REACTIVITY, THERMOCHEMISTRY AND KINETICS of 2-BUTANONE RADICALS: $CH_2•C(=O)CHCH_3$, $CH_3C(=O)CH•CH_3$ and $CH_3C(=O)CH_2CH_2•$

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Abstract

Thermochemistry and reaction paths for the radicals of 2-butanone and for species resulting from the reactions of 2-butanone-1yl, -3yl and -4yl radicals with $^3O_2$ are reported. Standard enthalpies, bond energies and kinetic parameters are evaluated using ab initio (G3MP2B3 and G3), and Density Functional (B3LYP/6-311g(d,p)) calculation. The $CH_2•C(=O)CH_2CH_3$, $CH_3C(=O)CH•CH_3$ and $CH_3C(=O)CH_2CH_2•$ radicals + O_2 association results in chemically activated peroxy radicals with 27, 26 and 35 kcal mol^{-1} excess of energy, respectively. The chemically activated adducts can react back to butanone-yl + O_2, form cyclic ethers, eliminate HO_2 to form an olefinic ketone, or undergo rearrangement via intramolecular abstraction of hydrogen to form hydroperoxide-alkyls. The hydroperoxide-alkyl radical intermediates can undergo further reactions forming cyclic ethers ketones (lactones) and OH radicals. Quantum RRK analysis is used to calculate k*(E)* and master equation analysis is used for evaluation of pressure fall-off in these chemical activated reaction systems.

Introduction

Ketones are important in the chemistry of the atmosphere and in combustion systems. Their photo-dissociation in the lower atmosphere results in formation of free radicals and that influence the oxidation capacity of the atmosphere. Ketones are also used as fuel tracers for monitoring fuel properties such as concentration, temperature, density, pressure, velocity, and distribution using laser-induced fluorescence [1, 2] and as fuel additives in reducing soot emissions [3,4]. Important atmospheric and combustion loss processes for ketones involve hydrogen abstractions by OH radicals, a process that is partially controlled by carbon-hydrogen bond energies, and by photolysis resulting from absorption by the carbonyl group [5, 6, 7]. The photolysis is reported to account for significant overall global presence of OH and HO_2 radicals particularly in the upper troposphere [8, 9]. To our knowledge, there are no studies describing the thermochemistry of these carbonyl alkyl radicals or the effect of the carbonyl group on the radical association reactions with O_2 in atmospheric or combustion systems. The peroxy radicals, resulting from the association of the radicals with oxygen (Figure 1), can undergo propagation and/or chain branching reactions through their chemical activated (energized)) and stabilized adducts.

In this study the C—H and C—OO bond energies are determined for the three carbons of the 2-butanone and the respective peroxy radicals. The thermochemistry of reaction intermediates and the oxidation reaction paths of the 2-butanone 1-, -3- and 4- yl radicals ($CH_2•C(=O)CH_2CH_3$, $CH_3C(=O)CH•CH_3$ and $CH_3C(=O)CH_2CH_2•$) with dioxygen is also determined. Structures and enthalpies of formation for important stable species and intermediate radicals resulting from this association reaction; reaction paths, transition state barriers and kinetics are reported. Standard enthalpies, $\Delta_f H^0_{298}$, are calculated using ab initio

and Density Functional calculations. Kinetics and intermediate paths are determined as a function of temperature and pressure using bimolecular chemical activation analysis.
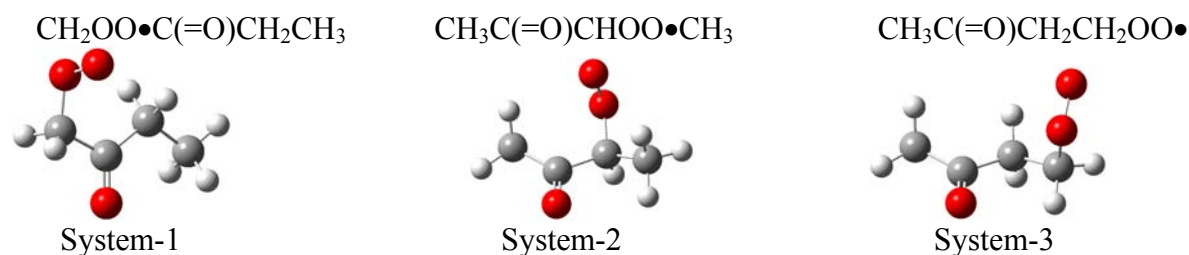
CH$_2$OO•C(=O)CH$_2$CH$_3$ CH$_3$C(=O)CHOO•CH$_3$ CH$_3$C(=O)CH$_2$CH$_2$OO•

System-1   System-2   System-3

Figure 1. Structure of the three peroxy radicals

Computational Methods

Molecular properties are calculated by using the Gaussian 03 program suite [10, 11, 12]. The hybrid DFT method B3LYP, which combines the three parameter Becke exchange functional, B3, with the Lee-Yang-Parr non-local correlation functional, LYP, with a double polarized basis, 6-311G(d,p) [13, 14, 15], the G3 and the modified G3 methods reported as G3MP2B3 which uses B3LYP geometries (G3MP2//B3LYP/6-31G(d,p)) [16, 17].

The accuracy of Density Functional Theory can be improved by use of isodesmic reactions, in which a hypothetical reaction that has the same number and type of bonds on both side, is used to calculate the enthalpy of the reaction ($\Delta H^0_{rxn,298}$). Here the errors on a given type of bond on each side of the reaction will cancel, and the resulting accuracy of $\Delta H^0_{rxn,298}$ will be high. The enthalpy of formation of a species is determined as follows:

$\Delta H^0_{rxn,298}$ = Σ (total energies at 298 K of products) – Σ (total energies at 298 K of reactants)

$\Delta H^0_{rxn,298}$ = Σ (experimental $\Delta_f H^0_{298}$ of products) – Σ (experimental $\Delta_f H^0_{298}$ of reactants)

A majority of the calculations in this study are based on isodesmic reactions, in which calculated values are coupled to experimental or computed enthalpies of formation of the reference species. In developing the isodesmic work reactions, efforts were made to preserve the bonding environment in the target species, so as to effectively cancel errors in bond energies and adjacent interaction energies across the work reactions.

Transition states were identified by their single imaginary frequency, whose mode of vibration connects the reactants and products. Enthalpies of formation on low energy geometries were calculated from isodesmic reaction analysis. For transition states, enthalpies of formation were obtained from the computational enthalpy of activation and from the calculated enthalpies of formation of the reactants or products.

Results and Discussion

Enthalpy of formation, $\Delta_f H^0_{298}$ calculations

Standard enthalpies of formation for reactants, transition states and products of the radical oxidation reaction systems CH$_2$•C(=O)CH$_2$CH$_3$, CH$_3$C(=O)CH•CH$_3$ and CH$_3$C(=O)CH$_2$CH$_2$• + O$_2$ are calculated using the total energies combined with isodesmic work reactions. The calculated enthalpy of formation for adducts, intermediates, products, and transition state structures are given in Table 1 and in the potential diagrams below (Figures 2 - 7). Some reference species, which could not be found in the literature, were also calculated. When comparing the enthalpy values of the radicals listed in Table 1, we note an excellent agreement among B3LYP, G3MP2B3 and G3, with a difference ≤ 1 kcal mol^{-1}.

Table 1. Calculated Standard Enthalpy of formation

Species	$\Delta_f H^0_{298}$ in kcal mol^{-1}		
	B3LYP	G3MP2B3	G3
$CH_2\bullet C(=O)CH_2CH_3$	-12.80	-13.57	-13.45
$CH_3C(=O)CH\bullet CH_3$	-19.24	-18.83	-18.17
$CH_3C(=O)CH_2CH_2\bullet$	-8.54	-8.47	-8.58
$CH_2OO\bullet C(=O)CH_2CH_3$	-41.42	-40.18	-40.52
$CH_3C(=O)CHOO\bullet CH_3$	-44.95	-44.24	-44.78
$CH_3C(=O)CH_2CH_2OO\bullet$	-44.1	-43.4	-43.7

The enthalpy values of the radicals and stable species reported in Figures 2 to 7, also show good agreement among the calculation methods as further developed and reported in other studies [18, 19]. The entropy and heat capacity for intermediates, transition state structures and final products are calculated using the rigid-rotor-harmonic-oscillator approximation [20, 21, 22] and based on the calculated parameters: frequencies, moments of inertia from the optimized lowest energy geometries, symmetry, spin degeneracy and optical isomers. These values are available from the authors [19]. The thermodynamic properties have been used for the determination of the reaction path energies and kinetic parameters in the kinetics.

Bond dissociation energies
The bond energies (BE) of C—H in the 2-butanone allow the estimation of abstraction kinetic parameters via rate constant rules using thermochemistry. The C—H bond energies for the $CH_3C(=O)CH_2CH_3$ are determined by DFT and ab-initio (G3MP2B3, G3) calculations. Table 2 shows an excellent agreement between the DFT and the ab initio BE values. Comparison of the C—H bonds in the 2-butanone, shows that bond energies are subject to a strong influence of the carbonyl group. As shown in previous studies [23, 24] and in Table 2, the sp^2 structure with π bonding of the carbon oxygen double bond, allows for resonance with the adjacent carbon radical resulting in lower bond energies. Only carbon 4 (C-4) shows a conventional C—H BE for a primary carbon of 100.6 kcal mol^{-1}. Table 2 shows that the C—H bond in the secondary carbon (C-3) adjacent to the carbonyl (–C=O) in $CH_3C(=O)CH(—\textbf{H})CH_3$ (2-butanone-3yl) has the lowest bond energy, 90 kcal mol^{-1}. The BE increases by near 6 kcal mol^{-1} for the primary carbon (C-1) in (**H**—)$CH_2C(=O)CH_2CH_3$ (2-butanone-1yl) and by 10 kcal mol^{-1} in the primary carbon (C-4), $CH_3C(=O)CH_2CH_2(—\textbf{H})$ (2-butanone-4yl) which is separated from the carbonyl by an sp^3 CH_2 group.

Table 2. Calculated C—H and R—OO bond energies in kcal mol^{-1}

	Species	B3LYP	G3MP2B3	G3
System-1	(**H**—)$CH_2C(=O)CH_2CH_3$	96.32	95.55	95.67
System-2	$CH_3C(=O)CH(—\textbf{H})CH_3$	89.88	90.29	90.95
System-3	$CH_3C(=O)CH_2CH_2(—\textbf{H})$	100.58	100.65	100.54
System-1	(**•OO**—)$CH_2C(=O)CH_2CH_3$	28.62	26.61	27.07
System-2	$CH_3C(=O)CH(—\textbf{OO•})CH_3$	25.71	25.41	26.61
System-3	$CH_3C(=O)CH_2CH_2(—\textbf{OO•})$	35.56	34.93	35.12

Table 2 compares the C—OO bonds in the peroxy radicals and we observe that the carbonyl group influences these C—OO bond energies as well. The results show a C—OO BE of 25 to 26 kcal mol^{-1} when the peroxy group is attached to the carbon adjacent to the carbonyl group

(systems 1 and 2) while the C—OO BE in 2-butanone-4-yl (system 3) is higher by near 10 kcal mol^{-1}. The same result was observed in the benzoyl + O$_2$ system [23].

Reaction Paths and Potential Diagrams

In this study, the major reaction pathways for oxidation of CH$_2\bullet$C(=O)CH$_2$CH$_3$, CH$_3$C(=O)CH$\bullet$CH$_3$ and CH$_3$C(=O)CH$_2$CH$_2\bullet$ radicals are determined. A detailed kinetic evaluation of the three systems is reported in a further study [19]. Reactions available to the energized adducts include:

a- Formation of a stable peroxy radical (Figure 2)
b- Reverse reaction back to butanone-yl radical + O$_2$ (no reaction)
c- Intramolecular abstraction of H from each (three) carbons by the peroxy site (Figures 3-6).
d- Peroxy radical addition at the carbonyl carbon forming a cyclic peroxide ring (Figure 7).
e- RO—O bond cleavage, (only important at very high T, not included in this study).

1. Formation of peroxy radical

The association reaction of the 2-butanone radical with O$_2$ results is in formation of an activated peroxy radical. 2-butanone has three radical sites for the addition of O$_2$. The reaction forms the activated peroxy [CH$_2$OO$\bullet$C(=O)CH$_2$CH$_3$]$^{\#}$, [CH$_3$C(=O)CHOO$\bullet$CH$_3$]$^{\#}$ and [CH$_3$C(=O)CH$_2$CH$_2$OO$\bullet$]$^{\#}$ intermediates with no barrier and a relatively loose transition state. In a previous study [23], we have determined the PES for the dissociation of C$_6$H$_5$C(=O)OO$\bullet$ to C$_6$H$_5$C$\bullet$(=O) + O$_2$ by calculating the structure of C$_6$H$_5$C(=O)OO$\bullet$ at different C—OO distances. Our DFT calculations did not show a saddle point for the benzoyl system and we reproduce the potential of the phenyl radical + O$_2$ association / phenylperoxy dissociation reaction [25, 26].
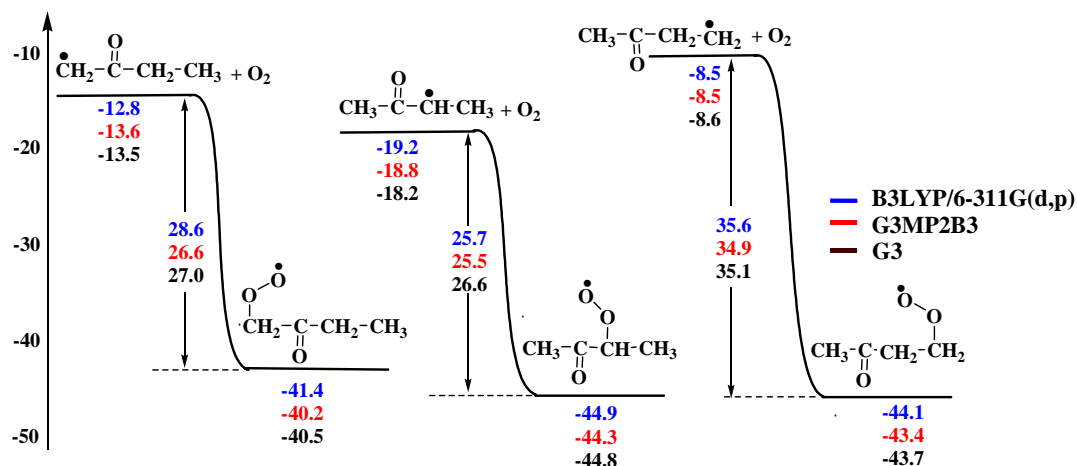

Figure 2. Well depth of the 2-butanone-yl + O$_2$ association reaction,

Two of the peroxy intermediates CH$_2$OO$\bullet$C(=O)CH$_2$CH$_3$ and CH$_3$C(=O)CHOO$\bullet$CH$_3$ have a fairly shallow well depth of 25-27 kcal mol^{-1} at 298K (due to loss of resonance with the carbonyl group), relative to G3 calculations as shown in Figure 2. The CH$_3$C(=O)CH$_2$CH$_2$OO$\bullet$ radical has a significantly deeper chemical activation well at 35 kcal mol^{-1} which provides added energy for further reaction of peroxy radical. This deeper well is explained by the primary radical, which has no resonance stabilization. These results are interesting since the bond energies are showing that the 2-butanone-4-yl is the less reactive radical. As reported above CH$_3$C(=O)CH$_2$CH$_2\bullet$ is formed after breaking over 100 kcal mol^{-1} C—H bond energy while the other radicals need some 90 and 95 kcal mol^{-1}. The Kinetic analysis below shows that the temperature plays an important role in the kinetics.

2. Intramolecular hydrogen abstraction via a 4-member ring.

All three systems will undergo intramolecular hydrogen abstractions which consist of transferring a hydrogen atom from the primary (C-1 and C-4) or secondary (C-3 adjacent to the carbonyl group) carbon to the peroxy oxygen site via a 4-member, 5-member, 6-member and 7-member ring structure. These reactions are described in Figures 3 to 6 which also show further reactions available to these adducts and compare the energetics of the three systems. Figure 3 describes the hydrogen shift from the carbon of the peroxy group (ipso carbon) to the peroxy oxygen site via a strained 4-member ring structure. These ipso radicals CH•(OOH)C(=O)CH$_2$CH$_3$, CH$_3$C(=O)C•(OOH)CH$_3$ and CH$_3$C(=O)CH$_2$CH•(OOH) formed for system 1, 2 and 3 respectively, are unstable. They radicals dissociate immediately, because the weak RO—OH bond (45 kcal mol^{-1}) cleaves allowing the strong C=O bond to form at 80 kcal mol^{-1} via e$^{\tilde{}}$ rearrangement. These adducts eliminate an OH and form: CH$_3$CH$_2$C(=O)CH=O, CH$_3$C(=O)C(=O)CH$_3$ and CH$_3$C(=O)CH$_2$CH=O for 2-butanone -1yl, -3yl and -4yl respectively.
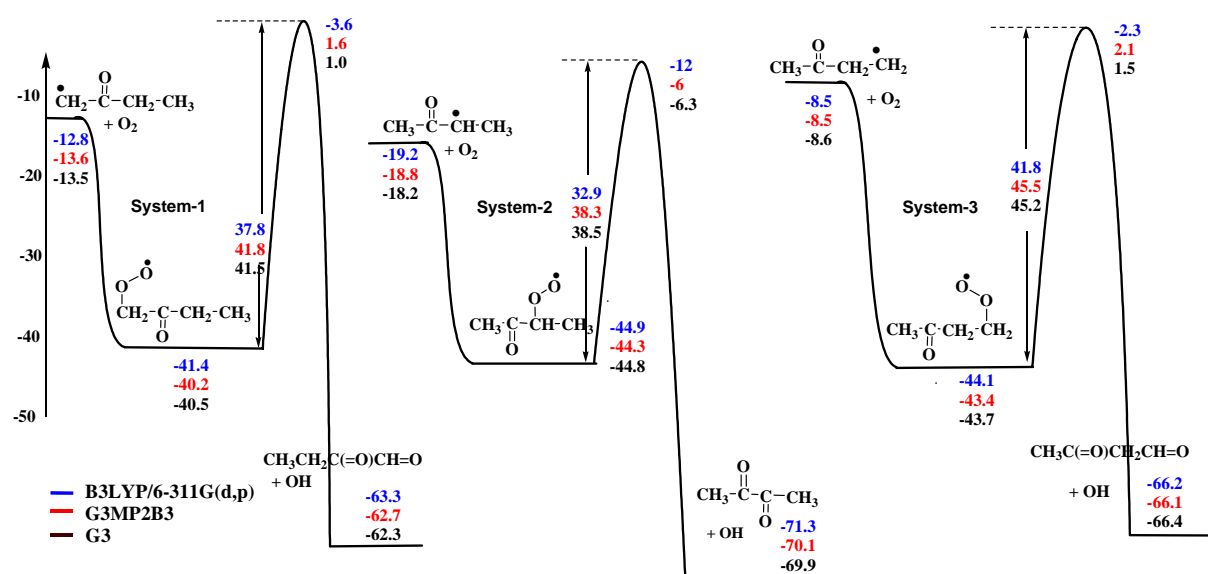
Figure 3. Intramolecular H atom abstraction / OH elimination reaction; Barrier strongly dependent on C—H bond energy

For all three systems the overall reaction is exothermic and releases some 22 to 25 kcal mol^{-1} relative to the stable peroxy radicals CH$_2$(OO•)C(=O)CH$_2$CH$_3$, CH$_3$C(=O)CH(OO•)CH$_3$ and CH$_3$C(=O)CH$_2$CH$_2$(OO•). However, these abstractions have high barriers, above the entrance channel, at 41, 38 and 45 kcal mol^{-1} respectively. The high barriers and shallow chemical activation well limit the importance of this reaction path at low temperature, but the importance increases at higher temperatures.

3. Intramolecular hydrogen abstraction via a strained 5 member ring.

An intramolecular abstraction of a H atom via a strained 5-member ring structure is a possible channel for CH$_3$C(=O)CH(OO•)CH$_3$ and CH$_3$C(=O)CH$_2$CH$_2$OO• (Figure 4). This abstraction transfers a hydrogen atom from the primary carbon (C-4) or from the secondary carbon (C-3) (adjacent to the C=O group) to the peroxy oxygen radical and forms an alkyl radical: CH$_3$C(=O)CH(OOH)CH$_2$• for 2-butanone-3yl and CH$_3$C(=O)CH•CH$_2$OOH for 2-butanone-4yl. The 2-butanone-3yl system with 26 kcal mol^{-1} well needs to overcome about 33 kcal mol^{-1} barrier while 2-butanone-4yl system has a lower barrier of 27 and 35 kcal mol^{-1} well. This low barrier for a 5 member ring H transfer results from the low C—H bond energy of the C-3

carbon. The barrier for the H-shift reaction in $CH_3C(=O)CH\bullet CH_2OOH$ at -17 kcal mol^{-1} is 9 kcal mol^{-1} under the entrance channel while the reaction of $CH_3C(=O)CH(OO\bullet)CH_3$ to $CH_3C(=O)CH(OOH)CH_2\bullet$ is 6 kcal mol^{-1} above the entrance channel. The 2-butanone-4yl shows a clear energetic advantage to forward reaction (oxidation) relative to the 2-butanone -1yl or -3yl radicals.
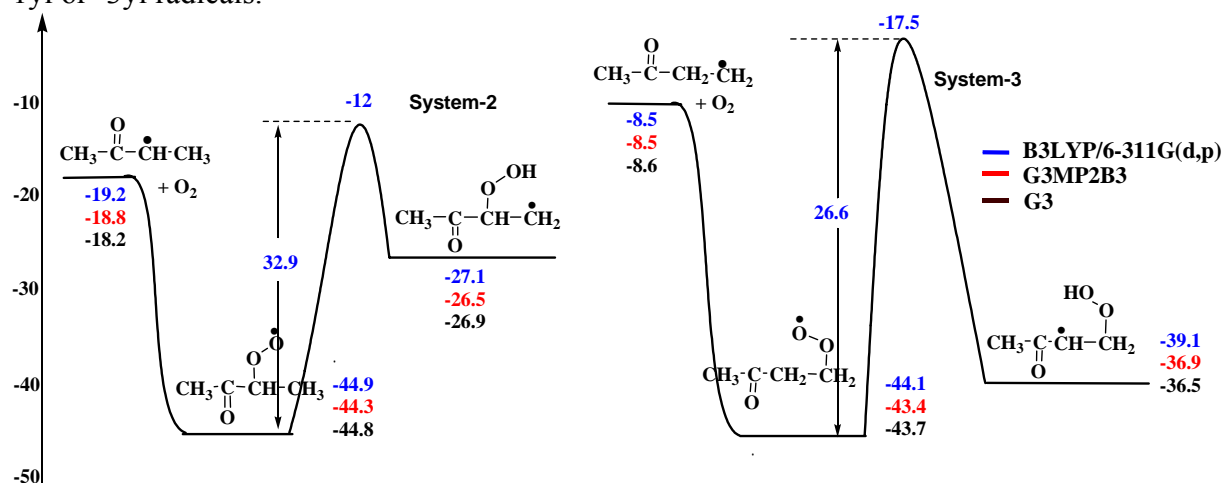

Figure 4. H-shift reaction via 5-member ring

4. Intramolecular hydrogen abstraction via a 6-member ring.

A second intramolecular abstraction via a less strained 6-member ring structure is possible for 2-butanone-1-yl, $CH_2OO\bullet C(=O)CH_2CH_3$ on the secondary C-3 (system 1) carbon and for 2-butanone-3yl, $CH_3C(=O)CHOO\bullet CH_3$ and on the primary C-1 carbon (system 2) as illustrated in Figure 5.
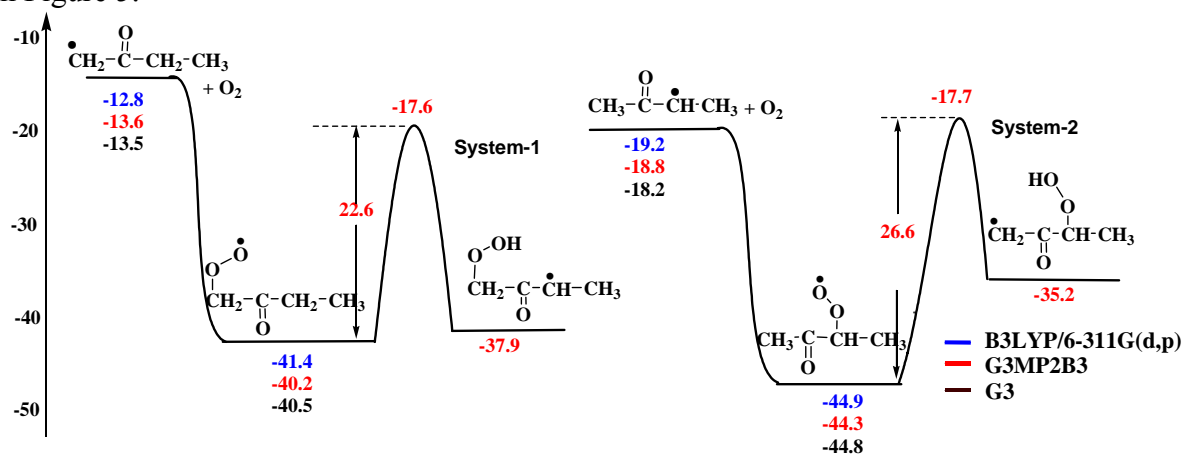

Figure 5. H-shift reaction via 6-member ring

It results in the formation of a resonantly stabilized hydroperoxide radical, $CH_2(OOH)C(=O)CH\bullet CH_3$, formed at -38 kcal mol^{-1} at a barrier slightly below the entrance channel by 4 kcal mol^{-1}. The $CH_2\bullet C(=O)CH(OOH)CH_3$ hydroperoxide alkyl radical formed at -35 kcal mol^{-1}, resulting from 2-butanone-3yl, has a barrier that is at the same energetic level as the entrance channel at -17.7 kcal mol^{-1}.

5. Intramolecular hydrogen abstraction via a 7-member ring.

Abstraction of a hydrogen atom via a 7-member ring is possible from the primary carbons (C-4) in 2-butanone-1-yl and in 2-butanone-4yl forming $CH_2(OOH)C(=O)CH_2CH_2\bullet$ and from $CH_2\bullet C(=O)CH_2CH_2(OOH)$ respectively (Figure 6). To abstract the hydrogen from the primary carbons (C-1 and C-4) barriers and energies show that systems 1 and 3 involve some

25-26 kcal mol^{-1} relative to the stable peroxy. The barrier for 2-butanone-1-yl is 26.5 at -14.7 kcal mol^{-1}, 1 kcal mol^{-1} below the entrance channel while in 2-butanone-4-yl, the TST structure is at -17.5 kcal mol^{-1} which is 9 kcal mol^{-1} below the entrance channel. This difference is explained by the C—H bond energy. As shown in Table 2, in 2-butanone-1-yl, the H to extract has a C—H bond which is 4 kcal mol^{-1} stronger than in 2-butanone-4-yl.
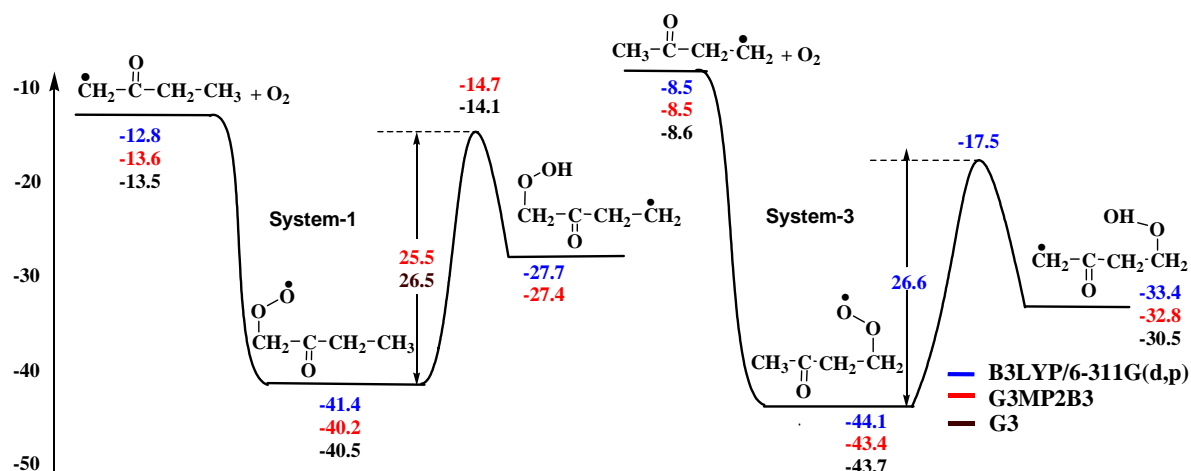

Figure 6. H-shift reaction via 7-member ring

6. Addition of the peroxy-oxygen radical to the C=O carbonyl group carbon C-2

Addition of the peroxy oxygen radical site on the carbonyl group is endothermic relative to the R• + O$_2$ entrance channel energy (Figure 7). The addition to the carbonyl involves a barrier of 33 to 38 kcal mol^{-1} relative to the peroxy radical as it breaks the strong (80 kcal mol^{-1}) carbonyl π bond. This addition forms a reactive dioxetane radical with a tight transition state for 2-butanone -1yl and 3-yl systems. This dioxetane radicals, when formed dissociates
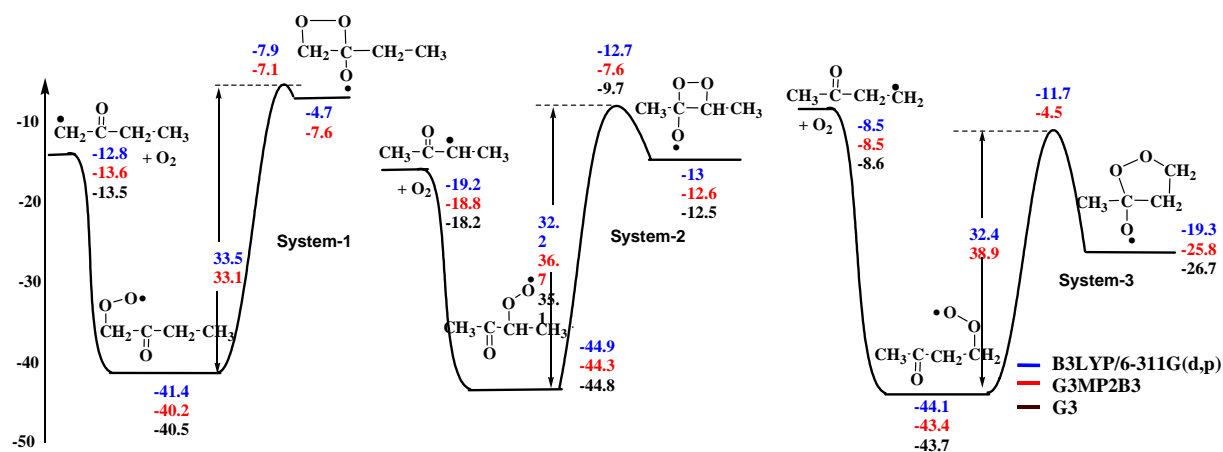

Figure 7. Addition to the carbonyl group carbon

rapidly through a very low or no barrier. Addition of the peroxy oxygen on the carbonyl group carbon in 2-butanone-4yl incurs the same barrier but with the deeper well, the barrier is near the entrance channel (R• + O$_2$) which is at -8.5 kcal mol^{-1}. In addition, the formation of a reduced strain, 5- member ring, results in the formation of a less reactive radical.

Kinetic calculations on the three systems

High Pressure limit kinetic parameters are obtained from canonical Transition State Theory calculations. Multifrequency Quantum Rice-Ramsperger-Kassel (QRRK) [27] analysis is used to calculate $k(E)$ data and master equation analysis (CHEMASTER code) is applied for fall-off on the CH$_2$•C(=O)CH$_2$CH$_3$, CH$_3$C(=O)CH•CH$_3$ and CH$_3$C(=O)CH$_2$CH$_2$• + O$_2$, reaction

systems. These form the energized peroxy radical intermediates $[CH_2OO\bullet C(=O)CH_2CH_3]^{\#}$, $[CH_3C(=O)CHOO\bullet CH_3]^{\#}$ and $[CH_3C(=O)CH_2CH_2OO\bullet]^{\#}$ which undergo further reaction. The calculations provide sets of rate constants for the formation of the stabilized adducts or reaction products as a function of pressure and temperature. Pressure dependence is important because different pressures are experienced throughout reactions in many combustion and engine systems. For example, scram jet engines run at 0.3 atm, turbines run at 10 to 15 atm, internal combustion engines can experience pressures to 100 atm and higher pressures are suggested for improved efficiency. These kinetic parameters are preliminary values and several channels are undergoing further analysis to increase accuracy.
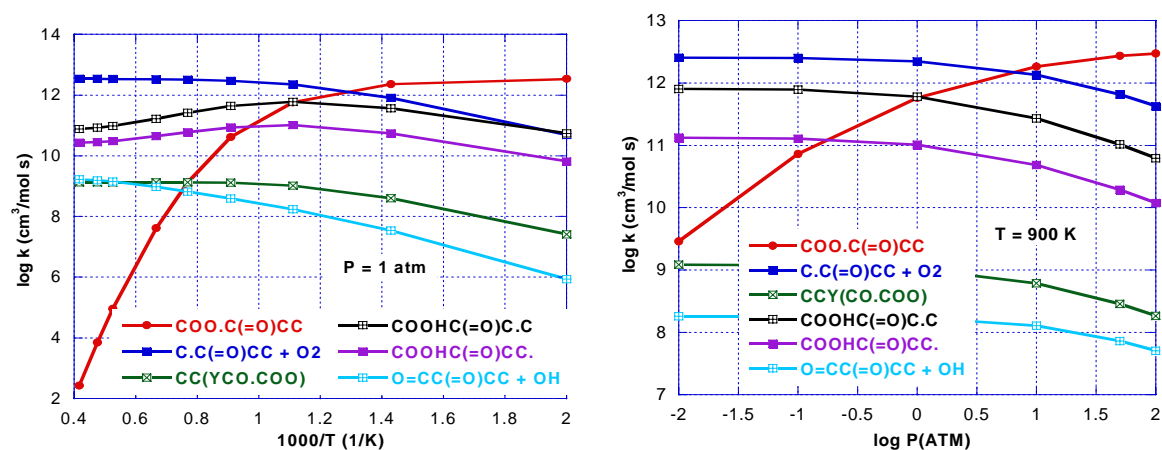

Figure 8: Chemical activation reaction for the products as a function of temperature at P=1atm and as a function of pressure at T = 900K for $CH_2\bullet C(=O)CH_2CH_3 + O_2$

Figure 8 illustrates the chemical activation reaction of $CH_2\bullet C(=O)CH_2CH_3 + O_2$ system as functions of temperature and of pressure. The results show that the important forward reactions paths are the stabilization reactions to the peroxy radical $CH_2OO\bullet C(=O)CH_2CH_3$. The reverse reaction back to $CH_2\bullet C(=O)CH_2CH_3 + O_2$ is also Fast. The H-shift reaction from the secondary carbon (C-3) shows the same dominance as the reverse reaction at low temperature; it decreases slightly at higher Temperature. The 7–member ring hydrogen abstraction reaction on the fourth primary carbon to form $CH_2OOHC(=O)CH_2CH_2\bullet$ have also some importance. Two channels start to show importance at higher temperature, at which sufficient energy is available for the energized radical to attack the oxygen site on the peroxy group carbon. This intermediate is unstable and beta scissions of an OH to form $O=CHC(=O)CH_2CH_3$ occurs.

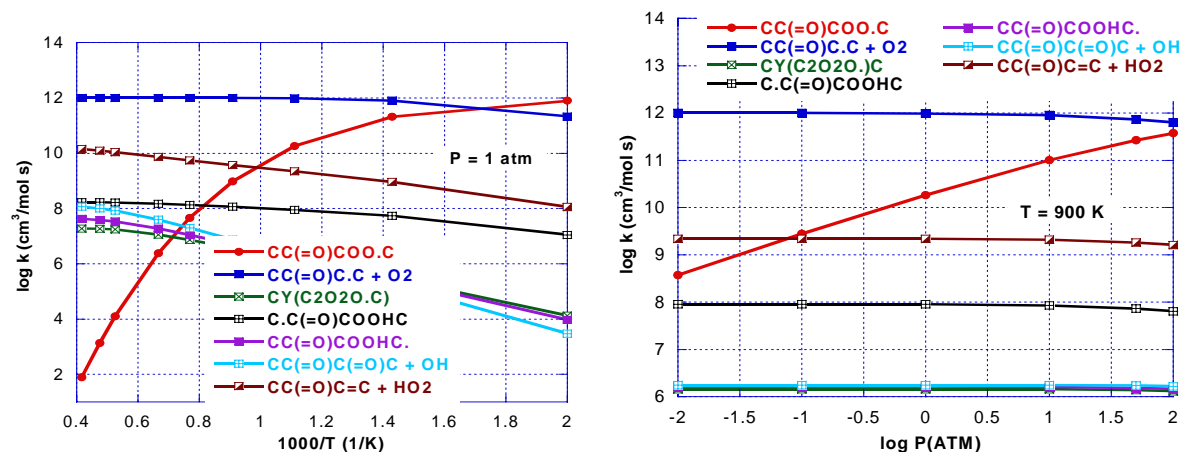**Figure 9**: Chemical activation reaction for the products as a function of temperature at P=1atm and as a function of pressure at T = 900K for $CH_3C(=O)CH\bullet CH_3 + O_2$

The chemical activation reaction of $CH_3C(=O)CH\bullet CH_3 + O_2$ system illustrated in Figure 9, shows that the important forward reaction paths are the stabilization reactions to the $CH_3C(=O)CHOO\bullet CH_3$ peroxy radical. The next two important channels are the OOH molecular elimination form $CH_3C(=O)CH=CH_2$ and the hydrogen abstraction reaction on the first primary carbon to form $CH_2\bullet C(=O)CHOOHCH_3$. More minor product a few orders of magnitude slower, are the butanedione + OH, the hydrogen abstraction from the primary carbon (C-4) and the oxygen attack on the carbonyl group carbon. These three reactions are in competition at higher temperature.
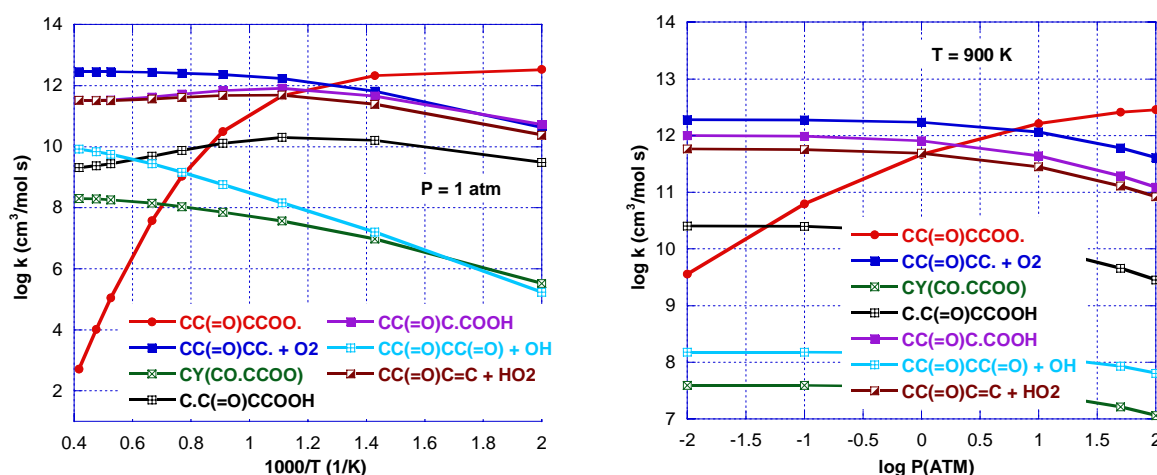

Figure 10: Chemical activation reaction for the products as a function of temperature at P=1atm for $CH_3C(=O)CH_2CH_2\bullet + O_2$

Figure 10 illustrates the product profiles from the 2-butanone-4yl peroxy radical, $CH_3C(=O)CH_2CH_2\bullet$, reaction with O_2 versus temperature at 1 atm and pressure at 900K. The reaction to stabilization of the $CH_3C(=O)CH_2CH_2OO\bullet$ peroxy radicals, is the most important forward reaction at low temperature. Two new product channels show importance also: intramolecular H-abstraction from C-3 to form $CH_3C(=O)CH\bullet CH_2OOH$ and molecular elimination of HO_2 forming $CH_3C(=O)CH=CH_2$. Abstraction of H-atom from C-1 is lower in magnitude but still of importance. The formation of the butadione + OH from the ipso abstraction channel is markedly increased with increasing temperature and is an important path at high temperature. The channel of less importance is as expected the attack of the oxygen radical on the carbonyl group carbon breaking the 80 kcal mol^{-1} C=O double bond.

Conclusions

Enthalpy of important intermediates, transition state structures and products resulting from the reaction of 2 butanone carbon radicals: $CH_2\bullet C(=O)CH_2CH_3$, $CH_3C(=O)CH\bullet CH_3$ and $CH_3C(=O)CH_2CH_2\bullet$ radicals with O_2, were studied by using DFT (B3LYP/6-311G(d,p) level) and ab-initio (G3MP2B3 and G3). These are illustrated in the PE diagrams of this study and are also reported separately in tabular form [19]. The R$\bullet$ + O_2 association of the three systems results in chemically activated peroxy radicals with 26 kcal mol^{-1} for 2-butanone-1yl and 2-butanone-3yl and with 35 kcal mol^{-1} for the 2-butanone-4yl radical. Important forward reaction channels of these chemically activated radical are: stabilization to peroxy radicals, OH and HO_2 plus olefin and intramolecular paths. Ether (lactone) ring formation occurs subsequent to the intramolecular hydrogen abstraction reactions. Stabilization to the peroxy radical is the most important channel.

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