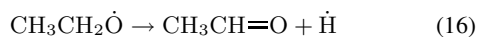


In conjunction with computed reaction enthalpies of -67.4 and -65.9 kJ mol⁻¹ we estimate barriers of 84.6–85.4 kJ mol⁻¹ for the reverse reaction which is in very good agreement with the activation energy of 88 ± 6 kJ mol⁻¹ of Hack *et al.* [47]. Thus although this route to butanal is energetically favoured it must be remembered that the alkoxide radical is not a major by-product of the initial H abstraction reactions from n-butanol. Neither is the δ or 4-hydroxybutyl radical which could lead to additional quantities of the butoxide being formed via a 1,5 H-shift reaction:



for which we calculate reaction barriers of 46.6–44.9 kJ mol⁻¹. The relative rates of radical production at 1,000 K by H abstraction from the parent butanol by the O₂ molecule are $\alpha : \beta : \gamma : \delta : \text{O}$ as 130:20:6:9:1 as estimated by Moss *et al.* [8].

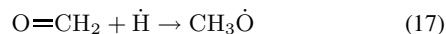
For C-centred addition to ethanal the same conclusions are arrived at; namely that the barrier heights of 19.6 and 22.0 kJ mol⁻¹ are considerably smaller than for O-centred addition. The elimination of a hydrogen atom from the ethoxy radical:



thus has barrier heights of 84.2–88.4 kJ mol⁻¹ essentially identical to those computed above for n-butoxy decomposition.

Thus for the two alkyl-substituted carbonyl compounds the results are independent of the nature of the alkyl group; to what

extent is this the case for methanal? It is also true for the competition in the reaction between H-atom and formaldehyde:



but to a lesser extent — we calculate that the formation of the methoxy radical requires surmounting an energy barrier, $\Delta H^{\circ,\ddagger}$, of 11.0–13.7 whilst formation of the hydroxymethylene radical, via addition at the O-centre, has an energy barrier of 38.0–39.6 kJ mol⁻¹.

Hippler *et al.* [48] computed barrier heights, $\Delta H^{\circ,\ddagger}$ (650K), ranging from 100.4 to 109.8 kJ mol⁻¹ for the dissociation of the methoxy radical, that is reaction (-18), which is in reasonable agreement with our results of 96.8–102.5 kJ mol⁻¹.

Hippler and Viskolcz [49] found that the barrier height was consistently approximately 35 kJ mol⁻¹ higher for addition to the oxygen atom relative to the carbon atom in the C=O bond. They concluded that, at temperatures below 1000 K, addition to the oxygen atom can be neglected.

Note that barrier heights for H-atom addition to the O-centre are effectively the same for formaldehyde (38.0–39.6), acetaldehyde (38.5–38.9) and butanal (38.5–36.9) but for C-centred addition the formaldehyde (11.0–13.7), acetaldehyde (19.6–22.0) and butanal (17.2–19.5) barriers differ.

Conclusions

Activation enthalpies for methyl addition to the CH₂ group of CH₂=CHX where X = H, OH and CH₃ average at 26.3 ± 1.0 kJ mol⁻¹ and are not influenced by the nature of X; addition to the CHX end is energetically costlier and does show the influence of group X = OH and CH₃. Replacing the attacking methyl radical by ethyl makes very little difference to addition at CH₂ and follows the same trend of a higher barrier for addition to the CH(OH) end.

In the case of H-addition it is more problematic to draw general conclusions since the DFT-based methodology, CBS-QB3, struggles to locate transition states for reactions (11) and (12). However the increase in barrier heights in reaction at the CHX end in comparison to addition at the methylene end is evident.

For hydrogen atom reaction with the carbonyl group in the compounds methanal, ethanal and butanal we see that for addition at the O-centre the barrier heights are not influenced by the nature of the alkyl group whereas addition at the C-centre is different on going from H → alkyl but seems to be invariant once alkylated.

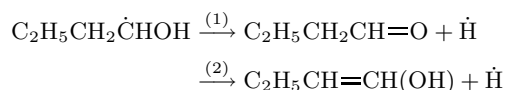
Computed reaction enthalpies are in excellent agreement with experimental values in all those cases where comparisons can be made.

For the β -scission of 1-hydroxybutyl which eliminates an ethyl radical:



we compute an enthalpy of activation of 122.3 ± 1.7 kJ mol⁻¹. This is very similar to the reverse of reactions (4)–(8), that is elimination of methyl radical through β -scission.

For H-atom elimination from the α -radical there are two competing processes; the first leads to the formation of butanal whilst the second parallel reaction yields butenol:



for which we predict barriers of (1) 147.0 kJ mol⁻¹ and (2) 150.6 kJ mol⁻¹. An estimation of the relative reaction rates can

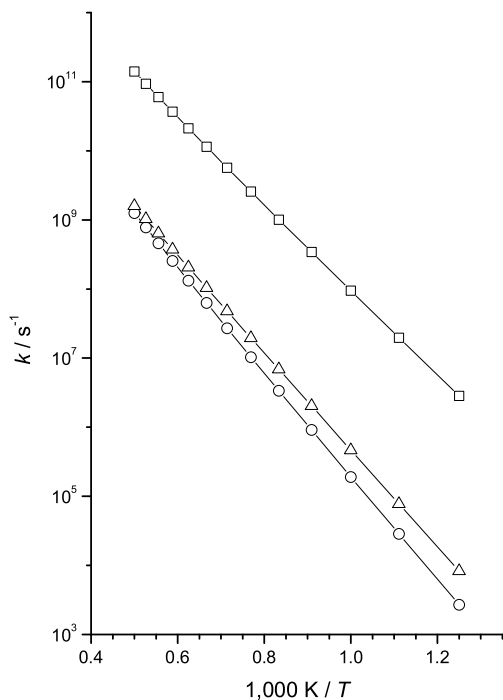
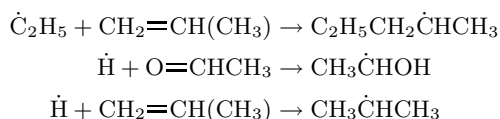


Figure 1: Estimated rate constants for 1-hydroxybutyl decomposition leading to the formation of \square ethenol, \triangle butanal, \circ butenol.

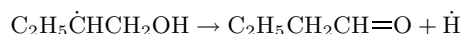
be obtained from the ratio of rotational and vibrational partition functions for the two transition states and the difference in barrier heights which indicate that $k_1/k_2 \approx 3.1$ at 1,000 K.

The rate constants for the three reactions (19), (1) and (2) can be estimated as follows. We use the correspondences established *here*, as regards barrier heights, to model the rate constants on the reactions taken from Curran [50]:



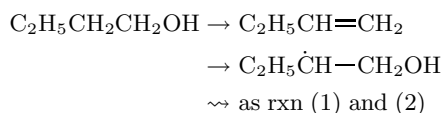
The results are shown in Fig. 1; at 1,000 K this method of estimation predicts an aldehyde to isomeric enol ratio of 2.5 which is in good agreement with the partition function evaluation.

For the β -radical $\dot{\text{H}}$ elimination also yields butenol:



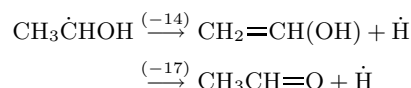
with ΔH^{\ddagger} of $136.3 \pm 1.6 \text{ kJ mol}^{-1}$.

The direct production of either butanal or butenol from n-butanol is unlikely to be of significance; although a reaction sequence such as:

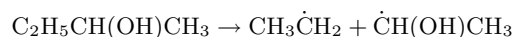


is possible, it is scarcely credible. The direct interconversion of butenol to butanal with a barrier of ca. 242 kJ mol^{-1} is also unlikely to feature in reactions in flames or shock waves (but see below).

For the analogous reactions of the 1-hydroxyethyl radical:



the corresponding barriers are (-17) 144.7–148.0 (Bhaskaran *et al.* [51] quote $E_a = 91.5 \text{ kJ mol}^{-1}$) and (-14) 155.5 kJ mol^{-1} and therefore $k_{-17}/k_{-14} \approx 3.8$ at the same temperature. Clearly reaction (-14) competes with reaction (-17); its omission from current models of ethanol combustion is therefore unfortunate. As a result of this latter calculation the 40:60 ratio of ethenol:ethanal found by Yang and co-workers [5] in iso-butanol flames can be easily explained since the favoured β -scission of the parent leads directly to a 1-hydroxyethyl radical:



which in turn eliminates a hydrogen atom to form the enol and the aldehyde.

Hence we conclude that enols should be almost as abundant as their isomeric counterparts, aldehydes, during the combustion of alcohols; this conclusion is predicated on the not unreasonable expectation that the rates of destruction of an enol and its corresponding aldehyde are comparable. Very recently however Zhou *et al.* [52] have shown that the dominant unimolecular fate of propen-2-ol is to isomerise to acetone which then produces acetyl and methyl radicals. If this is typical then the only kinetic distinction between an enol and its isomeric aldehyde (or ketone) will arise from different rates of abstraction. These are not known at this time and clearly represent a major experimental and computational challenge.

Acknowledgements

Financial support from an EU Marie Curie Transfer of Knowledge grant (MKTD-CT-2004-517248) is acknowledged. Computational resources were provided by the Irish Centre for High-End Computing, ICHEC.

References

- [1] J.M. Simmie, *Prog. Energy Combust. Sci.* 29 (2003) 599–634.
- [2] S.K. Ritter, *Chem. Eng. News* 17 November (2008) 57–61.
- [3] S. Atsumi, T. Hanai, J.C. Liao, *Nature* 451 (2008) 86–89.
- [4] C.S. McEnally, L.D. Pfeifferle, *Proc. Combust. Inst.* 30 (2005) 1363–1370.
- [5] B. Yang, P. Osswald, Y.Y. Li, J. Wang, L.X. Wei, Z.Y. Tian, F. Qi, K. Kohse-Hoinghaus, *Combust. Flame* 148 (2007) 198–209.
- [6] V. Zhukov, J.M. Simmie, H.J. Curran, G. Black, S. Pichon, 21st Int. Colloquium Dynamics Explosions Reactive Systems, Poitiers, France, July 2327, 2007.
- [7] G. Black, J.M. Simmie, H.J. Curran, 32nd Int. Symp. Combustion, Montreal, Canada, August 38, 2008. Work-in-progress Poster W5P67
- [8] J.T. Moss, A.M. Berkowitz, M.A. Oehlschlaeger, J. Biet, V. Warth, P.-A. Glaude, F. Battin-Leclerc, *J. Phys. Chem. A* 112, (2008) 10843–10855.

- [9] P. Dagaut, S.M. Sarathy, M.J. Thomson, *Proc. Combust. Inst.* (2009) doi:10.1016/j.proci.2008.05.005
- [10] B.E. Turner, A.J. Apponi, *Astrophysical J. Letts.* 561, (2001) L207–L210.
- [11] J. Wang, Y. Li, T. Zhang, Z. Tian, B. Yang, K. Zhang, F. Qi, A. Zhu, Z. Cui, C-Y. Ng, *Astrophysical J.* 676, (2008) 416–419.
- [12] C.A. Taatjes, N. Hansen, A. McIlroy, J.A. Miller, J.P. Senosiain, S.J. Klippenstein, F. Qi, L. Sheng, Y. Zhang, T.A. Cool, ; J. Wang, P.R. Westmoreland, M.E. Law, T. Kasper, K. Kohse-Hoeinghaus, *Science* 308, (2005) 1887–1889.
- [13] T.A. Cool, A. McIlroy, F. Qi, P.R. Westmoreland, L. Poisson, D.S. Peterka, M. Ahmed, *Rev. Sci. Instr.* 76 (2005) 094102/1–094102/7.
- [14] C.A. Taatjes, N. Hansen, J.A. Miller, T.A. Cool, J. Wang, P.R. Westmoreland, M.E. Law, T. Kasper, K. Kohse-Hoeinghaus, *J. Phys. Chem. A* 110 (2006) 3254–3260.
- [15] D.L. Osborn, P. Zou, H. Johnsen, C.C. Hayden, C.A. Taatjes, V.D. Knyazev, S.W. North, D.S. Peterka, M. Ahmed, S. R. Leone, *Rev. Sci. Instr.* 79 (2008) 104103/1–104103/10.
- [16] A.T. Archibald, M.R. McGillen, C.A. Taatjes, C.J. Percival, D.E. Shallcross, *Geophysical Res. Letts.* 34 (2007) L21801/1–L21801/4.
- [17] Private communication Prof. F. Qi, October 2008.
- [18] J. Moc, G. Black, J.M. Simmie, H.J. Curran, *Int. Conf. Computational Methods Sci. Engng.* 25–30 Sep. (2008) Hersonissos, Crete.
- [19] J.A. Montgomery Jr., M.J. Frisch, J.W. Ochterski, G.A. Petersson, *J. Chem. Phys.* 112 (2000) 6532–6542.
- [20] J.W. Ochterski, G.A. Petersson, J.A. Montgomery Jr., *J. Chem. Phys.* 104 (1996) 2598–2619.
- [21] Gaussian 03, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Menucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A. D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- [22] W.M.F. Fabian, *Monat. Chem.* 139, (2008) 309–318.
- [23] Y. Zhao, D.G. Truhlar, *Acct. Chem. Res.* 41, (2008) 157–167.
- [24] H. Fischer, L. Radom, *Angew. Chem. Int. Ed.* 40, (2001) 1340–1371.
- [25] M. Rodler, *J. Mol. Spectros.* 114, (1985) 23–30.
- [26] G. da Silva, C. H. Kim, J. W. Bozzelli, *J. Phys. Chem. A* 110, (2006) 7925–7934.
- [27] R. Gómez-Balderas, M.L. Coote, D.J. Henry, L. Radom, *J. Phys. Chem. A* 108,(2004) 2874–2883.
- [28] M. Saeys, M.F.O. Reyniers, G.B. Marin, V. Van Speybroeck, M. Waroquier, *J. Phys. Chem. A* 107, (2003) 9147–9159.
- [29] D.J. Henry, M. L. Coote, R. Gómez-Balderas, L. Radom, *J. Am. Chem. Soc.* 126, (2004) 1732–1740.
- [30] A.M. Hogg, P. Kebarle, *J. Am. Chem. Soc.* 86, (1964) 4558–4562.
- [31] P.M. Holt, J. A. Kerr, *Int. J. Chem. Kinet.* 9, (1977) 185–200.
- [32] M. Miyoshi, R. K. Brinton, *J. Chem. Phys.* 36, (1962) 3019–3030.
- [33] R.J. Cvetanović, R. S. Irwin, *J. Chem. Phys.* 46, (1967) 1694–1702.
- [34] J.M. Tedder, Walton, J. C.; Winton, K. D. R., *J. Chem. Soc. Farad. Trans. I* 68, (1972) 1866–1873.
- [35] V. D. Knyazev, I. A. Dubinsky, I. R. Slagle, D. Gutman, *J. Phys. Chem.* 98, (1994) 11099–11108.
- [36] R.R. Baldwin, A. Keen, R.W. Walker, *J. Chem. Soc. Faraday Trans. II* 83, (1987) 759–766.
- [37] D.L. Baulch, C.T. Bowman, C.J. Cobos, R.A. Cox, T. Just, J.A. Kerr, M.J. Pilling, D. Stocker, J. Troe, W. Tsang, R.W. Walker, J. Warnatz, *J. Phys. Chem. Ref. Data* 34, (2005) 757–1397.
- [38] W. Tsang, *J. Phys. Chem. Ref. Data* 20, (1991) 221–273.
- [39] M.K. Sabbe, A.G. Vandeputte, M.F.O. Reyniers, V. Van Speybroeck, M. Waroquier, G.B. Marin, *J. Phys. Chem. A* 111, (2007) 8416–8428.
- [40] A. Burcat, B. Ruscic, *Ideal Gas Thermochemical Database with updates from Active Thermochemical Tables*, 14 July 2008.
- [41] H. Sun, J.W. Bozzelli, *J. Phys. Chem. A* 106, (2002) 3947–3956.
- [42] J.A. Kerr, A. F. Trotman-Dickenson, *J. Chem. Soc.* (1960) 1611.
- [43] J.A. Kerr, M.J. Parsonage, “Evaluated Kinetic Data on Gas Phase Addition Reactions. Reactions of Atoms and Radicals with Alkenes, Alkynes and Aromatic Compounds”, Butterworths, London, (1972).
- [44] W.E. Morganroth, J. G. Calvert, *J. Am. Chem. Soc.* 88, (1966) 5387–5392.
- [45] J.A. Miller, S.J. Klippenstein, *Phys. Chem. Chem. Phys.* 6, (2004) 1192–1202.
- [46] H.Gg. Wagner, R. Zellner, *Ber. Bunsenges. Phys. Chem.* 76, (1972) 447–456.
- [47] W. Hack, K. Hoyermann, C. Kersten, M. Olzmann, B. Viskolcz, *Phys. Chem. Chem. Phys.* 3, (2001) 2365–2371.
- [48] H. Hippler, F. Striebel, B. Viskolcz, *Phys. Chem. Chem. Phys.* 3, (2001) 2450–2458.
- [49] H. Hippler, B. Viskolcz, *Phys. Chem. Chem. Phys.* 4, (2002) 4663–4668.
- [50] H.J. Curran, *Int. J. Chem. Kinet.* 38, (2006) 250–275.
- [51] K.A. Bhaskaran, R. Ravikumar, K.M. Karuppanan, K. Natarajan, *Colloq. Int. Berthelot-Vieille-Mallard-Le Chatelier*, 1, (1981) 278–283.
- [52] C-W. Zhou, Z-R. Li, C-X. Liu, X-Y. Li, *J. Chem. Phys.* 129, (2008) 234301.