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Enthalpies of Formation, Bond Dissociation Energies and Reaction Paths for the Decomposition of Model Biofuels: Ethyl Propanoate and Methyl Butanoate[†]

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The complete basis set method CBS-QB3 has been used to study the thermochemistry and kinetics of the esters ethyl propanoate (EP) and methyl butanoate (MB) to evaluate initiation reactions and intermediate products from unimolecular decomposition reactions. Using isodesmic and isogeitonic equations and atomization energies, we have estimated chemically accurate enthalpies of formation and bond dissociation energies for the esters and species derived from them. In addition it is shown that controversial literature values may be resolved by adopting, for the acetate radical, $CH_3C(O)\dot{O}$, $\Delta H_f^\circ(298.15K) = -197.8$ kJ mol^{-1} and for the *trans*-hydrocarboxyl radical, $\dot{C}(O)OH$, -181.6 ± 2.9 kJ mol^{-1}. For EP, the lowest energy decomposition path encounters an energy barrier of ~210 kJ mol^{-1} (~50 kcal mol^{-1}), which proceeds through a six-membered ring transition state (retro-ene reaction) via transfer of the primary methyl H atom from the ethyl group to the carbonyl oxygen, while cleaving the carbon−ether oxygen to form ethene and propanoic acid. On the other hand, the lowest energy path for MB has a barrier of ~285 kJ mol^{-1}, producing ethene. Other routes leading to the formation of aldehydes, alcohols, ketene, and propene are also discussed. Most of these intramolecular hydrogen transfers have energy barriers lower than that needed for homolytic bond fission (the lowest of which is 353 kJ mol^{-1} for the $C_\alpha-C_\beta$ bond in MB). Propene formation is a much higher energy demanding process, 402 kJ mol^{-1}, and it should be competitive with some C−C, C−O, and C−H bond cleavage processes.

Introduction

Biofuels provide alternative fuels for the transport sector and are hoped to both lessen our dependence on petroleum and also minimize climate change because they consume significantly less fossil energy and produce fewer greenhouse gases than gasoline/petrol or diesel and also have the potential to reduce particulate matter emissions.[1] Thus the European Union has, for example, mandated that biofuels should comprise 5.75% of the automotive fuel market by 2010.

It is not likely that biofuels will totally replace conventional fuels in the foreseeable future because that would require more than 20% of the current terrestrial net primary productivity of the biosphere[2] to sustain such a target. In addition, there is a major environmental concern that cheap biofuel produced in palm oil plantations will have a severe impact on the tropical rainforest,[3] thus essentially wiping out whatever gains are made elsewhere.

However, there is a good case to be made for the modest usage of renewable fuels sourced not only from crops that are not used as human foodstuffs such as the seeds from *Mesua ferrea* or *Pongania glabra*[4] but also from waste vegetation and recycled animals fats. In a major U.S. study Hill et al.[5] conclude that biodiesel sourced from soybeans offers significant advantages over bioethanol from corn as it yields 54% more energy compared to the energy invested in its production, releases only a fraction of the agricultural nitrogen, phosphorus and pesticides, and also emits much smaller quantities of air pollutants.

For this reason and for the fact that biodiesel is the most heavily used biofuel within the EU we have embarked on a study of its combustion chemistry. This effort complements and extends earlier work on a number of oxygenated compounds by our group.[6−26]

Direct studies of typical biodiesels, usually methyl or ethyl esters of fatty acids, are currently beyond our capabilities both because the laboratory experiments would have to be carried out on complex, largely involatile, mixtures and also because the modeling and simulation is not sufficiently developed to be able to tackle such large molecules.[27] Hence, we have chosen to work on model compounds, methyl butanoate or butyrate (MB), and ethyl propanoate or propionate (EP), which encapsulate all the essential chemical motifs of the real biodiesel and can therefore be used to provide insights into the combustion chemistry of the natural product.

Here we explore the thermochemistry and the kinetics of unimolecular decomposition reactions of MB, $CH_3CH_2CH_2C(O)OCH_3$, and EP, $CH_3CH_2C(O)OCH_2CH_3$, including the standard enthalpies of formation for stable molecules, intermediates and transition states using ab initio theories. The determination of bond dissociation energies[28] allows the identification of the weakest bonds, and the formation enthalpies help in finding the most reactive hydrogen atoms in the parent molecule; this enables the evaluation of initiation reactions—important for subsequent modeling work. Because less than 0.02% of known organic species have had their heats of formation measured,[29] the application of quantum methods is both inevitable and desirable provided that reasonable accuracy can be obtained.

There is surprisingly little known about the energetics of ethyl propanoate in the literature. Luo[29] quotes a bond dissociation energy (BDE) of the C−H bond adjacent to the C═O group of

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TABLE 1: Assumed ΔH_f°(298K) (kJ mol^{-1})

species	ΔH_f°	ref	species	ΔH_f°	ref
$CH_3CC(O)OCH_3$	-413.5 ± 1.2	75	$CH_3CH_2C(O)OCH_3$	-432.5	69
CH_3OH	-201.1 ± 0.2	76	C_3H_7OH	-255.1	52
CH_3CHO	-166.1 ± 0.5	77	C_3H_7CHO	-204.4 ± 1.4	49
$CH_3C(O)OH$	-432.2 ± 0.4	52	$C_3H_7C(O)OH$	-475.7 ± 1.1	78
$CH_3\dot{O}$	$+21.0 \pm 2.1$	79	$CH_3CH_2C(O)OH$	-455.7	52
CH_3CH_3	-83.8 ± 0.3	80	$CH_3\dot{C}H_2$	$+118.8 \pm 1.3$	81
$CH_3CH_2\dot{C}H_2$	$+100.0 \pm 2.0$	82	$\dot{C}H_3$	$+146.7 \pm 0.3$	79
CH_3OCH_3	-184.1 ± 0.5	83	$CH_3\dot{O}CH_2$	-0.4	52
$CH_3CH_2CH_3$	-104.7 ± 0.5	80	$HC(O)OCH_2CH_3$	-398.3	84
$CH_3C(O)CH_3$	-217.9 ± 0.7	48, 77	$CH_3C(O)\dot{C}H_2$	-34.9 ± 1.9	46
$CH_3C(O)OCH_2CH_3$	-444.8 ± 0.4	83	$\dot{C}H_2CH_2OH$	-29.3	85
$HCHO$	-109.0 ± 1.8	86	$H\dot{C}O$	$+43.5$	87
$CH_3C(O)\dot{O}$	-207.5 ± 4.2	62	$CH_3\dot{C}O$	-10.3 ± 1.8	79
$HC(O)OH$	-378.6	88	$HC(O)\dot{O}$	-129.7 ± 12.6	89
$\dot{C}H_2CHO$	$+14.7 \pm 1.6$	90	$\dot{C}(O)OH$	-194.6 ± 2.9	91
C_2H_5OH	-234.8 ± 0.5	92	$C_2H_5\dot{O}$	-13.6 ± 4.0	79
C_2H_5OOH	-175.4 ± 12.9	93	$C_2H_5O\dot{O}$	-27.4 ± 9.9	93
C_2H_5CHO	-188.7 ± 0.8	48	$\dot{C}H_2OH$	-17.1 ± 3.4	91

400 kJ mol^{-1} (95.6 kcal mol^{-1}), a value derived from a study of ESR hyperfine coupling constants.[30]

There is also a real paucity of suitable experiments—apart from some early work on the rate of oxidation of methyl butanoate in static reactors with results mainly of a qualitative nature[31−34] and very recent work by Gaïl et al.[35] who studied the oxidation in a jet-stirred reactor, in an opposed-flow diffusion flame and in a variable pressure plug flow reactor. Their mechanism, a slightly modified version of an earlier one by Fisher et al.,[22] indicates that homolytic cleavage of the $O-CH_3$ bond is favored over that of the $C_2H_5-CH_2C(O)OCH_3$ bond, which in turn is more important than breaking the H_3C-CH_2 or the $C_3H_7-C(O)OCH_3$ bonds.

Blades and Sandhu[36] obtained a rate constant for the formation of methyl acetate from the unimolecular decomposition of MB of $\approx 1 \times 10^{-3}$ s^{-1} at 989 K and estimated an *A*-factor of 3.16×10^{12} and an activation energy greater than 293 kJ mol^{-1} (>70 kcal mol^{-1}). Blades and Gilderson[37] measured the pyrolysis of EP between 780 and 875 K in a toluene carrier flow system, obtaining a rate constant of $5.2 \times 10^{12} \exp(-24\,410 \pm 180/T)$ s^{-1} based on the formation of propionic acid (later shock wave experiments are in substantial agreement with this value),[38] and O'Neal and Benson[39] estimated an *A*-factor of 4.0×10^{12} s^{-1} and an activation energy of 201 kJ mol^{-1} based on transition-state theory for a series of six-center eliminations.

More recently, Schwartz et al.[40] have studied the effect of doping a methane/air premixed flame with 5000 ppm of MB and EP. In the case of EP they find that a unimolecular six-centered dissociation reaction explains their results:

$$C_2H_5COOCH_2CH_3 \rightarrow C_2H_5COOH + CH_2{=}CH_2$$

whereas MB has a decomposition rate that is consistent with a unimolecular simple fission reaction:

$$C_3H_7COOCH_3 \rightarrow C_3H_7C(O)\dot{O} + \dot{C}H_3$$

Computational Methods

All electronic structure calculations have been performed by ab initio multilevel procedures with the CBS-QB3 methodology[41,42] as implemented in the Gaussian-03 applications.[43] The CBS-QB3 model chemistry combines the results of several electronic structure calculations and empirical terms to predict molecular energies to around 4 kJ mol^{-1} accuracy.[44] The required electronic structure calculations are outlined below:

- B3LYP/6-311G(2d,d,p) geometry optimization and frequencies
- MP2/6-311G(3df,2df,2p) energy and CBS extrapolation
- MP4(SDQ)/6-31G(d(f),p) energy
- CCSD(T)/6-31G† energy

We used a number of isodesmic and isogyric reactions, which although a less elegant procedure than the atomization method can result in higher accuracies due to cancelation of errors, and it does not require quite such heroic levels of theory,[45] to compute the reaction enthalpies. In addition, the thermodynamic contributions from hindered rotors, which can be difficult to compute, fortuitously cancel out.

Our choices for the isodesmic reactions were governed by two considerations: first, the chemistry, which is best fulfilled by choosing reactions that conserve neighboring groups about heavy atoms (we have labeled these *isogeitonic*),[46] and second, by the quality of the experimental data available for the three reference species. These twin aims are often mutually exclusive.

The search for the transition states for unimolecular dissociation of EP and MB have been carried out using several techniques, including the synchronous transit-guided quasi-Newton (QST2 and QST3) and the eigenvalue-following (EF) optimization procedures as implemented in the Gaussian programs. For each stationary point, we carried out vibrational frequency calculations to characterize their nature as minima (positive frequencies) or transition states (one negative frequency) and to correct energies for zero-point and thermal contributions at 298 K. The vibrational modes were examined using the ChemCraft application[47] to verify the existence of the transition states.

Results and Discussion

The enthalpies of formation of stable and transient species (all at the reference temperature of 298.15 K), which were used in this work, are detailed in Table 1. In the majority of cases these values are well established but for some there is considerable uncertainty; for example, for butanal Wiberg et al.[48] reported a ΔH_f° of -211.8 ± 0.9 whereas Buckley and Cox[49] measured -204.4 ± 1.4 kJ mol^{-1}. For propanal, measurements[48−51] span the range from -186 to -192 kJ mol^{-1}; we have used the Wiberg et al. value, which is close to the mean, whereas an authoritative handbook[52] prefers -185.6 kJ mol^{-1}.

TABLE 2: CBS-QB3 Standard Enthalpies of Reaction and Formation at 298 K (kJ mol^{-1}) for Propanoate Radical Based on $\Delta H_f^\circ[CH_3C(O)\dot{O}]$ at (a) −207.5 kJ mol^{-1} and (b) −197.8 kJ mol^{-1}

	ΔH_r°	ΔH_f° (a)	ΔH_f° (b)
(24)	+15.1	−221.9	−221.9
(25)	+0.6	−231.6	−221.9
(26)	−13.0	−222.4	−222.4
(27)	−80.4	−219.5	−219.5
(28)	+0.6	−230.7	−221.0
(29)	−14.5	−219.1	−219.1
(30)	−15.3	−225.9	−216.2
(31)	−10.2	−224.3	−224.3
(32)	−96.3	−211.4	−211.4
(33)	−30.4	−222.7	−222.7
mean		−222.9	−220.0
σ		±5.8	±3.8

Ethyl Propanoate. The heat of formation of EP has been experimentally determined at −463.6 ± 0.7 kJ mol^{-1} by Månsson[53] and at −466.5 ± 0.4 kJ mol^{-1} by Wiberg and Waldron.[54] To "calibrate" our procedure, we have used work reactions (1−4):

$$C_2H_5C(O)OCH_2CH_3 + CH_3OH \rightarrow CH_3C(O)OCH_3 + C_3H_7OH \quad (1)$$

$$C_2H_5C(O)OCH_2CH_3 + CH_3CHO \rightarrow CH_3C(O)OCH_3 + C_3H_7CHO \quad (2)$$

$$C_2H_5C(O)OCH_2CH_3 + CH_3C(O)OH \rightarrow CH_3C(O)OCH_3 + C_3H_7C(O)OH \quad (3)$$

$$C_2H_5C(O)OCH_2CH_3 + CH_3CH_2OH \rightarrow CH_3C(O)OCH_2CH_3 + C_3H_7OH \quad (4)$$

to compute the heat of formation of ethyl propanoate. The enthalpy changes of 1.2, 13.1, 12.8 and 2.4 kJ mol^{-1}, respectively, lead to $\Delta H_f^\circ(EP) = -468.7, -464.9, -469.8, -467.5 \Rightarrow -467.8 \pm 2.1$ kJ mol^{-1}; this is in very good agreement with the measured values and lends confidence in the application of this method to the case of MB for which there are no experimental values at all. In addition, there is good agreement with the group additivity estimate of −467.8 kJ mol^{-1} from the Stein and Brown database.[55] Here and elsewhere a simple arithmetic averaging procedure has been used, the results of which compare favorably with the weighted mean approach based on experimental errors alone. Because the error associated with the theoretical computation of reaction enthalpy is unknown, it cannot be included and so we prefer the simpler method.

C−H. An enthalpy change of −7.9 and −1.6 kJ mol^{-1} was computed for the work reactions (5) and (6), leading to an

$$EtC(O)OCH_2\dot{C}H_2 + CH_3CH_3 \rightarrow EtC(O)OCH_2CH_3 + CH_3\dot{C}H_2 \quad (5)$$

$$EtC(O)OCH_2\dot{C}H_2 + CH_3CH_2OH \rightarrow EtC(O)OCH_2CH_3 + \dot{C}H_2CH_2OH \quad (6)$$

average enthalpy of formation of the radical $EtC(O)OCH_2\dot{C}H_2$ of −254.8 kJ mol^{-1}, and from it the bond dissociation energy of the primary C−H bond in the ester was evaluated from

$$D(C-H) = \Delta H_f^\circ(EtC(O)OCH_2\dot{C}H_2) + \Delta H_f^\circ(\dot{H}) = \Delta H_f^\circ(EtC(O)OCH_2CH_3)$$

$$= -254.8 + 218.0 - (-463.6) = 427 \text{ kJ mol}^{-1}$$

whereas the secondary C−H energy was determined from both (7), enthalpy change of −5.9 giving −274.0, and (8) giving +13.7 and −274.7; the average enthalpy of formation of −274.4 kJ mol^{-1} yields a bond energy of 407 kJ mol^{-1}:

$$EtC(O)O\dot{C}HCH_3 + CH_3OCH_3 \rightarrow EtC(O)OCH_2CH_3 + CH_3O\dot{C}H_2 \quad (7)$$

$$EtC(O)O\dot{C}HCH_3 + CH_3CH_3 \rightarrow EtC(O)OCH_2CH_3 + CH_3\dot{C}H_2 \quad (8)$$

Reactions (9) and (10) were used to determine the secondary C−H bond energy in the C(O)−alkyl moiety of the molecule.

$$CH_3\dot{C}HC(O)OEt + CH_3CHO \rightarrow C_2H_5C(O)OEt + \dot{C}H_2CHO \quad (9)$$

$$CH_3\dot{C}HC(O)OEt + CH_3C(O)CH_3 \rightarrow C_2H_5C(O)OEt + CH_3C(O)\dot{C}H_2 \quad (10)$$

The ΔH_r° of +4.3 and +8.2 yield ΔH_f° of −287.1 and −288.8 kJ mol^{-1} and therefore a BDE of 394 kJ mol^{-1}, in moderate agreement with a previous value of 400 kJ mol^{-1} obtained from a reanalysis of pyrolysis data.[30] Reactions (11) and (12) were employed for the primary C−H BDE, with reaction

$$\dot{C}H_2CH_2C(O)OEt + CH_3CH_3 \rightarrow C_2H_5C(O)OEt + CH_3\dot{C}H_2 \quad (11)$$

$$\dot{C}H_2CH_2C(O)OEt + CH_3CH_2OH \rightarrow C_2H_5C(O)OEt + \dot{C}H_2CH_2OH \quad (12)$$

enthalpies of −4.3 and +2.0 kJ mol^{-1} leading to an average formation enthalpy of −258.4 kJ mol^{-1} and a bond energy of 423 kJ mol^{-1}. Note that all of the above D(C−H) bond energies are independent of the actual value for ΔH_f°(EP).

C−C. The C−C bond energy was evaluated from reactions (13) and (14) for which $\Delta H_r^\circ = -13.3$ and −13.9 and $\Delta H_f^\circ = -235.1$ kJ mol^{-1} on average; hence, $D[EtC(O)OC(H_2)-CH_3]$ = 375 kJ mol^{-1}.

$$EtC(O)O\dot{C}H_2 + CH_3OCH_3 \rightarrow EtC(O)OCH_3 + CH_3O\dot{C}H_2 \quad (13)$$

$$EtC(O)O\dot{C}H_2 + CH_3OH \rightarrow EtC(O)OCH_3 + \dot{C}H_2OH \quad (14)$$

Enthalpies of +8.3, −44.6 and +4.7 kJ mol^{-1} for reactions (15−17) yield formation enthalpies of −204.0, −200.9 and −219.6 kJ mol^{-1}. The result obtained for reaction (17) is clearly at variance with those from reactions (15) and (16). We had

$$\dot{C}(O)OEt + CH_3CH_3 \rightarrow HC(O)OEt + CH_3\dot{C}H_2 \quad (15)$$

$$\dot{C}(O)OEt + CH_3CHO \rightarrow HC(O)OEt + CH_3\dot{C}O \quad (16)$$

$$\dot{C}(O)OEt + HC(O)OH \rightarrow HC(O)OEt + \dot{C}(O)OH \quad (17)$$

used the most recent recommendations[29,52] of ΔH_f° for the *trans*-hydrocarboxyl radical, $\dot{C}(O)OH$, of $\geq -194.6 \pm 2.9$ kJ mol^{-1} derived from work by Ruscic and Litorja.[56] However, recent theoretical calculations[57−60] suggest that a higher value of −181.6 kJ mol^{-1}, which is also supported by the experiments of Ruscic and Litorja, is the more appropriate choice. The adoption of this value changes the result for reaction (17) to −206.0 kJ mol^{-1} and leads to an overall $\Delta H_f^\circ[\dot{C}(O)OEt]$ of -203.6 ± 2.6 kJ mol^{-1} and a BDE for $D[Et-C(O)OEt]$ of 379 kJ mol^{-1}.

However, comparisons of both enthalpy of formation and bond dissociation energy with data obtained for the molecule methyl butanoate produce inconsistencies (vide infra). Therefore, we chose a new set of isodesmic reactions (18)−(20),

$$\dot{C}(O)OEt + CH_3CH_3 \rightarrow CH_3C(O)OCH_3 + CH_3\dot{C}H_2 \quad (18)$$

$$\dot{C}(O)OEt + CH_3CHO \rightarrow CH_3C(O)OCH_3 + CH_3\dot{C}O \quad (19)$$

$$\dot{C}(O)OEt + CH_3C(O)OH \rightarrow CH_3C(O)OEt + \dot{C}(O)OH \quad (20)$$

with reactants of a structure more similar to that of the species under investigation; these gave values of ΔH_r°, ΔH_f° of −11.3 and −199.6 kJ mol^{-1} for (18), −61.3 and −196.4 kJ mol^{-1} for (19) and +5.5 and −199.7 kJ mol^{-1} for (20), with an average enthalpy of formation of ΔH_f° of -198.5 ± 1.9 kJ mol^{-1} and $D[Et-C(O)OEt]$ of 384 kJ mol^{-1}.

For reactions (21−23) enthalpy changes of 11.7, −15.1 and −11.3 kJ mol^{-1} resulted in an average formation enthalpy of -251.1 ± 2.6 kJ mol^{-1} for $\dot{C}H_2C(O)OEt$ (electrochemical[61] measurements had previously determined $\Delta H_f^\circ[\dot{C}H_2C(O)OEt]$ of -260 ± 13 and $D[H_3C-CH_2C(O)OEt]$ of 359 kJ mol^{-1}):

$$\dot{C}H_2C(O)OEt + CH_3CH_3 \rightarrow CH_3C(O)OEt + CH_3\dot{C}H_2 \quad (21)$$

$$\dot{C}H_2C(O)OEt + CH_3CHO \rightarrow CH_3C(O)OEt + \dot{C}H_2CHO \quad (22)$$

$$\dot{C}H_2C(O)OEt + CH_3C(O)CH_3 \rightarrow CH_3C(O)OEt + CH_3C(O)\dot{C}H_2 \quad (23)$$

C−O. From reactions (24−33), the enthalpy of formation of $EtC(O)\dot{O}$ was computed, from a total of ten isodesmic

$$EtC(O)\dot{O} + HC(O)OH \rightarrow EtC(O)OH + HC(O)\dot{O} \quad (24)$$

$$EtC(O)\dot{O} + CH_3C(O)OH \rightarrow EtC(O)OH + CH_3C(O)\dot{O} \quad (25)$$

$$EtC(O)\dot{O} + HCHO \rightarrow EtCHO + HC(O)\dot{O} \quad (26)$$

$$EtC(O)\dot{O} + CH_3CHO \rightarrow EtC(O)OH + CH_3\dot{C}O \quad (27)$$

$$EtC(O)\dot{O} + CH_3CHO \rightarrow EtCHO + CH_3C(O)\dot{O} \quad (28)$$

$$EtC(O)\dot{O} + CH_3OH \rightarrow EtC(O)OH + CH_3\dot{O} \quad (29)$$

$$EtC(O)\dot{O} + CH_3OH \rightarrow EtOH + CH_3C(O)\dot{O} \quad (30)$$

$$EtC(O)\dot{O} + EtOH \rightarrow EtC(O)OH + Et\dot{O} \quad (31)$$

$$EtC(O)\dot{O} + EtOOH \rightarrow EtC(O)OH + EtO\dot{O} \quad (32)$$

$$EtC(O)\dot{O} + CH_3CH_3 \rightarrow EtC(O)OH + CH_3\dot{C}H_2 \quad (33)$$

reactions, as an average of -222.9 ± 5.8 kJ mol^{-1}, column (a) in Table 2. Note that the values produced by reactions (25), (28) and (30) are considerably larger than the rest; the common factor is the enthalpy of formation of the acetate radical that we had adopted from an authoritative source[29] as -207.5 ± 4.2 kJ mol^{-1} derived ultimately from work by Benson and O'Neill.[62] Other authorities[52] prefer the Blanksby and Ellison recommendation[28] of -179.9 ± 12.6 kJ mol^{-1}, which is based on an analysis of an acidity and electron affinity cycle using the Wang et al.[63] 1998 value for electron affinity, EA, of 3.35 ± 0.08 eV (but see below).

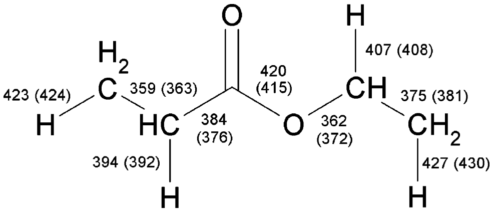

Figure 1. Ethyl propanoate bond energies (kJ mol^{-1}) (group additivity estimates).

Because the literature values for this species range from −179.9[28] to -216.3 ± 12.6[64] with a high degree of uncertainty, we decided to re-compute this value via the atomization method at the CBS-QB3 level of theory. We have recently used this procedure to calculate the heat of formation for the acetonyl radical at −32.5 kJ mol^{-1}, which compares well with the best experimental value of -34.9 ± 1.9 kJ mol^{-1}.[46] On the basis of this approach, the enthalpy of formation of $CH_3C(O)\dot{O}$ is computed to be −197.8 kJ mol^{-1}.

Furthermore, the very recent experimental determination, using anion photoelectron spectroscopy, by Wang and coworkers[65] of the electron affinity of $CH_3C(O)\dot{O}$ of 3.250 ± 0.010 eV (313.6 ± 1.0 kJ mol^{-1}) coupled to the recent estimation from gas-phase acidity data of the enthalpy of formation of the acetate anion $CH_3C(O)O^-$ of -510.8 ± 7.5 kJ mol^{-1} by Aleixo et al.,[66] leads to an enthalpy of formation of $CH_3C(O)\dot{O}$ of −197.2 kJ mol^{-1}, which is in very good agreement with our value from atomization energies.

We have therefore adopted −197.8 kJ mol^{-1} as the appropriate value and re-computed the results from reactions (25), (28) and (30); the enthalpy of formation of $EtC(O)\dot{O}$ is now -220.0 ± 3.8 kJ mol^{-1}, column (b) in Table 2 (cf. -228.4 ± 6.4 kJ mol^{-1} [29]). The new value is used to obtain $D[EtC(O)O-Et]$ = 362 kJ mol^{-1}.

Finally, reactions (34) and (35) with ΔH_r° of −12.1 and −0.7 kJ mol^{-1} were used to determine an average ΔH_f° = −30.3 kJ mol^{-1}, from which $D[EtC(O)-OEt]$ kJ mol^{-1} can be extracted.

$$Et\dot{C}O + MeOH \rightarrow EtOH + Me\dot{C}O \quad (34)$$

$$Et\dot{C}O + MeC(O)OMe \rightarrow EtC(O)OMe + Me\dot{C}O \quad (35)$$

Summary. A comparison of computed and estimated, using group additivity,[67] BDEs is instructive, Figure 1. In general, there is acceptable agreement between the two approaches save for the O−C and the C−C (O) bonds where differences of 10 kJ mol^{-1} are apparent. The reason for these discrepancies is not known. In this particular case this is inconsequential because elimination of ethene from the O-alkyl moiety is the dominant reaction channel.

Methyl Butanoate. The enthalpy of formation of methyl butanoate has not been determined experimentally but only estimated as −451.9 kJ mol^{-1} by Tumanov and colleagues[68] from γ -irradiation rate measurements by Witter and Neta[69] and from group additivity considerations[55] as −454.8 kJ mol^{-1}. On the

TABLE 3: Bond Energies and Formation Enthalpies (kJ mol^{-1})

R−X	this work	lit.	$\Delta H_f^\circ[\dot{\mathbf{R}}]$	lit.
	ethyl propanoate			
$CH_3CH_2C(O)OCH_2C(H_2)-H$	427		−254.8	
$CH_3CH_2C(O)O(CH_3)C(H)-H$	407		−274.4	
$H-C(H)(CH_3)C(O)OCH_2CH_3$	394	400[30]	−288.0	
$H-C(H_2)CH_2C(O)OCH_2CH_3$	423		−258.4	
$CH_3CH_2C(O)OC(H_2)-CH_3$	375		−235.1	
$CH_3C(H_2)-C(O)OCH_2CH_3$	384		−198.5	
$H_3C-CH_2C(O)OCH_2CH_3$	359		−251.1	−260[61]
$CH_3CH_2C(O)O-CH_2CH_3$	362		−220.0	−228.4[29]
$CH_3CH_2C(O)-OCH_2CH_3$	420		−30.3	
	methyl butanoate			
$CH_3CH_2CH_2C(O)OC(H_2)-H$	414		−257.9	
$H-C(H)(CH_2CH_3)C(O)OCH_3$	394	395[68]	−278.0	−275[68]
$H-C(H)(CH_3)CH_2C(O)OCH_3$	413		−259.0	
$H-C(H_2)CH_2CH_2C(O)OCH_3$	423		−249.2	
$CH_3CH_2C(H_2)-C(O)OCH_3$	391		−163.5	
$CH_3C(H_2)-CH_2C(O)OCH_3$	353		−219.8	−236.8,[72] −222[64]
$H_3C-CH_2CH_2C(O)OCH_3$	373		−228.1	
$CH_3CH_2CH_2C(O)O-CH_3$	364		−237.0	−249[29]
$CH_3CH_2CH_2C(O)-OCH_3$	424		−51.8	

basis of work reactions (36−39), calculations yield $\Delta H_f^\circ(\mathrm{MB}) = -452.1, -455.8, -457.0$ and -452.6 kJ mol^{-1}, respectively, average -454.4 kJ mol^{-1}. This is in excellent agreement with

$$CH_3CH_2CH_2C(O)OCH_3 + CH_3CHO \rightarrow CH_3C(O)OCH_3 + CH_3CH_2CH_2CHO \quad (36)$$

$$CH_3CH_2CH_2C(O)OCH_3 + CH_3OH \rightarrow CH_3C(O)OCH_3 + CH_3CH_2CH_2OH \quad (37)$$

$$CH_3CH_2CH_2C(O)OCH_3 + CH_3C(O)OH \rightarrow CH_3C(O)OCH_3 + CH_3CH_2CH_2C(O)OH \quad (38)$$

$$CH_3CH_2CH_2C(O)OCH_3 + CH_3CH_2OH \rightarrow CH_3CH_2C(O)OCH_3 + CH_3CH_2CH_2OH \quad (39)$$

the work of Liu and Cheng[70] who used a test set of 35 straight-chained alkyl carboxylic acids and esters and determined their atomization energies from DFT and ab initio calculations; the atomization energies were then fitted, via a three-parameter calibration equation, against known heats of formation with the result that they can predict enthalpies of formation for methyl butanoate of −454.4 and −455.7 kJ mol^{-1} from B3LYP/6-311++G(3df,2pd)//B3LYP/4-31G(d) and MP2/6-31+G(d)//HF/4-31G(d) computations respectively.

C−H. From reactions (40) and (41), with $\Delta H_r^\circ = -13.1$ and $+6.5$ kJ mol^{-1}, an average enthalpy of formation of −257.9 kJ mol^{-1} can be obtained for the radical to yield

$$CH_3CH_2CH_2C(O)O\dot{C}H_2 + CH_3OCH_3 \rightarrow CH_3CH_2CH_2C(O)OCH_3 + CH_3O\dot{C}H_2 \quad (40)$$

$$CH_3CH_2CH_2C(O)O\dot{C}H_2 + CH_3CH_3 \rightarrow CH_3CH_2CH_2C(O)OCH_3 + CH_3\dot{C}H_2 \quad (41)$$

$D[CH_3CH_2CH_2C(O)OC(H)_2-H] = 414$ kJ mol^{-1}. The equivalent bond in the methyl ester of acetic acid has been estimated at 405 kJ mol^{-1}.[71]

The three different C−H bonds on the alkyl chain of the molecule were evaluated as follows. First, they were evaluated from (42) and (43), whose reaction enthalpy of 3.6 and 7.4 kJ mol^{-1} translates into an average formation enthalpy of −278.0kJ mol^{-1} and consequently a bond energy of 394 kJ mol^{-1}. Tumanov et al.[68] reported −275 kJ mol^{-1} for the

$$CH_3CH_2\dot{C}HC(O)OCH_3 + CH_3CHO \rightarrow CH_3CH_2CH_2C(O)OCH_3 + \dot{C}H_2CHO \quad (42)$$

$$CH_3CH_2\dot{C}HC(O)OCH_3 + CH_3C(O)CH_3 \rightarrow CH_3CH_2CH_2C(O)OCH_3 + CH_3C(O)\dot{C}H_2 \quad (43)$$

$\Delta H_f^\circ[CH_3CH_2\dot{C}HC(O)OCH_3]$ and an R−H bond strength of 395 kJ mol^{-1}. Second, reaction enthalpies of 8.9 and 7.7 kJ mol^{-1} for (44) and (45) lead to ΔH_f° of −259.0 kJ mol^{-1} and a

$$CH_3\dot{C}HCH_2C(O)OCH_3 + CH_3CH_3 \rightarrow CH_3CH_2CH_2C(O)OCH_3 + CH_3\dot{C}H_2 \quad (44)$$

$$CH_3\dot{C}HCH_2C(O)OCH_3 + CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2C(O)OCH_3 + CH_3CH_2\dot{C}H_2 \quad (45)$$

bond energy of +413 kJ mol^{-1}. The final C−H energy was calculated from the enthalpy change of −1.0 and −2.2 kJ mol^{-1} for reactions (46) and (47), which results in $\Delta H_f^\circ = -249.2$ on

$$\dot{C}H_2CH_2CH_2C(O)OCH_3 + CH_3CH_3 \rightarrow CH_3CH_2CH_2C(O)OCH_3 + CH_3\dot{C}H_2 \quad (46)$$

$$\dot{C}H_2CH_2CH_2C(O)OCH_3 + CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2C(O)OCH_3 + CH_3CH_2\dot{C}H_2 \quad (47)$$

average and $D[H-CH_2CH_2CH_2C(O)OCH_3] = 423$ kJ mol^{-1}.

C−C. Reactions (48) (ΔH_r° and ΔH_f° of −25.5 and −164.5 kJ mol^{-1}), (49) (−44.0 and −159.9 kJ mol^{-1}), and (50) (+3.2 and −166.1 kJ mol^{-1}) gave an average of −163.5 ± 3.2 and a $D[\mathrm{Et}-C(O)O\mathrm{Et}]$ of 391 kJ mol^{-1}.

$$\dot{C}(O)OCH_3 + CH_3CH_2CH_3 \rightarrow CH_3C(O)OCH_3 + CH_3\dot{C}H_2 \quad (48)$$

$$\dot{C}(O)OCH_3 + CH_3CHO \rightarrow CH_3C(O)OCH_3 + H\dot{C}O \quad (49)$$

$$\dot{C}(O)OCH_3 + CH_3C(O)OH \rightarrow CH_3C(O)OCH_3 + \dot{C}(O)OH \quad (50)$$

For the $\dot{C}H_2C(O)OCH_3$ radical work reactions (51−53) with enthalpy changes of +11.7, −15.1 and −11.2 kJ mol^{-1} were used to give $\Delta H_f^\circ = -222.6, -217.6, -219.3 \Rightarrow -219.8 \pm 2.6$ kJ mol^{-1}, which is in severe disagreement with the recent value of −236.8 ± 8.4 kJ mol^{-1} derived from ion cyclotron mass spectrometric experiments by Karty et al.[72] but is close to an earlier electron impact measurement of −222 kJ mol^{-1} by

$$\dot{C}H_2C(O)OCH_3 + CH_3CH_3 \rightarrow CH_3C(O)OCH_3 + CH_3\dot{C}H_2 \quad (51)$$

$$\dot{C}H_2C(O)OCH_3 + CH_3CHO \rightarrow CH_3C(O)OCH_3 + \dot{C}H_2CHO \quad (52)$$

$$\dot{C}H_2C(O)OCH_3 + CH_3C(O)CH_3 \rightarrow CH_3C(O)OCH_3 + CH_3C(O)\dot{C}H_2 \quad (53)$$

TABLE 4: Differences in ΔH_f° for RC(O)OX−R′C(O)OX (kJ mol^{-1})

	Et−Me	Pr−Me
X = H	−23.5	−43.5
X = Me	−19.0	−41.9
X = Et	−18.8	−40.2
this work	−22.4	−39.2

TABLE 5: Differences in ΔH_f° for XC(O)OEt−XC(O)OMe (kJ mol$^{-1)}$

	Et−Me
X = H	−42.8
X = Me	−31.3
X = Et	−31.1
X = Pr	−29.6
X = EtMeCH	−30.1
X = MeCHCH	−29.3
X = *n*-Bu	−35.0
this work	−35.0

TABLE 6: Bond Lengths (Å) in EP and in the Radical Obtained by the Removal of An α-Hydrogen from Either the C(O)-Alkyl or the O-Alkyl Moiety

C(O)-alkyl moiety				O-alkyl moiety			
bond	EP	radical	diff	bond	EP	radical	diff
C═O	1.206	1.219	−0.013	C═O	1.206	1.202	+0.004
C_α−C(O)	1.515	1.449	+0.066	O−C_α	1.450	1.386	+0.064
C_α−C_β	1.526	1.482	+0.044	C_α−C_β	1.520	1.487	+0.033
C_β−H	1.092	1.098	−0.006	C_β−H	1.093	1.101	−0.008
				O−C(O)	1.352	1.369	−0.017

TABLE 7: Bond Lengths (Å) in MB and in the Radical Obtained by the Removal of An α-Hydrogen from Either the C(O)-Alkyl or the O-Alkyl Moiety

C(O)-alkyl moiety				O-alkyl moiety			
bond	EP	radical	diff	bond	EP	radical	diff
C═O	1.205	1.218	−0.013	C═O	1.206	1.201	+0.005
C_α−C(O)	1.514	1.449	+0.065	O−C_α	1.439	1.366	+0.073
C_α−C_β	1.528	1.485	+0.043				
C_β−H	1.094	1.101	−0.007				

Holmes and co-workers.[64] The corresponding C−C bond energy, $D[C_2H_5{-}CH_2C(O)OCH_3]$, is 353 kJ mol^{-1}.

Work reactions (54) and (55) were used to compute an average formation enthalpy of −228.1 kJ mol^{-1} based on enthalpy changes of −3.5 and 2.9, respectively; in turn this leads to $D[H_3C{-}CH_2CH_2C(O)OCH_3]$ = 373 kJ mol^{-1}.

$$\dot{C}H_2CH_2C(O)OCH_3 + CH_3CH_3 \rightarrow C_2H_5C(O)OCH_3 + CH_3\dot{C}H_2 \quad (54)$$

$$\dot{C}H_2CH_2C(O)OCH_3 + CH_3CH_2OH \rightarrow C_2H_5C(O)OCH_3 + \dot{C}H_2CH_2OH \quad (55)$$

C−O. The following reactions were chosen:

$$CH_3CH_2CH_2C(O)\dot{O} + HC(O)OH \rightarrow CH_3CH_2CH_2C(O)OH + HC(O)\dot{O} \quad (56)$$

$$CH_3CH_2CH_2C(O)\dot{O} + CH_3OH \rightarrow CH_3CH_2CH_2OH + CH_3C(O)\dot{O} \quad (57)$$

to investigate the butanoate radical with reaction (56) yielding $\Delta H_r^\circ = +\ 10.8$ and $\Delta H_f^\circ = -237.6$ and reaction (57) −15.3 and −236.5 kJ mol^{-1} which average to −237.0 kJ mol^{-1} (cf. −249 ± 4[29]) equivalent to a $O{-}CH_3$ bond energy of 364 kJ mol^{-1} which is the same as the $O{-}CH_3$ in methyl acetate calculated with the updated value of −197.2 kJ mol^{-1} for the acetate radical.

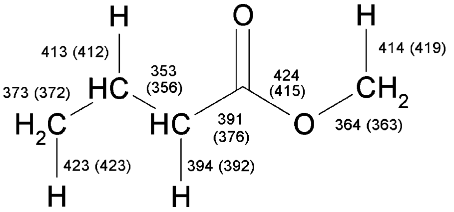

Figure 2. Methyl butanoate bond energies (kJ mol^{-1}) (group additivity estimates).

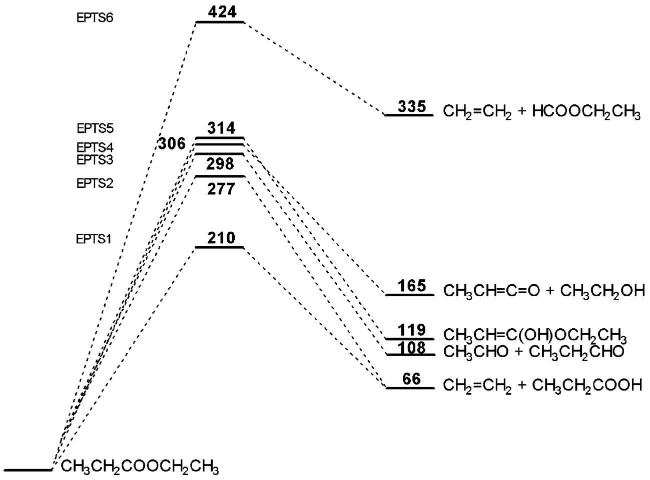

Figure 3. EP reaction profile diagram. Enthalpies of the TS and products are relative to EP (kJ mol^{-1}).

Reaction (59) is almost exactly thermoneutral. Together with reaction (58) it gives rise to a heat of formation of −51.8 kJ mol^{-1} for $Pr\dot{C}(O)$. Consequently, $D[PrC(O){-}OCH_3]$ of 424 kJ mol^{-1}. This number and the one for $D[EtC(O){-}OEt]$ of 420 kJ mol^{-1} found earlier from reactions (34) and (35) are in harmony with literature values for methyl acetate and ethyl chloroformate.[29] Furthermore, for the series of isogeitonic[46] reactions of type

$$Pr\dot{C}(O) + MeOH \rightarrow PrOH + Me\dot{C}(O) \quad (58)$$

$$Pr\dot{C}(O) + MeC(O)OMe \rightarrow PrC(O)OMe + Me\dot{C}(O) \quad (59)$$

$$Pr\dot{C}(O) + EtX \rightarrow PrX + Et\dot{C}(O)$$

which one would expect to be approximately thermoneutral, it follows that

$$\Delta H_f^\circ[Pr\dot{C}(O)] - \Delta H_f^\circ[Et\dot{C}(O)] \approx \Delta H_f^\circ[PrX] - \Delta H_f^\circ[EtX] \quad (60)$$

Literature values for the differences in the heats of formation of the stable molecules, the right-hand side of eq (60), for X = H, OH, C(O)OH and C(O)OMe range from −20 to −22 kJ mol^{-1}. Our computations for the differences in the radical species, the left-hand side of eq (60), gives −51.8 − (−30.3) = −21.5 kJ mol^{-1}.

Interestingly, using either one or the other of the experimental values[48,49] for butanal (PrX, with X = CHO) gives rise to differences that lie outside the above-mentioned range. A very recent theoretical study of *n*-aldehydes by da Silva and Bozzelli[73] recommends a ΔH_f° for butanal of −206.1 ± 0.7 kJ mol^{-1}, closer to the Buckley and Cox measurement[49] than to the Wiberg

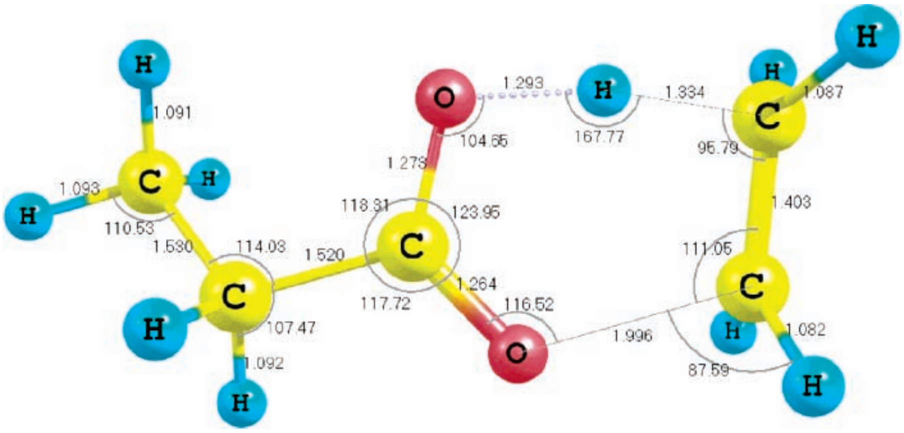

Figure 4. EPTS1: formation of ethene and propanoic acid from the O-alkyl moiety via a six-membered transition state.

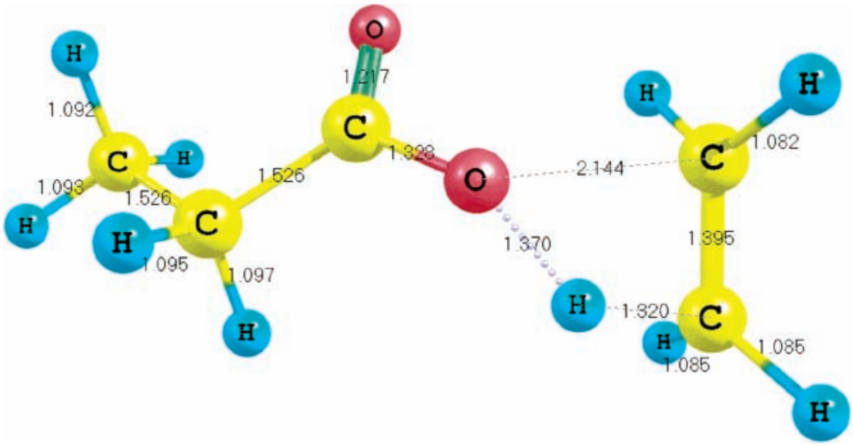

Figure 5. EPTS2: formation of ethene and propanoic acid from the O-alkyl moiety via a four-membered transition state.

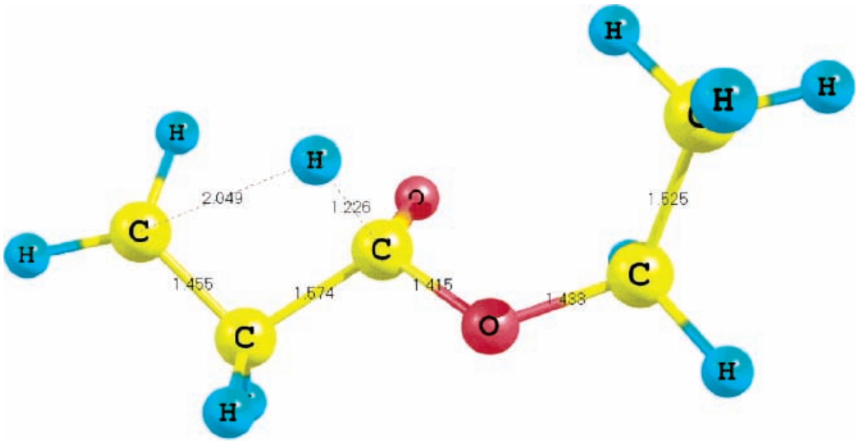

Figure 6. EPTS6: formation of ethene and ethyl formate from the C-alkyl moiety via a four-membered transition state.

et al.[48] one; adoption of this value improves the calculation outlined above but only slightly.

Reconciliation: RC(O)O−X. The enthalpies of formation of the species $RC(O)\dot{O}$, where R = methyl (Me), ethyl (Et) or *n*-propyl (Pr), have been calculated, but to what extent can the resultant values be reconciled? If it is *assumed* that the alkyl group does not affect the *D*(O−X) bond dissociation energy in a series of compounds RC(O)OX, then it can be shown that

$$\Delta H_f^\circ[RC(O)\dot{O}] - \Delta H_f^\circ[R'C(O)\dot{O}] = \Delta H_f^\circ[RC(O)OX] - \Delta H_f^\circ[R'C(O)OX] \quad (61)$$

hence the right-hand side of eq (61) can be evaluated from the literature, via Table 1 or the NIST database[55] and compared to the value computed in this work, that is, the left-hand side of eq (61). The results of such a comparison are shown in Table 4; clearly there is good agreement for both Et−Me and Pr−Me, which suggests that the computed values are in concordance with each other.

Reconciliation: X−C(O)OR. As before, it is assumed that *D*(X−C) in a series of compounds of general formula X−C(O)OR is unaffected by the precise identity of the R group whence

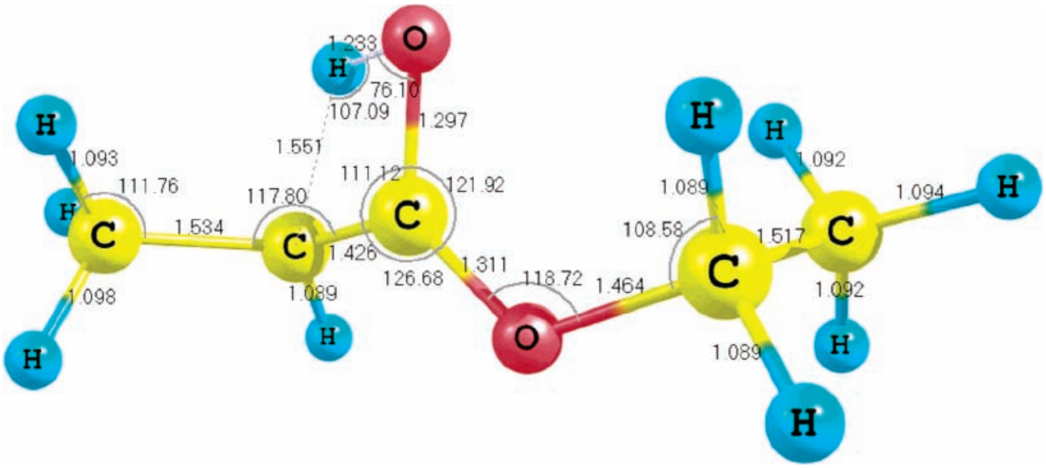

Figure 7. EPTS5: formation of enol.

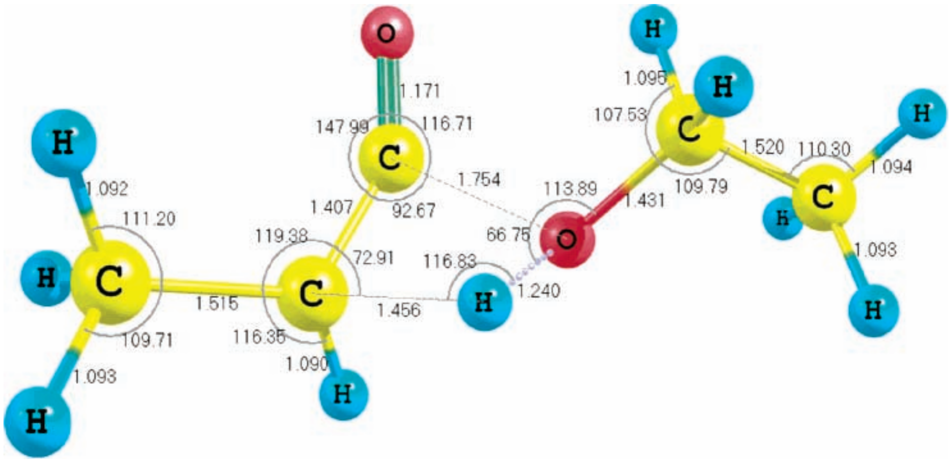

Figure 8. EPTS4: formation of ketene and ethanol.

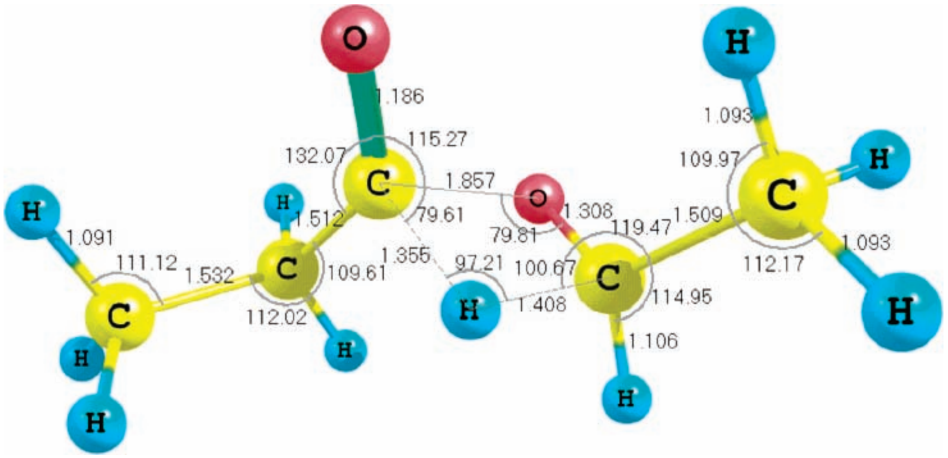

Figure 9. EPTS3: formation of aldehydes.

$$\Delta H_f^\circ[\dot{C}(O)OEt] - \Delta H_f^\circ[\dot{C}(O)OMe] = \Delta H_f^\circ[XC(O)OEt] - \Delta H_f^\circ[XC(O)OMe]$$

The differences for the stable molecular species, $\Delta H_f^\circ[XC(O)OEt] - \Delta H_f^\circ[XC(O)OMe]$, cluster around ~-32 kJ mol^{-1} for six pairs of esters (Table 5), excluding the formyl esters, which might reasonably be expected not to conform. The different behavior of formyl esters was pointed out earlier when using reactions (15−17) and, in the case of the molecule methyl butanoate, the equivalent reactions (51)−(53). When those reactions were used, a difference for the radical pair $\Delta H_f^\circ[\dot{C}(O)OEt] - \Delta H_f^\circ[\dot{C}(O)OMe]$ of -44 kJ mol^{-1} was computed, which is clearly out of line. However, using the more appropriate sets of reactions (18)−(20) and (51)−(53), our computed difference for the radical pair now amounts to -35 kJ mol^{-1}, which is in satisfactory accord with expectations.

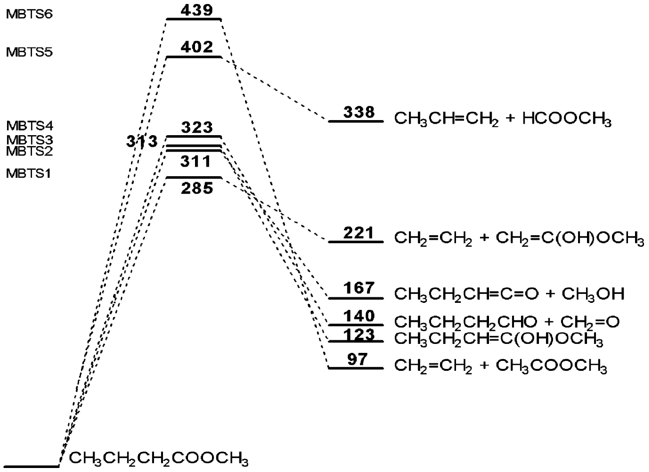

Figure 10. MB reaction profile diagram. Enthalpies of the TS and products are relative to MB (kJ mol^{-1}).

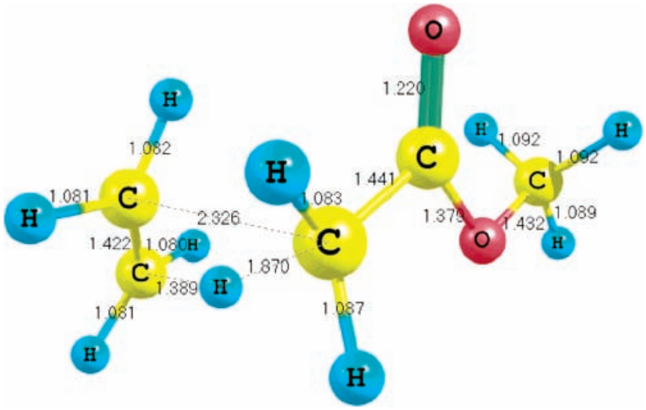

Figure 11. MBTS6: formation of ethene and methyl acetate via a four-membered transition state.

Summary. The CBS-QB3 computed bond energies for MB are summarized in Figure 2 together with values estimated from group additivity considerations. Generally there is good agreement except for the C−C(O) and the O−C(O) bonds where differences of 15 and 9 kJ mol^{-1} arise. The central C−C bond is identifed as the weakest by some 10 kJ mol^{-1} over the next weakest ($O-CH_3$) by both methods.

Additionally, a comparison of the BDEs of similar bonds in EP and MB reveals good agreement (Table 3). This lends further credence to our results.

Structures. In both ethyl propanoate and methyl butanoate there are two types of C−H bonds, abstraction of these H atoms gives primary and secondary radicals. The interaction of the resulting odd electron at the radical center occurs through conjugation with double bonds or lone pairs of electrons or through hyperconjugation with the adjacent CH bonds. This interaction is reflected in geometrical changes especially to the bond lengths. As shown in Table 6 for ethyl propanoate, abstraction of an α−hydrogen on the C(O)−alkyl side of the molecule gives elongation of the C═O and the $C_\beta-H$ bonds, but shortening is observed for the $C_\alpha-C$ and O−C compared to the parent molecule. Abstraction of an α-hydrogen on the O-alkyl side leads to shortening of the C═O, O−C and $C_\beta-C_\beta$ bonds while elongation of the $C_\beta-H$ and O−C(O) bonds occurs.

For methyl butanoate the effects of the abstraction of the α-hydrogen on the C(O)−alkyl side of the molecule are in the same trend as in the case of ethyl propanoate, Table 7. The removal of the hydrogen produces elongation of the C═O and the $C_\beta-H$ bonds and shortening of the $C_\alpha-C$ and the O−C bonds. On the other side of the O-alkyl molecule, both bonds, C═O and $O-C_\alpha$, are reduced in length by the α-hdrogen substraction on this side, as in the case of ethyl propanoate.

Energetics. The calculated values for the heats of formation of the four C-centered radicals derived from ethyl propanoate, are, in order of increasing energy, the secondary radicals $CH_3\dot{C}HC(O)OEt$ at −288.0 and $EtC(O)O\dot{C}HCH_3$ at −274.4 followed by the primary radicals $\dot{C}H_2CH_2C(O)OEt$ at −258.4 and $EtC(O)OCH_2\dot{C}H_2$ at −254.8, all in kJ mol^{-1}, Table 3. The order reflects the bond strengths, with primary C−H stronger than secondary C−H, and as expected the most stable arises because of the twin interaction of the unpaired electron with the adjacent C═O and with the terminal methyl group.

For methyl butanoate $Et\dot{C}HC(O)OCH_3$ at −278 kJ mol^{-1} is more stable than $CH_3\dot{C}HCH_2C(O)OCH_3$ at −259 kJ mol^{-1}, which is more stable than $PrC(O)O\dot{C}H_2$ at −258 kJ mol^{-1} and in turn than $\dot{C}H_2CH_2CH_2C(O)OCH_3$ at −249 kJ mol^{-1}. As before, the secondary radicals are more stable by some 2−28 kJ mol^{-1} than the primary ones, and the conjugatively delocalised $\dot{C}-C=O$ species is the most stable.

Transition States. *Ethyl Propanoate.* Five reaction channels, Figure 3, were examined for ethyl propanoate:

$$\rightarrow C_2H_5C(O)OH + CH_2{=}CH_2 \tag{62}$$

$$\rightarrow C_2H_5C(O)OH + CH_3CHO \tag{63}$$

$$\rightarrow CH_3CH{=}C{=}O + C_2H_5OH \tag{64}$$

$$\rightarrow CH_3CH{=}C(OH)OC_2H_5 \tag{65}$$

$$\rightarrow HC(O)OC_2H_5 + CH_2{=}CH_2 \tag{66}$$

with the formation of ethene and propanoic acid from the O-alkyl moiety, reaction (62), as the most favorable, Figure 4, with a low barrier height of 210 kJ mol^{-1} and only 66 kJ mol^{-1} endothermic. In contrast, the four-centered eliminations of ethene from the O-alkyl and the C-alkyl side of the molecule, Figures 5 and 6, are much less favored at 277 and 424 kJ mol^{-1}, respectively.

The energy barrier for enolization, reaction 65 with the transition state shown in Figure 7, lies somewhat higher than that for ketene formation, (64) and Figure 8, which in turn is higher than the channel for aldehyde formation, (63) and Figure 9.

As regards homolytic bond fission, arising from Figure 1 the weakest bond is the $C_\alpha-C_\beta$ at 359 kJ mol^{-1} followed closely by the O−C bond on the O-alkyl side at 362 kJ mol^{-1}.

Methyl Butanoate. Six reaction channels, Figure 10, were examined for methyl butanoate:

$$\rightarrow CH_2{=}C(OH)OCH_3 + CH_2{=}CH_2 \tag{67}$$

$$\rightarrow C_2H_5CH{=}C{=}O + CH_3OH \tag{68}$$

$$\rightarrow C_2H_5CH{=}C(OH)OCH_3 \tag{69}$$

$$\rightarrow C_3H_7CHO + HCHO \tag{70}$$

$$\rightarrow HC(O)OCH_3 + CH_3CH{=}CH_2 \tag{71}$$

$$\rightarrow CH_3C(O)OCH_3 + CH_2{=}CH_2 \tag{72}$$

The formation of ethene, reaction (67), has a much higher barrier of 285 kJ mol^{-1} than was the case for EP but is still lower than the energy required to cleave the weakest bonds in the molecule, either the $C_\alpha-C_\beta$ at 353 kJ mol^{-1} or the $O-CH_3$ at 364 kJ mol^{-1}.

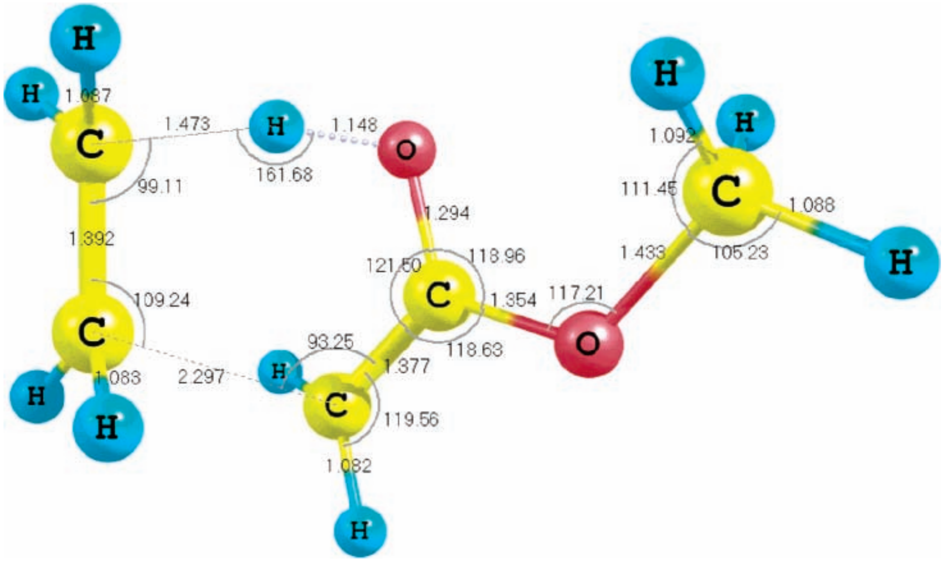

Figure 12. MBTS1: formation of ethene 1-methoxy-ethenol via a six-membered transition state.

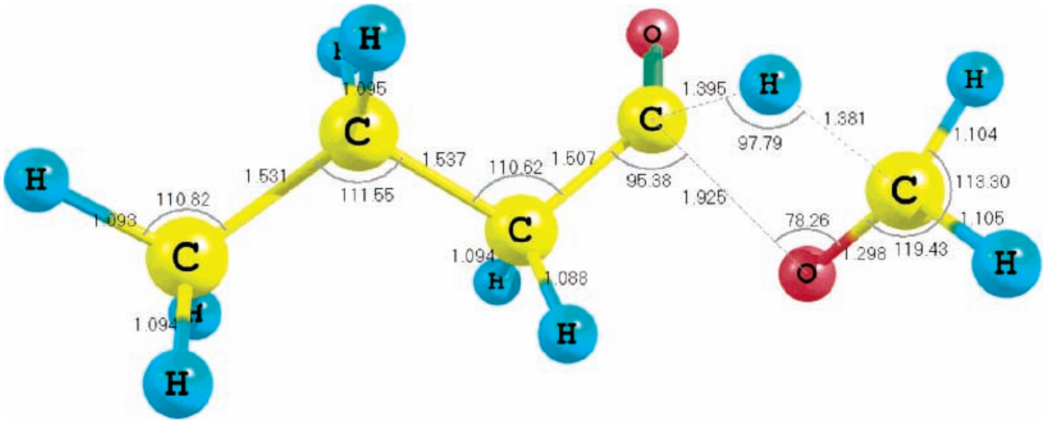

Figure 13. MBTS4: aldehyde formation.

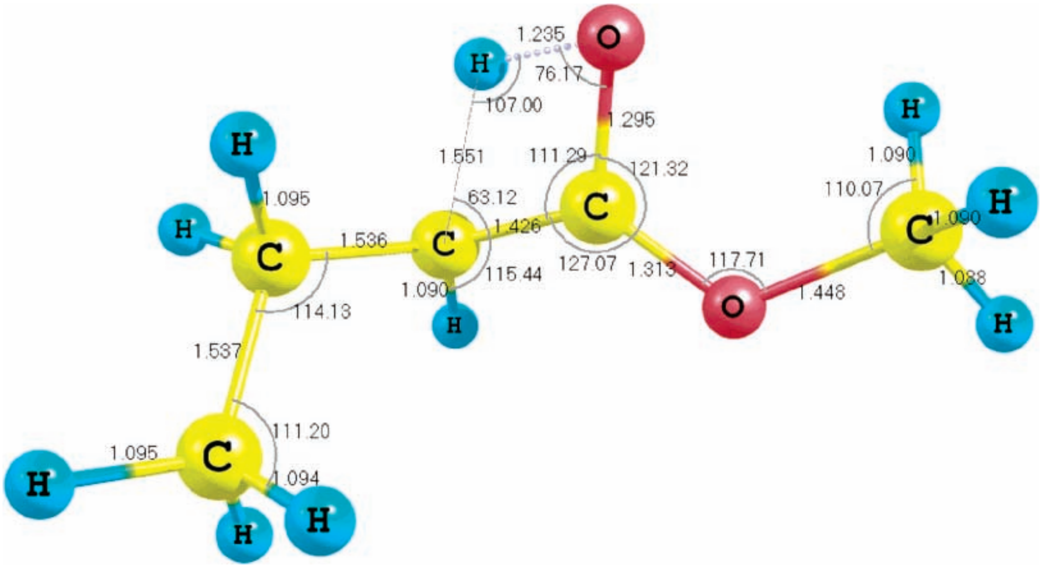

Figure 14. MBTS2: enol transition state.

For MB, aldehyde and ketene formation in reactions (70) and (68) are favored over alkene + ester formation, reactions (71) and (72), but the lowest barrier height for MB is 285 kJ mol^{-1} compared to 210 kJ mol^{-1} for EP, which is in concordance with the observed higher reactivity of the latter compared to the former.

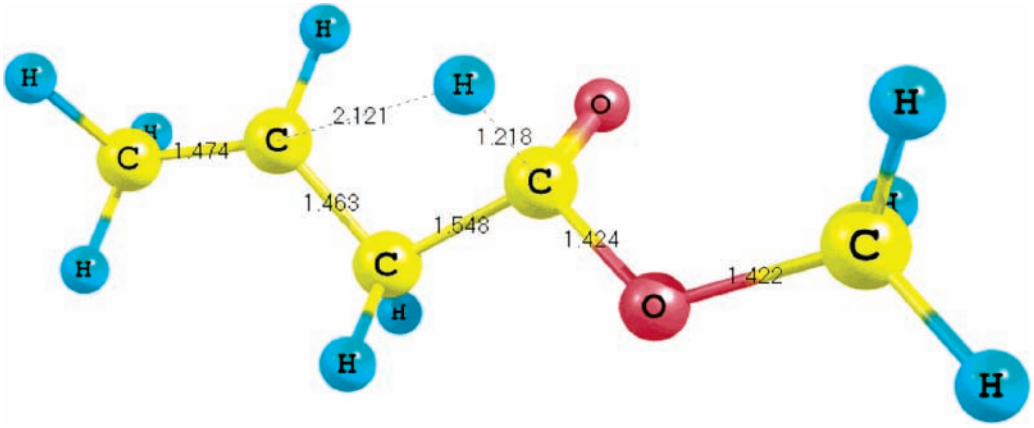

Figure 15. MBTS5: elimination of propene and methyl formate.

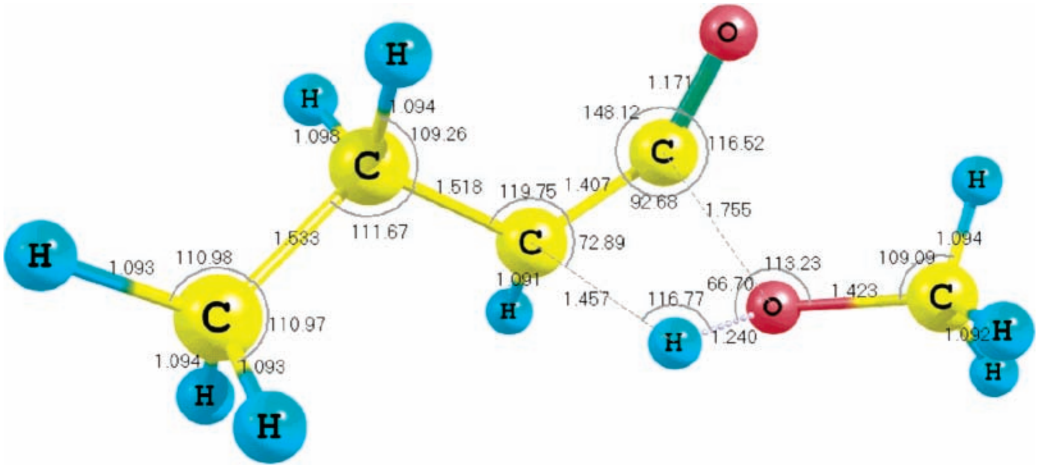

Figure 16. MBTS3: formation of ketene and methanol.

On the other hand, ethylene formation from MB is also examined but needs an energy barrier of 285 kJ mol^{-1}. Nevertheless, it is still lower in energy than breaking the weakest $C_\alpha-C_\beta$ of 353 kJ mol^{-1}. However, rupture of the latter bond gives rise to the formation of ethyl and methyl acetate radicals. The next weak bond is the $O-CH_3$ (364 kJ mol^{-1}), which gives rise to methyl and butanoate radicals.

The endothermicities of ketene formation are comparable, 165 kJ mol^{-1} for ethyl propanoate and 167 kJ mol^{-1} for methyl butanoate, and the barrier heights are comparable in both cases, 306 in EP as against 311 kJ mol^{-1} for MB. The $C_\alpha-H$ bond strengths are the same in both esters at 394 kJ mol^{-1}. Similarly, the barrier heights for enolization in both esters are comparable, 314 kJ mol^{-1} for EP vs 313 kJ mol^{-1} for MB.

Nevertheless, aldehyde formation from EP is easier than from MB because the C(O)−O bond is weaker in EP than in MB, 420 vs 424 kJ mol^{-1}, respectively, and the OC−H is weaker in EP than MB: 407 vs 414 kJ mol^{-1}. The C−O bond is weaker in EP than MB by 2 kJ mol^{-1}, giving rise to ethoxy and methoxy radicals, respectively, and the corresponding radical.

All of the investigated channels are endothermic and according to the Hammond postulate[74] the structures of the transition states, Figures 4−9 and 11−16, should be closer to the products rather than the reactants, that is, late transition states. The most endothermic reaction in the case of EP, with an enthalpy of reaction of +335 kJ mol^{-1}, transfers a β-H atom to the carbonyl carbon to form ethene and ethyl formate; see Figure 6. In this case, the $C-H_\beta$ bond is elongated by 87.6% from its value in the parent ethyl propanoate and the newly formed C−H bond is elongated only by 11.4% compared to its original value in the product, $HCOOC_2H_5$.

For methyl butanoate the most endothermic reaction is the formation of propene and methyl formate, Figure 15, at +338 kJ mol^{-1}. In this case, the $C-H_\beta$ bond is elongated by 93.9% from its value in methyl butanoate and the newly formed C−H bond is elongated by only 10.8% compared to its original value in the product, methyl formate.

The situation for the less endothermic pathways is ambiguous and the transition states optimize to structures intermediate between reactants and products. For the least endothermic reaction in ethyl propanoate decomposition, the formation of ethene and propionic acid through six-member transition state, Figure 6 (enthalpy of reaction of +66 kJ mol^{-1}), the $C-H_\beta$ bond is elongated by 22.0% from its value in the parent and the newly formed O−H bond is elongated by 34.1% compared to its original value in the product propionic acid.

In the transition state for the least endothermic reaction at +96 kJ mol^{-1} in the decomposition of MB, to give ethene and methyl acetate, Figure 11, the C−H bond is elongated by 26.0% from its value in the reactant and the newly formed C−H bond is elongated by 71.5% compared to its original value in the product methyl acetate.

Conclusions

The bond dissociation energies for the model biofuels ethyl propanoate and methyl butanoate have been determined through a series of isodesmic and isogeitonic reactions that computed the enthalpy of reaction and thereby the enthalpy of formation at the CBS-QB3 level of theory.

Arising out of these computations we have resolved a number of controversies regarding the heat of formation of the acetate or acetyloxy radical showing that $\Delta H_f^\circ[CH_3C(O)\dot{O};298.15K] = -197.8$ kJ mol^{-1} and that the higher of the two values supported by experiment for the *trans*-hydrocarboxyl radical of -181.6 ± 3.6 kJ mol^{-1} is to be preferred, although our calculations suggest that this is very much a lower limit.

Our calculations identify the weakest bond in MB as the central C−C, which conflicts with the work of Gaïl et al.[35] and Schwartz and co-workers[40] who both assumed that cleavage of the O−C would predominate.

Investigation of the various decomposition channels available to both molecules reveals that energy barriers and rate constants follow a similar trend favoring the channel to produce ethene via a six-membered transition state or from the O-alkyl moiety of the molecule if possible. These channels present the lowest barrier height and the highest rate constant. Following these channels, reactions to produce enols, ketenes and aldehydes were found to end with the reactions to produce alkenes via four-membered transition state in the C-alkyl part of both molecules.

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Supporting Information Available: Table of frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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