Energy Barriers for the Addition of H, $\dot{C}H_3$, and $\dot{C}_2H_5$ to CH_2=CHX [X = H, CH_3, OH] and for H-Atom Addition to RCH=O [R = H, CH_3, $\dot{C}_2H_5$, *n*-C_3H_7]: Implications for the Gas-Phase Chemistry of Enols

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Although enols have been identified in alcohol and other flames and in interstellar space and have been implicated in the formation of carboxylic acids in the urban troposphere in the past few years, the reactions that give rise to them are virtually unknown. To address this data deficit, particularly with regard to biobutanol combustion, we have carried out a number of ab initio calculations with the multilevel methods CBS-QB3 and CBS-APNO to determine the activation enthalpies for methyl addition to the CH_2 group of CH_2=CHX where X = H, OH, and CH_3. These 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 CH_3. Replacing the attacking methyl radical by ethyl makes very little difference to addition at CH_2 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 some reactions. 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, propanal, and butanal we see that for addition at the O-center the barrier heights of ca. 38 kJ mol^{-1} are not influenced by the nature of the alkyl group whereas addition at the C-center is different on going from H → alkyl but seems to be invariant at 20 kJ mol^{-1} once alkylated. Rate constants for H-atom elimination from 1-hydroxyethyl, 1-hydroxypropyl, and 1-hydroxybutyl radicals, valid over the range 800−2000 K, are reported. These demonstrate that enols are more prevalent than previously suspected and 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. Since the toxicity of enols is not known experiments and further theoretical studies are clearly desirable before the large-scale usage of alcohol biofuels commences. An enthalpy of formation for butanal of $\Delta_f H$(298.15 K) = −204.4 ± 1.4 kJ mol^{-1} [Buckley, E.; Cox, J. D. *Trans. Faraday Soc.* **1967**, *63*, 895−901] is recommended, the uncertainty surrounding that for the 2-hydroxypropyl radical has been markedly reduced, and new values for 1-buten-1-ol, 1-propen-1-ol, and 2-propen-2-ol of −171.8 ± 1.6, −151.8 ± 1.7, and −169.9 ± 1.5 kJ mol^{-1}, respectively, are proposed.

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Introduction

The development of detailed chemical kinetic mechanisms[1] to both understand and predict the behavior of existing and novel biofuels is of major current interest. The present-day market leader bioethanol, 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", biofuels[2] that do not impact adversely on the environment (atmosphere *and* hydrosphere), are not produced from animal or human foodstuffs, and have desirable performances in internal combustion engines or gas turbines.

One possible candidate is biobutanol (normal or 1-butanol) for which new methods of production through the manipulation of biological systems[3] offers significant advantages over the classical fermentation route.[4,5] Consequently a number of experimental studies have emerged very recently on the combustion of butanol.[6−12] 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 recognized that enols, strictly compounds with a hydroxyl group *adjacent* to a C=C double bond, R_1R_2C=CH(OH), are implicated in the combustion of oxygenated[7,13] and nitrogenous[14] compounds as well as hydrocarbons following on from their observation in flames.[15] In addition there is a growing recognition that enols may play a role in the chemistry of the interstellar medium with *syn*- and *anti*-ethenol (vinyl alcohol) first detected by microwave emissions from Sagittarius B2N in 2001[16] and a number of other enols in cold plasma discharges of alcohols very recently.[17] These latter experiments utilized tunable synchrotron radiation in the vacuum ultraviolet to selectively photoionize both stable and transient species and then detect these qualitatively, and quantitatively in some cases, via molecular-beam mass spectrometry.[18−22] Clearly this new technique, which has been recently incorporated into a flow reactor,[23] has provided additional capabilities in reactive flows and will generate extremely valuable data for the validation of reaction mechanisms[24]

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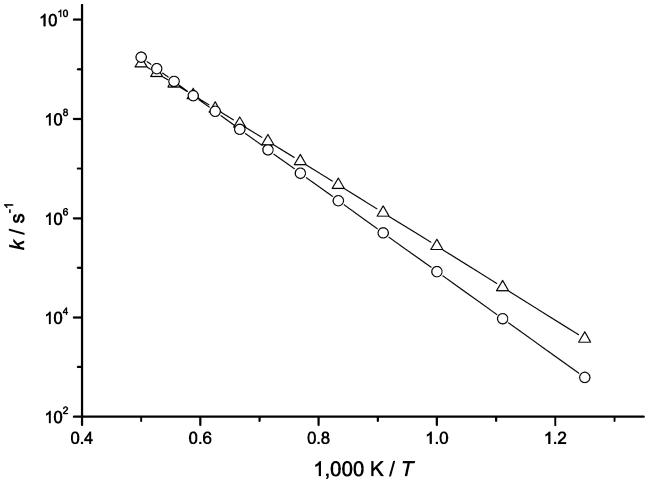

Figure 1. Estimated rate constants for 1-hydroxyethyl decomposition leading to the formation of (△) ethanal and (○) ethenol.

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(however, the perturbative effect of the sampling probe on the flame temperature is currently not known, and until this is resolved, successful chemical kinetic simulation is not possible). The new technique is particularly useful for the case for species like enols, which are thermodynamically extremely stable in comparison to their isomeric aldehydes yet nevertheless are known to rapidly isomerize in contact with Pyrex[25] and have much shorter lifetimes in condensed phases.

Taatjes et al.[20] found that the reaction of ȮH with ethene is the dominant route to ethenol formation in ethene flames and speculated that addition−elimination reactions of ȮH with other alkenes is likely to be responsible for enol formation in flames; this suggestion has recently been explored theoretically by Zhou and co-workers for propene + ȮH.[26] However, work by Wang et al.[17] on low-pressure cold-plasma discharges in alcohols (ethanol, propanols, and butanols) seems to suggest fairly conclusively that other pathways to enols are more likely. Interestingly, in molecular dynamics simulations of propene oxidation, Chenoweth et al.[27] do not observe any enol formation although ethynol, HC≡C−OH, is found. The 2-hydroxyethenyl radical HĊ=CH(OH) is proposed by Basiuk and Kobayashi[28] as a possible intermediate in the interstellar synthesis of ethenol via reaction sequences such as

$$HC{-}CH \xrightarrow{\dot{O}H} HC{-}CH(OH) \xrightarrow{\dot{H}} H_2C{-}CH(OH)$$

which, they argue, is based upon simple, commonly available and abundant interstellar species rather than the more direct channel proposed by Turner and Apponi[16] of

$$CH_3^+ + CH_2{=}O \rightsquigarrow CH_2{=}HOH$$

which involves much less abundant species.

The possible impact of enols on the chemistry of the atmosphere has been investigated by Archibald et al.[29] and a novel mechanism (not based, however, on elementary reactions) proposed by which the reactions of enols contribute significantly toward gas-phase carboxylic acid concentrations that 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.

The possible impact of enols on human health is moreover completely unknown; indeed, this is unsurprising given that only one naturally occurring stable aliphatic enol (devoid of conjugated or bulky aromatics and lacking a stabilizing 1,3-diketone structure) is known.[30]

In elegant flame speciation experiments[7] 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.[31] Almost certainly these intermediates are formed from $CH_3CH_2CH_2\dot{C}HOH$, the alpha- or 1-hydroxylbutyl which we have shown[32] in high-level theoretical calculations to be one of the predominant species formed in H-atom abstraction reactions by ȮH and $H\dot{O}_2$, from the parent. The α-radical can eliminate a H-atom to form butanal, reaction 1, or butenol, reaction 2,

$$CH_3CH_2CH_2\dot{C}HOH \rightarrow CH_3CH_2CH_2CH{=}O + \dot{H} \quad (1)$$

$$CH_3CH_2CH_2\dot{C}HOH \rightarrow CH_3CH_2CH{=}CH(OH) + \dot{H} \quad (2)$$

or break the $C_\beta{-}C_\gamma$ bond to form an ethyl radical + ethenol in a β-scission reaction 3:

$$CH_3CH_2CH_2\dot{C}HOH \rightarrow CH_3\dot{C}H_2 + H_2C{=}CH(OH) \quad (3)$$

Consequently, estimates of the barrier heights for such reactions are desirable and can best be achieved by treating reactions 1−3 in the *reverse* direction, that is, H-atom addition to both butenol and butanal and ethyl radical addition to ethenol.

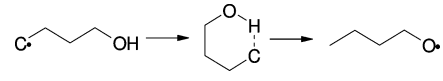
An additional route to butenol but not butanal that we have considered is H-atom elimination from the β-radical, 1-hydroxymethyl propyl

$$CH_3CH_2\dot{C}HCH_2OH \rightarrow CH_3CH_2CH{=}CHOH + \dot{H} \quad (4)$$

as well as a route to butanal from the 1-butoxy radical:

$$CH_3CH_2CH_2CH_2\dot{O} \rightarrow CH_3CH_2CH_2CH{=}O + \dot{H} \quad (5)$$

An additional channel for the formation of the butoxy (over and above that formed directly from *n*-butanol by H-atom abstraction) is via a facile six-center transition state from the δ-radical:



Studies of the initial radicals formed from *n*-butanol by hydrogen abstraction agree that abstraction from the methyl or the OH groups is much less likely than abstraction from the α, β, and γ carbons, although there is not a numerical consensus.[10,33−35]

Alkyl radical β-scission is an endothermic process and thus the rate constant is often measured in the reverse, exothermic direction, the addition of a radical species to an olefin with the forward rate constant then determined by microscopic revers-

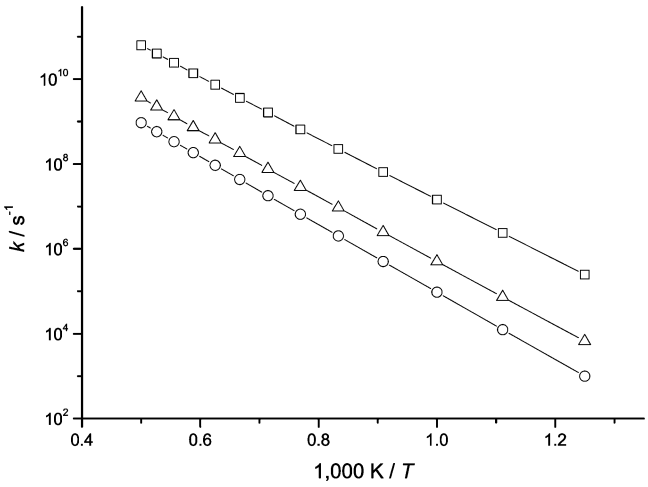


Figure 2. Estimated rate constants for 1-hydroxypropyl decomposition leading to the formation of (□) ethenol, (△) propanal, and (○) propenol.

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ibility. Cvetanović and Irwin[36] published some of the earliest work on the addition of methyl radicals to olefins. In addition, Tedder and Walton[37] considered the importance of polarity and steric effects in determining the rate and orientation of free radical addition to olefins. It was found that the rate constant for addition decreased as either the radical or the olefin to which it is adding becomes more branched or highly substituted.

More recently, Fischer and Radom[38] carried out a review of theoretical studies on the addition of carbon-centered radicals to alkenes and other unsaturated compounds. They found that frequency factors for additions to structurally related systems span a limited range and were of the order of 10^{11} cm^3 mol^{-1} s^{-1}. In addition, activation energies for addition are dominated by (i) steric effects of the radical and alkene substituents, (ii) effects of the overall reaction enthalpy and (iii) polar substituent effects. The reaction enthalpy, $\Delta_r H$, has a general and often dominating influence on the activation energy which, for many alkyl radical additions to a variety of alkenes, is well described by a linear Evans−Polanyi−Semenov[39] relationship, specifically E_a/kJ mol^{-1} = (0.244 ± 0.013)$\Delta_r H$ + (49.7 ± 1.3) for methyl and benzyl.[38]

To validate our results and to draw more wide ranging conclusions, we have computed the barrier heights for the addition of hydrogen atoms and methyl radicals to a series of alkenes, CH_2=CHX, where X = H, CH_3, and OH, and considered both "head" (CH_2) and "tail" (CHX) additions. In their review, Fischer and Radom[38] report that activation energy barriers computed for methyl addition to ethenol are very sensitive to the level of theory used and ranged very widely from 3.3 to 62.8 kJ mol^{-1}. Such a variation in barrier height represents a thousand-fold difference in the rate of reaction at 1000 K.

Computational Results

Estimates of the reaction barrier heights for the addition of methyl, ethyl, and hydrogen atoms to H_2C=CHX where X = H, OH, and CH_3 at both ends of the double bond and of H-atoms to RCH=O where R = H, CH_3, C_2H_5, and n-C_3H_7 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[40] and CBS-APNO,[41] were used, as implemented in the application Gaussian-03.[42] In the QB3 method geometry optimization 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 optimization and frequency calculations at HF/6-311G(d,p), followed by a geometry reoptimization at QCISD/6-311G(d,p) and five single point calculations including QCISD(T)/6-311++G(2df,p), MP2(Full)/CBSB6, HF/CBSB5A, and MP2/CBSB5 with CBS extrapolation.

There are a very large number of methods available[43,44] for the computation of reaction barriers and enthalpies ranging from general purpose ones to those specifically designed for thermochemistry and kinetics (Fischer and Radom[38] 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 and crucially, allow an objective measure of statistical significance.[45]

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 levels, respectively. The average of 4.64 kJ mol^{-1} with an uncertainty (defined as twice the standard deviation) of ±0.33 kJ mol^{-1}, is in very good agreement with the microwave measurements of Rodler[46] of 4.5 ± 0.6 kJ mol^{-1} and the recent theoretical calculations of da Silva and co-workers[47] of 4.6 kJ mol^{-1}.

Addition of Methyl. In the case of methyl group addition

$$\dot{C}H_3 + CH_2{=}CH_2 \rightarrow CH_3CH_2\dot{C}H_2 \quad (6)$$

$$\dot{C}H_3 + CH_2{=}CH(CH_3) \rightarrow CH_3CH_2\dot{C}H(CH_3) \quad (7)$$

$$\dot{C}H_3 + CH_2{=}CH(OH) \rightarrow CH_3CH_2\dot{C}H(OH) \quad (8)$$

$$\dot{C}H_3 + CH(CH_3){=}CH_2 \rightarrow (CH_3)_2CH\dot{C}H_2 \quad (9)$$

$$\dot{C}H_3 + CH(OH){=}CH_2 \rightarrow (CH_3)(OH)CH\dot{C}H_2 \quad (10)$$

both CBS-QB3 and CBS-APNO yielded consistent results, Table 1. Here and elsewhere a single imaginary frequency characterized the location of each transition state for which an optimized geometry could be found. The values obtained for methyl addition to ethene and propene at the CH_2 end, reactions 6 and 7, are in agreement with the vibrationless barriers previously reported by Gómez-Balderas et al.[48] at CBS-QB3. The CBS-RAD results of Fischer and Radom[38] for reactions 7 and 8 are within 0.5 kJ mol^{-1} of the vibrationless barriers computed in this work.

Saeys et al.[49] 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 CH_2 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 6−8 while the CBS-APNO results show an even smaller variation.

TABLE 1: Enthalpy of Activation, $\Delta H^{\circ,\ddagger}$, and of Reaction, $\Delta_r H$, at 298.15 K for Methyl and H-Atom Addition

	$\Delta H^{\circ,\ddagger}$/kJ mol^{-1}		$\Delta_r H$/kJ mol^{-1}		
reaction	CBS-QB3	CBS-APNO	CBS-QB3	CBS-APNO	lit.[61]
$\dot{C}H_3 + CH_2{=}CH_2$	25.7	26.7	−97.1	−100.3	−98.0 ± 1.0
$\dot{C}H_3 + CH_2{=}CH(CH_3)$	24.7	26.1	−98.0	−100.2	−97.9 ± 2.0
$\dot{C}H_3 + CH_2{=}CH(OH)$	26.8	27.7	−97.0	−99.4	−98.5 ± 3.5
$\dot{C}H_3 + CH(CH_3){=}CH_2$	30.6	31.5	−92.9	−95.2	−93.1 ± 1.1
$\dot{C}H_3 + CH(OH){=}CH_2$	36.4	37.3	−86.4	−84.3	−86.1 ± 11.9
$\dot{H} + CH_2{=}CH_2$	2.7	5.5	−148.4	−152.1	−150.9 ± 0.7
$\dot{H} + CH_2{=}CH(CH_3)$		3.4	−148.6	−151.5	−148.0 ± 2.0
$\dot{H} + CH_2{=}CH(OH)$		3.0	−149.8	−152.5	−149.7 ± 3.4
$\dot{H} + CH(CH_3){=}CH_2$	8.2	9.8	−135.9	−138.9	−136.9 ± 1.1
$\dot{H} + CH(OH){=}CH_2$	14.7	15.4	−119.3	−117.9	−118.5 ± 2.6

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, CH_3, 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.[50] who found that $\Delta H^{\circ,\ddagger}$(0 K) increased from 36.7 (for addition to CH_2) to 42.3 kJ mol^{-1} for $CH(CH_3)$ addition in G3X-RAD calculations performed on QCISD/6-31G(d) optimized geometries.

Comparison with Experiment. The addition of a methyl radical to ethylene to form n-propyl radical has been investigated experimentally by two groups. Hogg and Kebarle[51] determined a rate constant of 4.59×10^{11} exp(−3940/T) cm^3 mol^{-1} s^{-1} over the temperature range 392−434 K in a static reactor by normalizing the expression relative to the rate constant for methyl radical self-reaction producing ethane, $2\dot{C}H_3 \rightarrow C_2H_6$. Holt and Kerr[52] determined a rate constant of 2.09×10^{11} exp(−3670/T) cm^3 mol^{-1} 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 $E_a = \Delta H^{\circ,\ddagger} + (1 - \Delta n^{\ddagger})RT$, where $\Delta n^{\ddagger}$ 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 studied by a number of groups.[53−59] Miyoshi and Brinton[53] and Cvetanović and Irwin[54] 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.,[56] using the terminal/internal branching ratio measured by Baldwin et al.[57] at temperatures of 403 and 753 K, derived $k = 1.09 \times 10^{12}$ exp(−4240/T) cm^3 mol^{-1} s^{-1} and $E_a = 35.2$ kJ mol^{-1} attributable to both of these sets of data. The most recent review by Baulch et al.[58] recommends a rate constant of 2.11×10^{11} exp(−3700/T) cm^3 mol^{-1} 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 isobutyl radical. A rate constant of 5.79×10^8 cm^3 mol^{-1} s^{-1} was measured by Baldwin et al.[57] at 753 K, and they also recommended a rate constant of 2.0×10^{11} exp(−4390/T) cm^3 mol^{-1} s^{-1} in the temperature range 353−753 K for this reaction with an activation energy of 36.5 kJ mol^{-1}. Tsang,[59] in his review of propane oxidation kinetics, recommended a rate constant of 9.64×10^{10} exp(−4030/T) cm^3 mol^{-1} s^{-1} between 300 and 2500 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 CH_2 versus $CHCH_3$ 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. Generally speaking, computed reaction enthalpies are less sensitive than energy barriers to the level of theory employed,[38] so the excellent results for both methyl and H-atom addition to $CH_2{=}CHX$ are perhaps not that surprising, Table 1.

Enthalpy changes for reactions 6, 8, and 9 are in good agreement with values computed by Sabbe et al.[60] and with values calculated from enthalpies of formation taken from an authoritative source[61] in conjunction with ΔH_f for *syn*-ethenol of −125.5 kJ mol^{-1} from da Silva et al.[47] and −62.6 ± 11.7 kJ mol^{-1} for the 2-hydroxypropyl radical, $(CH_3)(OH)C\dot{H}CH_2$, from Sun and Bozzelli.[62] The uncertainty associated with the latter is quite high, so reaction enthalpies for the isogeitonic[63] reaction

$$(CH_3)(OH)C\dot{H}CH_2 + CH_3C(O)CH_3{=}(CH_3)(OH)CHCH_3 + CH_3C(O)\dot{C}H_2$$

were computed to be −27.6 and −26.9 kJ mol^{-1}. The average value of −27.3 kJ mol^{-1} together with an associated uncertainty of 0.88 kJ mol^{-1} (twice the standard deviation)[45] was then used in conjunction with known enthalpies of formation for acetone,[64] acetonyl,[63] and isopropanol[61] to calculate ΔH_f(298.15 K) of −61.3 ± 2.2 kJ mol^{-1}, which is in excellent agreement with the Sun and Bozzelli result but carries with it much less uncertainty.

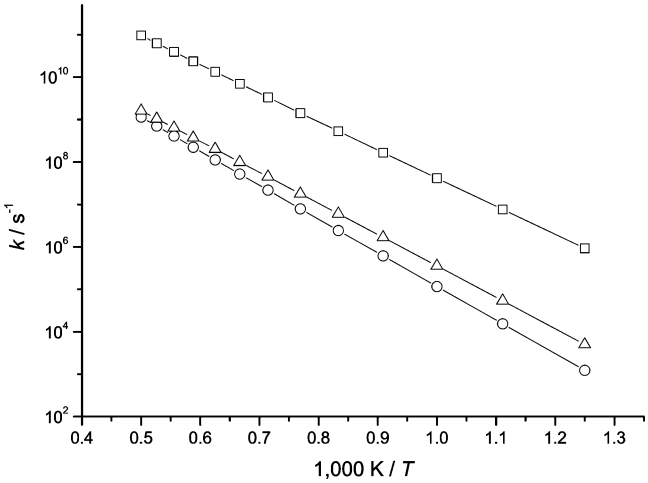

Figure 3. Estimated rate constants for 1-hydroxybutyl decomposition leading to the formation of (□) ethenol, (△) butanal, and (○) butenol.

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TABLE 2: Geometry of Transition States

	r(C···C)/Å		r(C—C)/Å		∠(C···C—C)/deg		i$\bar{\nu}$/cm^{-1}	
TS #	CBS-QB3	CBS-APNO	CBS-QB3	CBS-APNO	CBS-QB3	CBS-APNO	CBS-QB3	CBS-APNO
(6)	2.332	2.277	1.355	1.367	109.7	109.3	401	512
(7)	2.333	2.280	1.357	1.368	109.6	108.7	403	523
(8)	2.335	2.281	1.357	1.366	110.2	109.7	411	548
(9)	2.306	2.271	1.361	1.370	104.4	104.9	454	527
(10)	2.235	2.210	1.367	1.374	103.7	103.8	538	642

The activation and reaction enthalpies are correlated with a linear Evans—Polanyi—Semenov[39] relationship ($r = -0.976$) between them:

$$\Delta H^{\circ,\ddagger}/\text{kJ mol}^{-1} = (0.876 \pm 0.069)\Delta_r H + (112.4 \pm 6.6)$$

Transition State Geometries. The geometry and imaginary frequencies for transition states 6—10 are shown in Table 2; the forming $H_3C\cdots C$ distances are shorter and the breaking C═C bonds are longer for the QCISD/6-311G(d,p) or CBS-APNO geometries. This is in accord with previous findings that DFT geometries tend to predict earlier transition states with longer forming and shorter breaking bonds than QCISD methods.[48]

The shortest forming $H_3C\cdots C$ bond corresponds to the least exothermic reaction, 10, which agrees with the general correlation found for radical-addition reactions.[38]

The angles of approach of ≈109° for addition to the CH_2 end are close to the corresponding angle in the forming radical[38] and there are appreciable deviations from planarity of the H-atoms in the headgroup of 16.1 and 18.2° respectively for ethene and of 33.5 and 33.9° in the methyl radical for tail addition to ethenol. The angles of attack for tail addition are substantially more acute by about 5°, similar to the findings of Hirunsit and Balbuena[65] for $\dot{R} + CH_2{=}CF_2$.

Addition of Ethyl. The addition of ethyl radical to ethene leading to the formation of *n*-butyl

$$CH_3\dot{C}H_2 + CH_2{=}CH_2 \rightarrow CH_3CH_2CH_2\dot{C}H_2 \qquad (11)$$

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 ± 2.2 kJ mol^{-1}. Our standard CBS-QB3 result for $\Delta E(0\text{ K}) = 28.1$ kJ mol^{-1} is within 0.8 kJ mol^{-1} of the nonstandard CBS-QB3 calculation of 27.3 kJ mol^{-1} reported by Saeys et al.[49]

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 3.

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.[66—68] Kerr and Trotman-Dickenson[66] reported a rate constant of 1.12×10^{12} exp(−4330/T) cm^3 mol^{-1} s^{-1} in the temperature range 417—460 K, with an activation energy, E_a, of 36.0 kJ mol^{-1}. Later, Kerr and Parsonage[67] carried out an extensive literature review and recommended $k = 1.58 \times 10^{11}$ exp(−3670/T) cm^3 mol^{-1} s^{-1} from 348—482 K and a lower activation energy of 30.6 kJ mol^{-1}. Morganroth and Calvert[68] reported a rate constant of 2.90×10^{10} exp(−3270/T) cm^3 mol^{-1} s^{-1} from 430—520 K with an even lower $E_a = 27.2$ kJ mol^{-1}.

TABLE 3: Ethyl + Syn-Ethenol Activation Enthalpies (kJ mol^{-1})

reaction	dihedrals	CBS-QB3	CBS-APNO
$CH_2{=}CH(OH)$	TG	26.3	26.5
$CH_2{=}CH(OH)$	GG′	24.3	24.4
$CH_2{=}CH(OH)$	G′G	24.0	24.5
$CH(OH){=}CH_2$	GT	32.4	32.9
$CH(OH){=}CH_2$	TG′	32.9	33.3
$CH(OH){=}CH_2$	G′G	31.6	31.7

Our computed value for reaction 11 of $\Delta H^{\circ,\ddagger} = 24.2$ and $E_a = 30.9$ kJ mol^{-1} is thus in very good agreement with the Kerr and Parsonage[67] recommended activation energy.

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

$$\dot{H} + CH_2{=}CH_2 \rightarrow CH_3\dot{C}H_2 \qquad (12)$$

$$\dot{H} + CH_2{=}CH(CH_3) \rightarrow CH_3\dot{C}H(CH_3) \qquad (13)$$

$$\dot{H} + CH_2{=}CH(OH) \rightarrow CH_3\dot{C}H(OH) \qquad (14)$$

$$\dot{H} + (CH_3)CH{=}CH_2 \rightarrow (CH_3)CH_2\dot{C}H_2 \qquad (15)$$

$$\dot{H} + (OH)CH{=}CH_2 \rightarrow (OH)CH_2\dot{C}H_2 \qquad (16)$$

but transition states for reactions 13 and 14 could not be located in direct CBS-QB3 computations. The geometrical optimizer employed by this model chemistry is B3LYP/CBSB7 (effectively B3LYP/6-311G(2d,d,p)) 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 13. Miller and Klippenstein[69] in their comprehensive paper on the kinetics of reaction 12 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 14 for either expanded basis set.

Note that Saeys and co-workers[49] utilized 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 $\Delta E(0\text{ K})$

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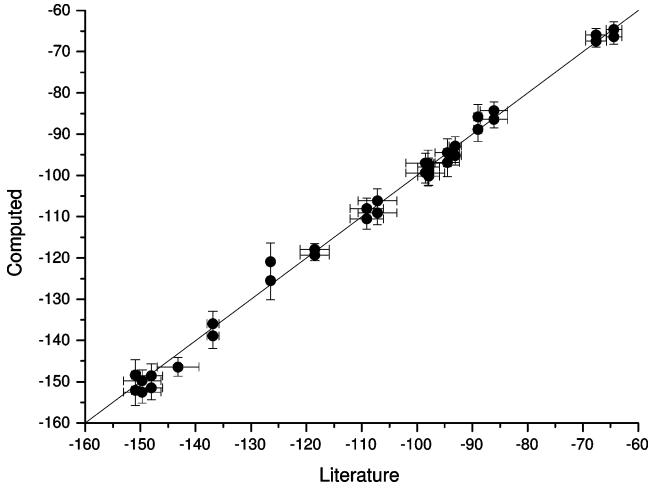

Figure 4. Computed reaction enthalpies compared to literature values (kJ mol^{-1}). The line is the unit slope through the origin.

of 10.1 kJ mol^{-1} for H-atom addition to ethene is substantially different from 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 summarized in Table 1. Good agreement is obtained between computed reaction enthalpies and values from the literature.

Clearly, accurate computations of the barrier heights for H addition are problematic (Miller and Klippenstein[69] list $\Delta E^{\ddagger}$(0 K) values from 11.7 to 22.2 kJ mol^{-1} from a number of very high-level calculations). Their most rigorous result of 11.7 kJ mol^{-1} was obtained from restricted quadratic configuration-interaction with perturbative inclusion of triplet contribution, QCISD(T), using correlation-consistent, polarized valence triple and quadruple-ζ basis sets and extrapolated to the basis set limit. This is in good agreement with our CBS-APNO result of $\Delta E^{\ddagger}$(0 K) = 9.9 kJ mol^{-1}.

The addition of H to butenol to form an α- or 1-hydroxybutyl radical, that is, the reverse of reaction 2,

$$CH_3CH_2CH{=}CH(OH) + \dot{H} \rightarrow CH_3CH_2CH_2\dot{C}HOH$$

did not present any problems, and a CBS-QB3 transition state could be found (ethyl trans to the OH group and with a syn OH). Barrier heights of 4.6 and 6.0 kJ mol^{-1} and reaction enthalpies of −144.1 and −146.4 kJ mol^{-1} compared with $\Delta_r H$ = −143.2 ± 3.8 kJ mol^{-1} (based on $\Delta_f H$(298.15 K) = −96.2 ± 3.4 kJ mol^{-1} for the α-radical and our own value for 1-buten-1-ol vide infra) were computed. Hence, for reaction 2 $\Delta H^{\circ,\ddagger}$ = 150.6 ± 3.7 kJ mol^{-1}.

Comparison with Experiment. The addition of a H atom to ethylene, reaction 12, was studied by Allen et al.[70] and complemented since by many further studies,[71−89] with most but not all fitting the expression of $1.70 \times 10^{10} T^{1.07}$ exp(−730/*T*) cm^3 mol^{-1} s^{-1} developed by Curran.[90] This also agrees well with the value of Baulch et al.[91] of $3.97 \times 10^{9} T^{1.28}$ exp(−650/*T*) cm^3 mol^{-1} s^{-1} with E_a = 5.4 kJ mol^{-1}.

"Head" addition of a H atom to propene, reaction 13, was studied by Wagner and Zellner,[92] who determined $k = 5.40 \times 10^{12}$ exp(−629/*T*) cm^3 mol^{-1} s^{-1}, which is consistently approximately 20% slower than that of Kurylo et al.[93] and has an effective activation energy of 5.2 kJ mol^{-1}. The rate constant recommended by Seakins et al.[94] of $5.70 \times 10^{9} T^{1.16}$ exp(−440/*T*) cm^3 mol^{-1} s^{-1} is a high-pressure extrapolation of a measurement of the rate constant in the pressure range 1−9 Torr. Curran[90] recommended a rate constant of $4.24 \times 10^{11} T^{0.51}$ exp(−619/*T*) cm^3 mol^{-1} s^{-1}, which is a best fit an to the experimental data of Kurylo et al.[93] and Tsang[95] and the high pressure extrapolation of Seakins et al.[94]

Wagner and Zellner[92] studied the reaction of a H atom with propene to form the *n*-propyl radical, "tail" addition, and determined $k = 4.40 \times 10^{12}$ exp(−1380/*T*) cm^3 mol^{-1} s^{-1} and E_a = 11.5 kJ mol^{-1}. Tsang[95] quotes $k = 1.3 \times 10^{13}$ exp(−1640/*T*) cm^3 mol^{-1} s^{-1} and E_a = 13.6 kJ mol^{-1} under the same conditions as those reported for the formation of isopropyl radical.

The clearest experimental evidence for the increase in barrier height in going from "head", reaction 13, to "tail" reaction 15, addition of H to propene,

$$CH_3\dot{C}HCH_3 \xleftarrow{(13)} CH_3CH{=}CH_2 \xrightarrow{(15)} CH_3CH_2\dot{C}H_2$$

thus comes from the work of Wagner and Zellner;[92] they indicate that E_a changes from 5.2 to 11.5 kJ mol^{-1} commensurate with our computations of $\Delta H^{\circ,\ddagger}$ going from 3.4 to 9.8 kJ mol^{-1}, Table 1.

H-Atom Addition to Lower Aldehydes. ***O-Centered Addition.*** Theoretical calculations of the energy barrier for H-atom addition to the aldehyde butanal at the O-center did not present any difficulties, Table 5; both CBS-QB3 and CBS-APNO methods yield transition states that lie 38.5 and 36.9 kJ mol^{-1} above the reactants. There are no experimental or theoretical values known against which we could compare this result.[96] In conjunction with computed reaction enthalpies of −108.0 and −110.5 kJ mol^{-1}, the enthalpy of activation is 147.0 ± 1.0 kJ mol^{-1}, for the reverse reaction:

$$CH_3CH_2CH_2\dot{C}HOH \xrightarrow{(1)} CH_3CH_2CH_2CH{=}O + \dot{H}$$

The enthalpy of formation of butanal ranges quite widely from the −211.8 ± 0.9 kJ mol^{-1} of Wiberg et al.[97] to the −204.4 ±

TABLE 4: Enthalpies of Formation (kJ mol^{-1}) of Reference Species

species	$\Delta_f H°$(298.15 K)	ref
$\dot{C}H_2OH$	−17.18 ± 0.37	61
$CH_3\dot{O}$	20.26 ± 0.42	101
CH_2O	−108.7 ± 05	101
CH_3OH	−201.2 ± 0.2	61
CH_2CH_2	52.6 ± 0.4	61
CH_3CHO	−166.6 ± 0.4	61
CH_2CHOH	−125.5 ± 2.0	47
$CH_3\dot{C}H_2$	119.7 ± 0.7	61
$CH_3\dot{C}HOH$	−55.8 ± 3.5	99
$CH_3CH_2\dot{O}$	−13.0 ± 1.3	45
CH_3CH_2OH	−234.61 ± 0.28	61
$CH_3CO\dot{C}H_2$	−34.9 ± 1.9	63
CH_3CHCH_2	−20.2 ± 0.4	61
CH_3COCH_3	−217.9 ± 0.7	64
$CH_3CH(OH)\dot{C}H_2$	−62.6 ± 11.7	62
$CH_3CH(OH)CH_3$	−272.8 ± 0.3	61
$CH_3CH_2CH_2OH$	−255.2 ± 1.3	61
$CH_3CH_2CH_2CHO$	−204.4 ± 1.4	98
$CH_3CH_2CHCH_2$	−0.03 ± 0.47	61
$(CH_3)_2CCH_2$	−17.57 ± 0.52	61
$CH_3CH_2CH_2CH_2\dot{O}$	−49.8 ± 1.3	45

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1.4 kJ mol^{-1} of Buckley and Cox;[98] hence the enthalpy change for reaction 1 is either -101.7 ± 2.8 or -109.1 ± 3.0 kJ mol^{-1} using a formation enthalpy of -96.2 ± 3.4 kJ mol^{-1} for the 1-hydroxybutyl radical, which is based on a number of isodesmic reactions at the CBS-QB3 level only. Our results would therefore tend to indicate that the Buckley and Cox value for butanal is more nearly correct and we have consequently adopted it.

For H-addition to *n*-propanal the energy barriers range from 37 to 40 kJ mol^{-1} depending on the rotamer chosen (the synperiplanar conformer is slightly favored); together with computed reaction enthalpies, an estimated energy barrier of 146.4 ± 3.3 kJ mol^{-1} results for the reaction:

$$CH_3CH_2\dot{C}HOH \rightarrow CH_3CH_2CH{=}O + \dot{H}$$

In the case of O-centered addition of a hydrogen atom to acetaldehyde/ethanal,

$$CH_3CH{=}O + \dot{H} \rightarrow CH_3\dot{C}HOH \qquad (17)$$

barriers heights of $38.5-38.9$ kJ mol^{-1} are found and reaction enthalpies of -106.2 to -109.1 are in good agreement with a literature value of -107.2 ± 3.5 kJ mol^{-1} (based on enthalpies of formation for ethanal/acetaldehyde[61] and for the 1-hydroxyethyl radical).[99] The reverse reaction, the H-elimination from 1-hydroxyethyl to form the aldehyde, has $\Delta H^{\ddagger} = 146.4 \pm 3.3$ kJ mol^{-1}.

These results show 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. Formation of the hydroxymethylene radical, via addition at the O-center,

$$H_2C{=}O + \dot{H} \rightarrow \dot{C}H_2OH \qquad (18)$$

has an energy barrier of $38.0-39.6$ kJ mol^{-1}; this is sharply different from that used by Tsuboi et al.[100] of 5.0 kJ mol^{-1}. For the reverse reaction the energy barrier is 162.0 ± 6.2 kJ mol^{-1} given that reaction enthalpies of -120.9 and -125.5 kJ mol^{-1} were computed for reaction 18, which are in good agreement with that calculated from the literature of -126.5 ± 0.6 kJ mol^{-1}, based on values for hydroxymethylene[101] and formaldehyde.[61]

C-Centered Addition. H-atom addition at the C-center of butanal is expected to be kinetically and thermodynamically favored over O-center addition as Henry and others[50] 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:

$$CH_3CH_2CH_2CH{=}O + \dot{H} \rightarrow CH_3CH_2CH_2CH_2\dot{O}$$

In conjunction with computed reaction enthalpies of -67.4 and -65.9 kJ mol^{-1} (compared with a $\Delta_r H$ of -67.6 ± 1.9 kJ mol^{-1} calculated from enthalpies of formation for the *n*-butoxyl radical[45] and the Buckley and Cox value for butanal)[98] we estimate barriers of 85.0 ± 0.8 kJ mol^{-1} for the reverse reaction

$$CH_3CH_2CH_2CH_2\dot{O} \xrightarrow{(5)} CH_3CH_2CH_2CH{=}O + \dot{H}$$

which is in very good agreement with the activation energy of 88 ± 6 kJ mol^{-1} of Hack et al.[102]

Thus, although this route to butanal is energetically favored, it must be remembered that the alkoxyl radical is not a major byproduct 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 butoxyl radical being formed via a facile 1,5 H-shift reaction,

$$\dot{C}H_2CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH_2CH_2\dot{O}$$

for which we calculate reaction barriers of $46.6-44.9$ kJ mol^{-1} (in excellent agreement with computations by Somnitz).[103] The relative rates of radical production at 1000 K by H-abstraction from the parent butanol by the O_2 molecule are $\alpha{:}\beta{:}\gamma{:}\delta{:}$O as 130:20:6:9:1, as estimated by Moss et al.[10]

Similar considerations apply for the other aldehydes; for C-centered addition to propanal barriers of $18.0-20.2$ kJ mol^{-1} are found, which translates to a barrier of 86.7 ± 2.6 kJ mol^{-1} for

$$CH_3CH_2CH_2\dot{O} \rightarrow CH_3CH_2CH{=}O + \dot{H}$$

This result is in excellent agreement with the work of Rauk et al.,[104] who reported enthalpy barriers of 21.3 and 83.4 kJ mol^{-1}, respectively. Their calculations utilized a variant of CBS-RAD, which is itself a variant of the CBS-QB3 composite method developed to overcome problems of spin contamination in the computation of the properties of radicals.[105] The geometry optimizer in CBS-RAD is based upon the functional B3LYP with a 6-31G(d) basis set whereas the standard CBS-QB3 method uses B3LYP/6-311G(2d,d,p). The net result is little different; such variability as exists can be attributed principally to the different enthalpy of formation used by Rauk et al. for the 1-propoxy radical.

For C-centered addition to ethanal, the same conclusions are arrived at; namely, the barrier heights of 19.6 and 22.0 kJ mol^{-1} (in good agreement with $E_a = 22.4 - 27.0$ kJ mol^{-1})[104,106] allied to reaction enthalpies of -64.6 and -66.4 kJ mol^{-1} (compared with a literature value of -64.4 ± 1.4 kJ mol^{-1} based on -13.0 ± 1.3 kJ mol^{-1} for the ethoxy radical)[45] are considerably smaller than for O-centered addition. The elimination of a hydrogen atom from the ethoxy radical

TABLE 5: Enthalpy of Activation, $\Delta H^{\circ,\ddagger}$, and of Reaction, $\Delta_r H$, at 298.15 K for H-Atom Addition to RCHO Where R = H, Methyl, Ethyl and *n*-Propyl

	$\Delta H^{\circ,\ddagger}$/kJ mol^{-1}		$\Delta_r H$/kJ mol^{-1}		
R	CBS-QB3	CBS-APNO	CBS-QB3	CBS-APNO	lit.[61]
			$\dot{H} + CHR{=}O \rightarrow RCH_2\dot{O}$		
H	11.0	13.7	−85.8	−88.3	-89.0 ± 0.7
Me	19.6	22.0	−64.4	−66.4	-64.4 ± 1.4
Et	18.0	20.2	−67.4	−67.8	-65.1 ± 2.1
nPr	17.2	19.5	−67.4	−65.9	-67.6 ± 1.9
			$\dot{H} + O{=}CHR \rightarrow HO\dot{C}HR$		
H	38.0	39.6	−120.9	−125.5	-126.5 ± 0.6
Me	38.5	38.9	−106.2	−109.1	-107.2 ± 3.5
Et	38.3	36.8	−106.3	−109.2	-107.4 ± 3.3
nPr	38.5	36.9	−108.0	−110.5	-109.1 ± 3.7

$$CH_3CH_2\dot{O} \rightarrow CH_3CH{=}O + \dot{H} \quad (19)$$

thus has barrier heights of 86.3 ± 4.2 kJ mol^{-1} essentially identical to those computed above for the other alkoxy radical decompositions and in excellent agreement with the Rauk et al.[104] value of 85.1 kJ mol^{-1} and the activation energy of 84 kJ mol^{-1} due to Caralp et al.[107] but not with the 101 kJ mol^{-1} of Hoyermann et al.[108] nor with the only experimental value of 98 kJ mol^{-1} due to Batt.[109]

Hence for the three alkyl-substituted carbonyl compounds the results are independent of the nature of the alkyl group; to what extent is this the case for methanal? For the reaction between H-atom and formaldehyde,

$$O{=}CH_2 + \dot{H} \rightarrow CH_3\dot{O} \quad (20)$$

we calculate that the formation of the methoxy radical requires surmounting an energy barrier, $\Delta H^{\circ,\ddagger}$, of 11.0−13.7 (in good agreement with $\Delta H^{\ddagger}$ = 13.8 kJ mol^{-1} of Rauk et al.[104] and with activation energies of 17.2,[90] 18.7,[104] and 22.0[106] kJ mol^{-1}), and hence for the reverse reaction a barrier of 99.4 ± 5.2 kJ mol^{-1} is computed on the basis of enthalpies of −85.8 and −88.8 kJ mol^{-1} for reaction 20 as compared to a literature value of −89.0 ± 0.7 kJ mol^{-1}.

The increase in barrier height seen in going from C-centered to O-centered addition parallels that found much earlier by Sosa and Schlegel;[110] they highlighted the fact that spin contamination of the transition state affects the calculation of barrier heights in these systems. The CBS multilevel methods used here do include empirical corrections for open shell species which should lessen the consequences of spin contamination.

Hippler et al.[111] computed barrier heights, $\Delta H^{\circ\ddagger}$(650 K), 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 99.4 ± 5.2 kJ mol^{-1}.

Hippler and Viskolcz[106] 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-center are effectively the same for methanal, ethanal, propanal, and butanal and higher than those for C-centered addition for which only the formaldehyde differs from the rest, Table 5. Rauk and co-workers[104] reported similar differences for H and methyl C-centered addition to formaldehyde and monosubstituted alkyl aldehydes.

The transition state geometries for both C- and O-centered addition show the close relationship between these reactions, Table 6. As before, the forming H···O and H···C bonds are shorter and the breaking O—C bonds are longer in the QCISD case than in the DFT one.

Enol/Keto Isomerization. The isomerization of butenol to butanal is slightly exothermic, −36.2 and −36.1 kJ mol^{-1}, but has barrier heights of 244.1−240.5 kJ mol^{-1} at CBS-QB3 and CBS-APNO, respectively; the propenol ↔ propanal numbers are virtually identical and differ considerably from the 290 kJ mol^{-1} barrier calculated by Qin et al.[112] Our values are not dissimilar from the −40.6 and +229.3 kJ mol^{-1} computed by da Silva et al.[47] for the vinyl alcohol (ethenol) ↔ acetaldehyde (ethanal) isomerization at CBS-APNO. Hence it appears that replacing the *trans*-hydrogen atom by an ethyl group in ethenol has very little effect as regards enol/keto isomerization. In addition, these values that we have obtained for exothermicities and barriers are fairly typical of enol/keto species; exceptions to this involve either conjugation of the double bond or steric considerations[113] or a quite unusual molecular architecture,[30] none of which apply in this situation.

Since the formation enthalpy of *syn*-(*E*)-1-buten-1-ol is not known[114] we have calculated it via a pair of isodesmic, but not isogeitonic, reactions:

$$CH_3CH_2CH{=}CH(OH) + CH_3OH \rightarrow CH_2{=}CH(OH) + (CH_3)(OH)CHCH_3 \quad (21)$$

$$CH_3CH_2CH{=}CH(OH) + CH_3OH \rightarrow CH_2{=}CH(OH) + CH_3CH_2CH_2OH \quad (22)$$

Computed reaction enthalpies of −26.1 and −25.9 kJ mol^{-1} for reaction 21 and −6.8 and −6.9 kJ mol^{-1} for reaction 22 lead to a final ΔH_f(298.15 K) = −171.8 ± 1.6 kJ mol^{-1} based on methanol, propanol, and isopropanol formation enthalpies.[61] Hence the predicted enthalpy change for butenol/butanal isomerization is −32.6 ± 2.1 kJ mol^{-1} in good agreement with our direct calculations of −36.1 kJ mol^{-1}.

A similar approach was used to determine the formation enthalpies for the other enols; for *syn*-propen-1-ol (*E*) using the reaction partners ethanol, ethenol, and propanol first and then second propene, ethenol, and but-1-ene yields a final enthalpy of formation of −151.8 ± 1.7 kJ mol^{-1}, which is not in good agreement with the −169 kJ mol^{-1} determined mass spectrometrically by Tureček.[115] In the case of propen-2-ol using the reaction partners ethanol, ethenol, and isopropanol and then propene, ethenol and isobutene yields −169.9 ± 1.5 kJ mol^{-1}, which is in fair agreement with the −176 ± 10 kJ mol^{-1} of Tureček and Havlas.[116]

All of the above results are anchored on the most reliable value for ethenol, which was obtained recently by da Silva et al. of −125.5 ± 2.0 kJ mol^{-1} from multiple determinations (at CBS-Q, CBS-APNO, and G3 levels) of the reaction enthalpies of three isodesmic reactions[47] and nicely spans the experimental measurements of Tureček and Havlas[116] (−128), of Holmes and Lossing[117] (−125 ± 8) and of Holmes et al. (−111 ± 8 kJ mol^{-1}).[118] A complete listing of the formation enthalpies of reference species employed can be found in Table 4.

Elimination Reactions. The barrier heights for the elimination of either hydrogen or water from *n*-butanol are expected to be quite large:

$$CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH_2CH{=}O + H_2 \quad (23)$$

$$CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH{=}CH_2 + H_2O \quad (24)$$

Computations show that this is indeed the case; for reaction 23 a barrier of 358.5 ± 2.5 kJ mol^{-1} is found while for reaction 24 the comparable value is 282.0 ± 4.5 kJ mol^{-1}.

In reality, the presence of a large number of rotamers for *n*-butanol makes precise calculation of these barriers quite complex; the subject is treated in more detail in Moc et al.[32] including all 14 energetically distinct conformers that lie within 9 kJ mol^{-1} of the lowest energy isomer TGt (labeling the CCCC, CCCO, CCOH dihedrals in sequence as trans T or gauche G).

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TABLE 6: Geometry of Transition States for H-Addition to RCHO

	$\dot{H} + O{=}CHR \rightarrow HO\dot{C}HR$							
	$r(H\cdots O)$		$r(O{-}C)$		∠HOC/deg		$i\bar{\nu}$/cm^{-1}	
	CBS-QB3	CBS-APNO	CBS-QB3	CBS-APNO	CBS-QB3	CBS-APNO	CBS-QB3	CBS-APNO
H	1.574	1.479	1.227	1.243	122.0	119.2	1182	1740
Me	1.543	1.467	1.233	1.245	119.7	115.9	1210	1848
Et	1.554	1.471	1.232	1.244	116.7	115.0	1193	1840
nPr	1.554	1.471	1.232	1.244	116.8	115.0	1193	1843
	$\dot{H} + CHR{=}O \rightarrow RCH_2\dot{O}$							
	$r(H\cdots C)$		$r(O\overset{\cdots}{-}C)$		∠HCO/deg		$i\bar{\nu}$/cm^{-1}	
	CBS-QB3	CBS-APNO	CBS-QB3	CBS-APNO	CBS-QB3	CBS-APNO	CBS-QB3	CBS-APNO
H	1.952	1.784	1.212	1.227	104.6	102.7	633	977
Me	1.845	1.738	1.220	1.231	99.6	98.8	813	1136
Et	1.860	1.749	1.220	1.231	100.0	99.3	785	1123
nPr	1.861	1.749	1.220	1.231	100.2	99.5	780	1124

TABLE 7: Enthalpy of Activation, $\Delta H^{\circ,\ddagger}$, for H Elimination Reactions

$\Delta H^{\ddagger}$/kJ mol^{-1}	product	reactant	product	$\Delta H^{\ddagger}$/kJ mol^{-1}
		$H\dot{C}HOH \rightarrow$	$H\dot{C}HO$	162.0 ± 6.2
154.2 ± 2.7	HCH=CHOH	$\leftarrow CH_3\dot{C}HOH \rightarrow$	CH_3CHO	146.4 ± 3.3
147.6 ± 2.7	$CH_3CH{=}CHOH$	$\leftarrow C_2H_5\dot{C}HOH \rightarrow$	C_2H_5CHO	145.3 ± 1.4
150.6 ± 3.7	$C_2H_5CH{=}CHOH$	$\leftarrow C_3H_7\dot{C}HOH \rightarrow$	C_3H_7CHO	147.0 ± 1.0

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Both reactions are endothermic with reaction enthalpies of 69.3 ± 4.4 kJ mol^{-1} for (23) and 39.1 ± 0.6 kJ mol^{-1} for (24). As previously noted, the Buckley and Cox value for butanal predicts a reaction enthalpy for reaction 23 of 70.3 kJ mol^{-1}, which is in excellent agreement with our computed mean value whereas the Wiberg et al. formation enthalpy leads to $\Delta_r H(23)$ of 62.9 kJ mol^{-1}.

Aldehydes versus Enols. On the basis of the results obtained above, we now consider the relative rates of formation of aldehydes and isomeric enols first from the 1-hydroxyethyl radical:

$$\dot{H} + CH_2{=}CH(OH) \overset{(-14)}{\leftarrow} CH_3\dot{C}HOH \overset{(-17)}{\rightarrow} CH_3CH{=}O + \dot{H}$$

the corresponding barriers are 144.7−148.0 for reaction −17 (Bhaskharan et al.[119] quote $E_a = 91.5$ kJ mol^{-1}) and 155.5 kJ mol^{-1} for reaction −14. A summary of the barrier heights for the 1-hydroxyalkyl radicals is given in Table 7, where possible the barrier for the reverse reaction, $\Delta_r H^{\ddagger}$, is derived from the mean of $(\Delta_f H^{\ddagger} - \Delta_r H)$ and the quoted error is twice the standard deviation. In those cases where the CBS-QB3 method did not yield a transition state, then the average enthalpy of reaction is used in conjunction with the CBS-APNO transition state; although perhaps not entirely satisfactory, this procedure does allow an uncertainty to be computed.

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[7] in isobutanol flames can be easily explained since β-scission of the parent leads directly to a 1-hydroxyethyl radical:

$$CH_3CH_2CH(OH)CH_3 \rightarrow CH_3\dot{C}H_2 + \dot{C}H(OH)CH_3$$

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

These rate constants can be estimated by using the correspondences established *here*, as regards barrier heights,

$$\Delta H^{\ddagger}\{\dot{H} + CH_2{=}CH(CH_3)\} \equiv \Delta H^{\ddagger}\{\dot{H} + CH_2{=}CH(OH)\}$$

to also apply to rate constants. The rate constants of the reverse reactions, k_r, are then obtained from the equilibrium constant, K, and the forward rate constant, k_f taken from a review article by Curran.[90] The equilibrium constants are computed from the usual thermodynamic parameters, which can be estimated from group additivity considerations or indeed from first principles.

Hence, for aldehyde production $k_{-17} = 2.92 \times 10^{14} T^{-0.46} \exp(-17600/T)$ and for enol formation $k_{-14} = 5.57 \times 10^{11} T^{0.504} \exp(-19190/T)$ s^{-1}. The results are shown in Figure 1; at 1000 K this method of estimation predicts an aldehyde to isomeric enol ratio of 3.2, which is in good agreement with an evaluation calculated directly from the ratio of rotational and vibrational partition functions and the difference in barrier heights.

For normal alcohols with more than two carbon atoms β-scission of the parent α-radical leads to a rather surprising result. For example in the case of the 1-hydroxypropyl radical:

$$CH_3CH_2\dot{C}HOH \rightarrow \dot{C}H_3 + CH_2{=}CHOH \qquad (25)$$

a rate constant, k_{25}, of $5.01 \times 10^{10} T^{1.04} \exp(-15325/T)$ s^{-1} can be estimated, on the basis of the work of Curran,[90] on the assumption that reaction 7 $\dot{C}H_3 + CH_2{=}CHCH_3$ behaves similarly to reaction 8 $\dot{C}H_3 + CH_2{=}CHOH$ and hence that the rate constants are transferable.

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The H-atom elimination channels

$$CH_3CH_2\dot{C}HOH \rightarrow CH_3CH_2CH{=}O + \dot{H} \quad (26)$$

$$CH_3CH_2\dot{C}HOH \rightarrow CH_3CH{=}CHOH + \dot{H} \quad (27)$$

can be similarly estimated to have rate constants of $k_{26} = 7.03 \times 10^9 T^{0.99} \exp(-16400/T)$ s^{-1} and $k_{27} = 5.46 \times 10^{11} T^{0.343} \exp(-17930/T)$ s^{-1}. Over the temperature range 800−2000 K, therefore, the formation of enols dominates over that of the aldehyde, Figure 2, by factors of about 100. Li and co-workers[13] have identified all these three products in lean *n*-propanol flames in addition to considerable quantities of acetaldehyde, which they consider to arise from the isomerization of ethenol. They report ethanal:ethenol:propanal:propenol(s) ratios of 40:5:125:1, albeit at different positions within the flame, and argue that ethanal or acetaldehyde can only be formed effectively from the isomerization of ethenol. We have shown that the formation of propanal is only slightly more favored than that of propenol thus it is probable that such ratios imply that the isomerization of propenol is also of importance.

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

$$CH_3CH_2CH_2\dot{C}HOH \rightarrow CH_3\dot{C}H_2 + CH_2{=}CH(OH) \quad (28)$$

we compute an enthalpy of activation of 122.3 ± 2.4 kJ mol^{-1}. This is very similar to the reverse of reactions 6−10, that is, elimination of methyl radical through β-scission, Table 8. As before, we can estimate a rate constant of $k_{28} = 1.52 \times 10^{12} T^{0.60} \exp(-14660/T)$ s^{-1}.

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

$$\dot{H}+CH_3CH_2CH{=}CH(OH) \xleftarrow{(2)} CH_3CH_2CH_2\dot{C}HOH \xrightarrow{(1)} CH_3CH_2CH_2CH{=}O + \dot{H}$$

for which we predict barriers of (1) 147.0 ± 1.0 kJ mol^{-1} and (2) 150.6 ± 3.6 kJ mol^{-1}, Table 7. Estimation leads to $k_1 = 3.07 \times 10^{14} T^{-0.45} \exp(-17460/T)$ and $k_2 = 4.07 \times 10^{11} T^{0.40} \exp(-17830/T)$ s^{-1}. An estimation of the relative reaction rates can also 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 1000 K. Note that Archibald et al. in their recent paper on the atmospheric transformation of enols[29] assumed an acetaldehyde to ethenol ratio of 2:1 from tailpipe-out emissions.

TABLE 8: Enthalpy of Activation, $\Delta H^{\circ,\ddagger}$, for Methyl Elimination Reactions

reaction	$\Delta H^{\circ,\ddagger}$/kJ mol^{-1} CBS-QB3	CBS-APNO
$CH_3CH_2\dot{C}H_2 \rightarrow \dot{C}H_3 + CH_2{=}CH_2$	122.8	127.0
$CH_3CH_2\dot{C}HCH_3 \rightarrow \dot{C}H_3 + CH_2{=}CH(CH_3)$	122.7	126.3
$CH_3CH_2\dot{C}H(OH) \rightarrow \dot{C}H_3 + CH_2{=}CH(OH)$	123.8	127.1
$(CH_3)_2CH\dot{C}H_2 \rightarrow \dot{C}H_3 + CH(CH_3){=}CH_2$	125.8	126.7
$CH_3CH(OH)\dot{C}H_2 \rightarrow \dot{C}H_3 + CH(OH){=}CH_2$	122.8	121.6

For the β-radical, H-elimination only yields butenol:

$$CH_3CH_2\dot{C}HCH_2OH \rightarrow CH_3CH_2CH{=}CHOH + \dot{H}$$

with $\Delta H^{\circ,\ddagger}$ of 135.2 and 137.4, respectively, or 136.3 ± 2.2 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

$$CH_3CH_2CH_2CH_2OH \xrightarrow{-H_2O} CH_3CH_2CH{=}CH_2 \xrightarrow{(i)+\dot{O}H(ii)-\dot{H}} CH_3CH_2CH{=}CHOH$$

is possible, it is scarcely credible. A similar conclusion has been recently reached by Wang et al.[17] from experiments of low-pressure cold plasma discharges in C2−C4 alcohols. It has been considered that the direct interconversion of butenol to butanal with a barrier of ca. 242 kJ mol^{-1} is unlikely to feature in reactions in flames or shock waves. However, very recently, Zhou et al.[120] have shown that the dominant unimolecular fate of propen-2-ol (they considered 12 possible decomposition channels) is to isomerize to acetone, which then produces acetyl and methyl radicals:

$$H_2C{=}C(CH_3)OH \rightarrow CH_3C(O)CH_3 \rightarrow CH_3\dot{C}O + \dot{C}H_3$$

If this is true of enols in general, then the only kinetic distinction between an enol and its isomeric aldehyde (or ketone) will arise from different rates of destruction. These are not known at this time and represent a considerable experimental and computational challenge. What is known is that the O−H bond strength in ethenol is weaker by about 16 kJ mol^{-1} than the aldehydic C−H bond in ethanal and is considerably weaker than the C−H bonds in ethenol.[47]

Conclusions

Activation enthalpies for methyl addition to the CH_2 group of $CH_2{=}CHX$ where X = H, OH, and CH_3 average 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 CH_3. Replacing the attacking methyl radical by ethyl makes very little difference to addition at CH_2 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 13 and 14. 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, propanal, and butanal we see that for addition at the O-center the barrier heights of ∼38 kJ mol^{-1} are not influenced by the nature of the alkyl group whereas addition at the C-center is different on going from H → alkyl but seems to be invariant at ∼20 kJ mol^{-1} once alkylated. The reverse reactions, H-elimination from $RCH_2\dot{O}$, thus have barriers of ∼86 kJ mol^{-1} for R = methyl through *n*-propyl but a higher barrier of 99 kJ mol^{-1} for R = H.

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.

Computed reaction enthalpies are in excellent agreement with experimental values in all those cases where comparisons can be made, Figure 4. Finally, as regards enthalpies of formation we recommend the Buckley and Cox value for butanal of $\Delta_f H(298.15\ \mathrm{K}) = -204.4 \pm 1.4\ \mathrm{kJ\ mol^{-1}}$, we have reduced the uncertainty surrounding the 2-hydroxypropyl radical to $\Delta_f H(298.15\ \mathrm{K}) = -61.3 \pm 2.2\ \mathrm{kJ\ mol^{-1}}$, and we propose for 1-buten-1-ol, 1-propen-1-ol and propen-2-ol $\Delta_f H(298.15\ \mathrm{K}) = -171.8 \pm 1.6$, -151.8 ± 1.7, and $-169.9 \pm 1.5\ \mathrm{kJ\ mol^{-1}}$, respectively.

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