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The Ground State Comparative Study of Proton Affinities and Associated Parameters of Conjugated α,β-unsaturated Carbonyl Compounds in Gas and Aqueous Phases by Density Functional Theory Method

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ABSTRACT

The proton affinities (PA) of a series of α,β-unsaturated carbonyl compounds (acrolein [ACL], 4-hydroxy-2-nonenal, methyl vinyl ketone, acrylamide [ACR], methyl acrylate, and ethyl methacrylate, and their O-protonated counterparts have been computed using density functional theory [Becke, Lee, Yang and Parr] method using 6-311G[d,p]) basis sets with complete geometry optimizations in both gaseous and aqueous phases. The O-protonation in both phases is observed to be exothermic, and the stereochemical disposition of proton is observed to be almost equal in each case. PA values are affected due to the presence of different length of alkyl chain and the different substituent at carbonyl carbon. In gas phase, PA of ACR is maximum, whereas it is minimum in ACL. In aqueous phase, the PA of the carbonyl compounds decrease in the order as $–H>–NH_2>–CH_3>–OC_2H_5>–OCH_3$ *substituent at carbonyl carbon. Atom electron density is recorded by natural population analysis along with Mulliken net charge. A proper correlation of PA with a number of computed system parameters like net charge on the carbonyl oxygen of unprotonated and protonated bases, charge on proton of protonated bases, and also the computed hardness (η) of the unprotonated bases in both phases have been explained thoroughly. The overall basicities are explicated considering the contribution from carbonyl group and distant atom.*

Key words: *Unsaturated, Natural population analysis, Aqueous, Becke; Lee; Yang and Parr, Density functional theory.*

1. INTRODUCTION

The α,β-unsaturated carbonyl compounds of type-2-alkene series (acrolein [ACL], 4-hydroxy-2-nonenal [HNE], methyl vinyl ketone [MVK], acrylamide [ACR], methyl acrylate [MA], and ethyl methacrylate [EMA]) are considered as soft electrophiles due to their corresponding pi-electron mobility. Members of this type-2-alkene series are treated as deadly environmental pollutants as they produce toxicity via common molecular mechanism [1]. Interaction of proton (Lewis acid) with carbonyl compounds (base) is an important part of biological science and chemistry. Proton affinity (PA) is the negative of the enthalpy change of proton-base interaction implying that higher the PA, higher the basicity. Gas phase basicity and PA are generally characterized by $B[g]+H^+[g]\rightarrow BH^+[g]$ and $B^-[g]+H^+[g]=BH$. Ground state basicities of carbonyl compounds are well recognized [2-4]. In recent study, the binding nature of ion with ligand (donor site) has been a research direction of physical organic chemistry and computational chemistry [5]. There are many instances of proton attack on carbonyl oxygen in the primary step of a carbonyl system [6-9]. Experimental data of PA are scarcely available [10] in ground state, and it is not an easy task to determine experimental PA values in a protonation reaction [11]. Ground state gas phase basicities of a series of aliphatic and aromatic conjugated carbonyl systems have been reported [12,13]. There are no such comparative theoretical results on PA which have still been found for several conjugated α,β-unsaturated carbonyl compounds of the type-2 alkene chemical class in both phases together. Therefore, we are compelled to turn to theory to investigate some quantitative thought on PA of a structurally related and biologically important carbonyl compounds in gas phase and in aqueous phases with the help of density functional theory Becke, Lee, Yang and Parr (B3LYP[DFT]) method at the 6-311G(d,p) basis set level [14]. We examine here

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theoretically, the PA of various carbonyl compounds toward Lewis acid H^+, and draw the comparison to the equivalent reaction with proton in gas phase as well as in aqueous phase. We are especially interested in the effect of solvation, geometric features, conjugation, and some other chemical properties. It is seen that computed chemical properties, geometrical features provided with this level of theoretical calculations are more accurate compared to other quantum mechanical methods such as *ab*-initio (Hartree-Fock [HF]) calculations, therefore, results obtained from HF calculation are not taken into account. Basis set superposition error corrections are not taken into account for this theoretical study. We have studied the interaction of H^+ ion with different electron rich sites present in the compound that is carbonyl oxygen-H^+ interaction, carbonyl π-H^+ interaction, and also the other electronegative atom-H^+ interaction. We observed that carbonyl oxygen-H^+ interaction energy is much lower in the series and this gives the most stable complexes. Gas phase PA determination reflects the thermodynamic and electronic properties of the compound are avoiding more complicated solvent effect [15], but in this study, we search the solvation effect on different molecular properties in the ground state. Charge on proton (q_H^+) in the protonated complexes in both gas and aqueous phases are noticed carefully, and it is seen that migration of charge density to the added proton has taken place. Computed PA values indicate that both preprotonation charge distribution local to chromophore and protonated complex relaxation charge density are involved to develop the overall basicity of the compounds. Since the selected carbonyl compounds are known as toxic pollutants, we have studied their comparative electrophilic nature by calculating some quantum mechanical parameters from their HOMO–LUMO energy gap. Compounds studied in this theoretical calculation are given below in Figure 1 with their respective abbreviated names.

2. METHODOLOGY

These quantum mechanical studies have been carried out using Gaussian "09" software (Gauss-view) [16]. The optimization has been done in B3LYP(DFT) method. Since the accuracy of the computed properties is sensitive to the quality of the basis set, we employ triplet split-valence basis set with polarization function 6-311G(d,p). Water was selected as a solvent from the solvent list for structural optimization of the free bases and their O-H^+ complexes using polarizable continuum model [17] at the same basis set. Mulliken population analysis [18] and NBO analysis (natural population analysis only) are used to determine equivalent charges on all atoms from the free bases and their protonated complexes.

3. RESULT AND DISCUSSION

The α,β-unsaturated carbonyl compounds given in Figure 1 and their O-H^+ complexes computed in B3LYP(DFT) method at 6-311G(d,p) basis set level in both gaseous and aqueous phases are observed to be exothermic, so reactions are thermodynamically favorable. The calculated PA values of the free bases with their respective names and proper abbreviation are listed in Table 1. Generated atomic charge is not important in this quantum mechanical calculation. Mulliken net charge density among the atoms has been observed. Charge among the atoms computes by separating orbital overlap equally between two shared atoms. Table 2 reports the net charge on carbonyl oxygen (q_O^-) of the compounds before protonation and of the protonated complexes and charge on proton (q_H^+) in protonated complexes. Data in Table 2 reflect that charge on O-atom decreases in the protonated species in both gaseous and aqueous phases and clear the high protonation tendency of the compounds. Charge on proton in the O-H^+ complexes decreases from actual value establish the fact of charge transfer from ligand to the added proton has taken place. Table 1 shows that PA is maximum for ACR (−218.56 kcal/mole) in gas phase where ACL exhibits the highest affinity

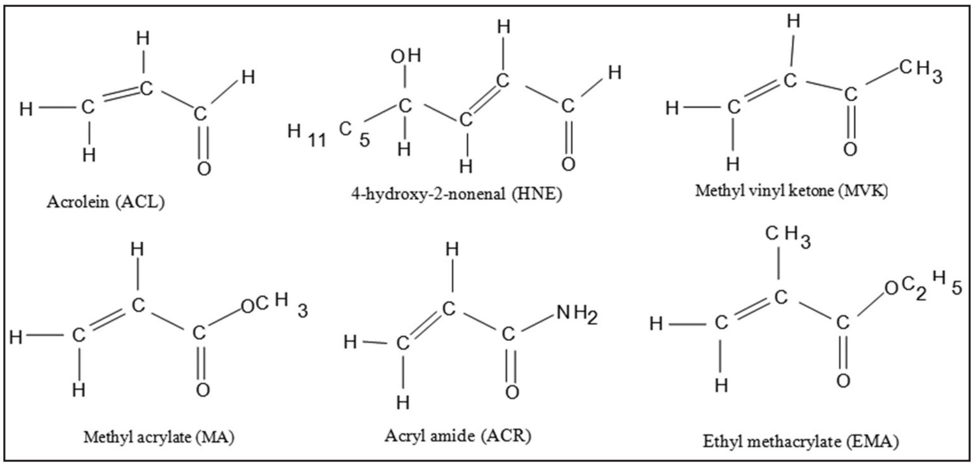


Figure 1: α,β-unsaturated carbonyl compounds.

Table 1: Computed PA=ΔE of six α,β-unsaturated carbonyl compounds for both gas and aqueous phases at the equilibrium geometry of the ground state. All data of PAs are in Hartree and kcal/mole unit.

Molecule	**Gas phase PA**		**Aqueous phase PA**	
	ΔE (Hartree)	**ΔE (kcal/mol)**	**ΔE (Hartree)**	**ΔE (kcal/mole)**
ACL	−0.3207	−201.24 (−194.019)*	−0.4526	−284.01
HNE	−0.3427	−215.04 (-)	−0.414	−259.78
MVK	−0.3336	−209.33 (−200.478)*	−0.4137	−259.60
ACR	−0.3483	−218.56 (−208.30)*	−0.4269	−267.88
MA	−0.3342	−209.71 (−199.28)*	−0.4104	−257.52
EMA	−0.3361	−210.90 (−203.11)*	−0.4114	−258.15

*Experimental PA values of the respective compounds are noted in the parenthesis. Ref: Grutzmacher *et al*. 1989.
PA: Proton affinities, ACL: Acrolein, HNE: 4-hydroxy-2-nonenal, MVK: Methyl vinyl ketone, ACR: Acrylamide, MA: Methyl acrylate, EMA: Ethyl methacrylate

Table 2: Computed Mulliken net charge on carbonyl oxygen atom (q_O–) of free base (B_1) and O-protonated complexes (B_1H_+) and net charge on proton (q_{H+}) of the O-protonated complexes at the equilibrium ground state and dipole moment (p) in debye of the free bases in both phases.

Molecule	**Gas phase**				**Aqueous phase**			
	(q_O^-)		**q_H+**	**p**	**(q_O^-)**		**qH^+**	**p**
	B_1	**B_1H^+**	**B1H+**		**B_1**	**B_1H^+**	**B_1H^+**	
ACL	−0.2864 (−0.5056)	−0.1465 (−0.5002)	0.3200 (0.5181)	3.15	−0.4675 (−0.5673)	−0.1742 (−0.5162)	0.3389 (0.5299)	4.04
HNE	−0.2944 (−0.5214)	−0.2101 (−0.5187)	0.3206 (0.5169)	2.12	−0.3490 (−0.5530)	−0.2090 (−0.5234)	0.3437 (0.5312)	2.83
MVK	−0.3022 (−0.5494)	−0.1995 (−0.5425)	0.3162 (0.517)	2.7	−0.3574 (−0.5979)	−0.2090 (−0.5538)	0.3354 (0.5298)	3.51
ACR	−0.3594 (−0.6048)	−0.2505 (−0.5837)	0.3171 (0.5152)	3.88	−0.4316 (−0.6714)	−0.2750 (−0.5979)	0.3307 (0.5230)	5.14
MA	−0.3157 (−0.5670)	−0.1889 (−0.5567)	0.2991 (0.5085)	4.32	−0.3778 (−0.6265)	−0.222 (−0.5757)	0.323 (0.5238)	5.56
EMA	−0.3553 (−0.5587)	−0.2192 (−0.5772)	0.3106 (0.5187)	1.78	−0.3701 (−0.6180)	−0.2374 (−0.5854)	0.3278 (0.5304)	5.51

Data written in parenthesis are obtained from NPA analysis. NPA: Natural population analysis, ACL: Acrolein, HNE: 4-hydroxy-2-nonenal, MVK: Methyl vinyl ketone, ACR: Acrylamide, MA: Methyl acrylate, EMA: Ethyl methacrylate

(−284.01 kcal/mole) toward proton in aqueous media. The different PA values of the α,β-unsaturated carbonyl compounds clear the nonunique effect of conjugated double bond and influenced by the different substituent at carbonyl carbon. In gas phase, the highest PA value in ACR is due to the presence of $–NH_2$ group at the carbonyl carbon. Along with C-C double bond effect, lone-pair electron on nitrogen atom also move toward binding oxygen makes it more electron rich and enhanced the PA. Gas phase PA increases in the order ACL<MVK<MA≤EMA<HNE<ACR, where it follows the decreasing order ACL>ACR>HNE>MVK>EMA>MA in the aqueous phase. In the presence of solvation effect, this order appeared by almost reversed due to the electronic relaxation effect. ACL shows the highest affinity to proton because there is no possibility of hydrogen bond formation at any center of the compound which can restrict the shifting of π electron at the binding site, so the resonance effect (+R) increases the electronegativity of binding oxygen and accelerate the proton-oxygen interaction. PA value of HNE (−259.78 kcal/mole) becomes less compared to ACL in aqueous phase because of the possibility of hydrogen bond formation with hydroxyl oxygen, but it has higher PA value than MVK, MA, and EMA, this is due to the positive inductive effect (+I) exhibited by the long alkyl chain attached to the carbonyl group shifting partial negative charge at oxygen binding site [19]. PA value varies due to the presence of different substituents at the carbonyl carbon, and it also affected slightly by the substituent (–H or $–CH_3$) present at the α-carbon of the molecule.

PA increases in gas phase following the order as $B=–H<–CH_3<–OCH_3<–OC_2H_5<–NH_2$. Effect of

Table 3: Geometrical features of the free base and O-protonated base (length in Å and angle in degree) at the equilibrium ground state in the gas phase.

Molecule	Free Base	O-protonated complexes		
	r (C-O)	r (C-O)	r (O-H+)	<C-O-H+)
ACL	1.208	1.277	0.9761	114.720
HNE	1.21	1.298	0.9771	113.560
MVK	1.213	1.291	0.9721	117.570
ACR	1.22	1.30	0.9686	113.275
MA	1.203	1.296	0.9684	113.577
EMA	1.208	1.298	0.9743	111.597

ACL: Acrolein, HNE: 4-hydroxy-2-nonenal, MVK: Methyl vinyl ketone, ACR: Acrylamide, MA: Methyl acrylate, EMA: Ethyl methacrylate

Table 4: Geometrical features of the free base and O-protonated base (length in Å and angle in degree) at the equilibrium ground state in aqueous phase.

Molecule	Freebase	O-protonated complexes		
	r (C-O)	r (C-O)	r (O-H$^+$)	<C-O-H$^+$
ACL	1.221	1.277	0.9762	113.970
HNE	1.21	1.288	0.9715	112.712
MVK	1.219	1.286	0.9728	113.1269
ACR	1.230	1.307	0.9687	112.432
MA	1.212	1.295	0.9694	113.4703
EMA	1.212	1.295	0.9749	111.397

ACL: Acrolein, HNE: 4-hydroxy-2-nonenal, MVK: Methyl vinyl ketone, ACR: Acrylamide, MA: Methyl acrylate, EMA: Ethyl methacrylate

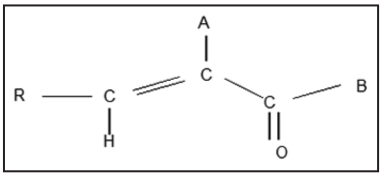


Figure 2: Structures for conjugated α,β-unsaturated carbonyl compounds of type-2-alkene chemical class (R=–H or alkyl group, A=–H or –CH$_3$ and B=–H,–CH$_3$,–OCH$_3$,–NH$_2$,–OC$_2$H$_5$).

B (–CH$_3$, –OCH$_3$ and –OC$_2$H$_5$) on PA is more or less same for these three unsaturated compounds. Positive inductive effect (+I) of methyl group at α position increase PA little bit in EMA (A=–CH$_3$) compared to methyl acrylate (A=–H). Lone-pair electron on the nitrogen of amide group lost their mobility toward carbonyl oxygen due to the hydrogen bond formation (N–H) in water, which is one of the causes for decreasing PA of ACR compared to ACL. +I character of methyl group enhance the PA of MVK (−259.6 kcal/mole). Effect of –OCH$_3$ at B is less on PA compare to –OC$_2$H$_5$ because both substituents have a negative inductive effect (–I) and resonance (+R) effect, but due to more resonance character (–OCH$_3$<–OC$_2$H$_5$) PA value of EMA (–258.15 kcal/mole) is little more compared to MA (−257.52 kcal/mole) in aqueous phase. For α,β-unsaturated carbonyl compounds, PA increases in the order B=–OCH$_3$<–OC$_2$H$_5$<–CH$_3$<–NH$_2$<–H (in ACL) in aqueous phase. From Table 2, it is obvious that net charge on O$^-$ atom is higher in free bases in each compound compared to their protonated complex indicate their high protonation tendency. Charge on proton of the protonated complexes revealed the fact of extensive charge transfer during protonation, proton added to the carbonyl oxygen form a strong covalent σ bond. Charge density on O-atom increases markedly in aqueous phase compared to the gas phase indicating the higher charge separation in water. It is well supported by increased dipole moment in aqueous phase than that in the gas phase. Charge on proton and oxygen atom in the complexes clearly shows that shifting of charge is not local; it comes from all over the molecules. Computed net charge on oxygen atom in free compound and protonated complexes are within the range −0.2864 to −0.3594 and −0.1465 to −0.2505 in gas phase. It is −0.3701 to −0.4635 and −0.1742 to −0.2750 for free base and their O–H$^+$ complexes in aqueous phase, respectively. Charge on adjunct proton lies within 0.2991-0.3206 in gas phase, a little increases in the aqueous phase (from 0.323 to 0.3437). Some selected optimized geometrical features such as bond distance (C–O and O–H), <C–O–H$^+$ bond angle surrounding carbonyl group of the computed compounds are reported in Tables 3 and 4. r(C–O) bond length effected with the protonation, it increases in protonated complexes by 0.069Å-0.092Å in gas phase and 0.067Å-0.097Å in aqueous phase. In complex r(O–H$^+$), bond distance remains almost equal for all compounds both in gas and aqueous phase; it varies iota (0.0062Å in gas phase and 0.0087Å in aqueous phase). The <C–O–H$^+$ bond angle for computed complexes lies within 111.59°-117.57° and 111.397°-113.97° in gas and aqueous phases, respectively. The local stereochemical and other quantum mechanical parameters obtained from DFT[B3LYP] theoretical study at 6-311G(d,p) basis set level suggest to conclude that the PA of the selected carbonyl compounds cannot be explained correctly by local carbonyl site properties only, it must consider the entire molecular contribution. We have also analyzed some other global quantum mechanical parameters to observe the comparative electrophilic nature by calculating electrophilic index (ω), hardness (η), and softness (σ) from HOMO–LUMO energy gap of the free carbonyl compounds in both gas and aqueous phases. It is observed from the data reported in Table 5 and

Table 5: Computed hardness, softness, chemical potential, and electrophilic index of the free base (B_1) in the gas phase ground state by DFT method.

$\{\text{Hardness}(\eta)=[\in_{LUMO}-\in_{HOMO}]\}/2$, Softness($\sigma$)=1/$\eta$ Chemical potential(μ)=$[\in_{LUMO}+\in_{HOMO}]/2$, Electrophilic index ($\omega$)=$\mu^2/2\eta$						
Molecule	$\in_{HOMO}$	$\in_{LUMO}$	**η**	**σ**	**μ**	**ω**
ACL	−0.2649	−0.0735	0.0957	10.44	−0.1692	0.1495
HNE	−0.2603	−0.0717	0.0943	10.60	−0.166	0.1461
MVK	−0.2565	−0.0639	0.0963	10.38	−0.1602	0.1332
ACR	−0.2593	−0.0477	0.1058	9.45	−0.1535	0.1113
MA	−0.2781	−0.0614	0.1083	9.23	−0.1697	0.1329
EMA	−0.2725	−0.0451	0.1137	8.79	−0.1588	0.1108

ACL: Acrolein, HNE: 4-hydroxy-2-nonenal, MVK: Methyl vinyl ketone, ACR: Acrylamide, MA: Methyl acrylate, EMA: Ethyl methacrylate, DFT: Density functional theory

Table 6: Computed hardness (Hartree), softness, chemical potential, and electrophilic index of the free base (B_1) in the aqueous phase ground state by DFT method.

$\{\text{Hardness }(\eta)=[\in_{LUMO}-\in_{HOMO}]/2\}$, Softness($\sigma$)=1/$\eta$, Chemical potential ($\mu$)=$[\in_{LUMO}+\in_{HOMO}]/2$, Electrophilic index ($\omega$)=$\mu^2/2\eta$						
Molecule	$\in_{HOMO}$	$\in_{LUMO}$	**η**	**σ**	**μ**	**ω**
ACL	−0.26124	−0.06480	0.0982	10.18	−0.1630	0.1352
HNE	−0.26641	−0.07356	0.0964	10.37	−0.1699	0.1496
MVK	−0.26312	−0.06646	0.0983	10.16	−0.1647	0.1379
ACR	−0.26802	−0.04818	0.1099	9.09	−0.1581	0.1136
MA	−0.2887	−0.06312	0.1127	8.36	−0.1759	0.1371
EMA	−0.27515	−0.04065	0.1172	8.52	−0.1579	0.1063

ACL: Acrolein, HNE: 4-hydroxy-2-nonenal, MVK: Methyl vinyl ketone, ACR: Acrylamide, MA: Methyl acrylate, EMA: Ethyl methacrylate, DFT: Density functional theory

Table 6 that ACL (ω=0.1495 and 0.1352 in gas and aqueous phases, respectively) and HNE (ω=0.1461 and 0.1496 in gas and aqueous phases, respectively) are two most strong electrophiles compared to rest four compounds and EMA (ω=0.1108 and 0.1063 in gas and aqueous phases) have the weakest electrophilic reactivity. Based on their corresponding quantum mechanical parameter, the selected carbonyl compounds follow the electrophilicity order as HNE≥ACL>>MVK≥MA>ACR>EMA in aqueous, albeit controversial in gaseous phase where ACL exhibit highest electrophilicity compared to HNE. The global parameter hardness (η) obtained from E_{LUMO}–E_{HOMO} energy gap is the scale of ground state stability of the relative compounds. Calculated quantum mechanical data tabulated in Tables 5 and 6 clear that EMA (η=0.1137 and 0.1172 in gas and aqueous phases) is most stable among the six compounds (Figures 2 and 3).

4. CONCLUSION

Investigated PA values of six α,β-unsaturated conjugated carbonyl compounds in both gas phase and aqueous phases using DFT(B3LYP) method employing triple valence basis set 6-311G(d,p) cannot be explained exactly considering only electronic and stereochemical optimized parameter at or around the carbonyl moiety, proton affinities are strongly affected by the different substituents (B=–H, $-CH_3$, $-OCH_3$, $-OC_2H_5$, and $-NH_2$) attached to the carbonyl carbon. Proton affinities of the bases markedly change due to solvation. Interaction enthalpies are more negative in water. +I effect of α-methyl group, +R (resonance) and –I effect of the $-OCH_3$, and $-OC_2H_5$ group are responsible for the small increase of PA in EMA. So, it can be concluded that PA of the α,β-unsaturated carbonyl compounds are obtained considering the different electronic properties strongly. It has been found that selected carbonyl derivatives are harder in aqueous phase. The electrochemical properties of the protonated complexes clear the fact that the interaction between binding oxygen site and proton is preferably an ion-induced dipole interaction and ion-dipole attraction as well rather than a covalent interaction. Overall protonation reactions are spontaneous.

Figure 3: Optimized structure of selected conjugated α,β-unsaturated carbonyl compounds and their carbonyl oxygen-H^+ complexes in gas and aqueous phases.

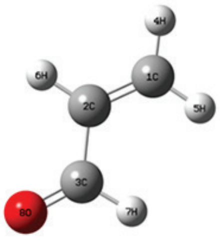
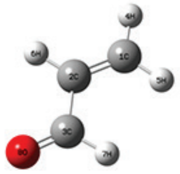
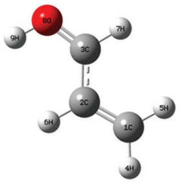
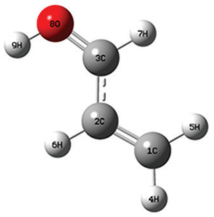
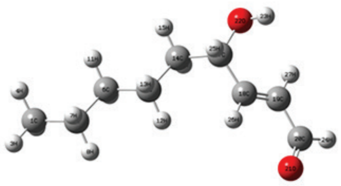
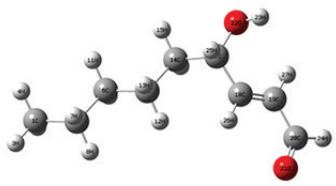
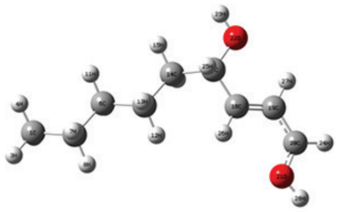
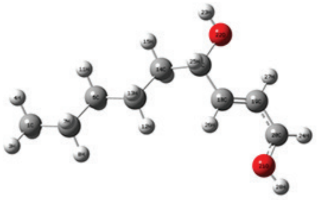
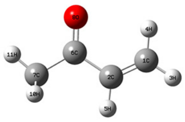
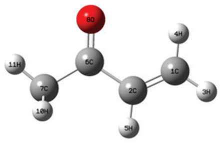
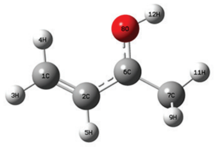
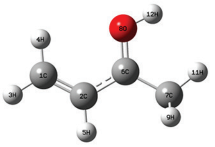
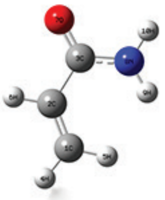
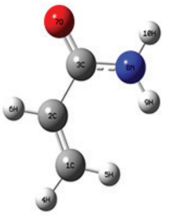
Carbonyl compounds	Gas phase	Aqueous phase
ACL		
ACL (O-H+)		
HNE		
HNE (O-H+)		
MVK		
MVK (O-H+)		
ACR		

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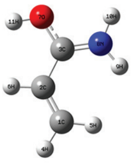
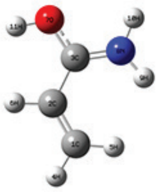
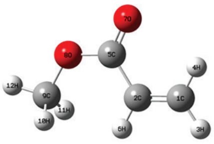
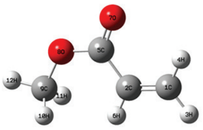
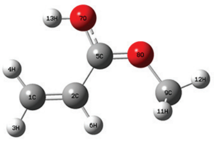
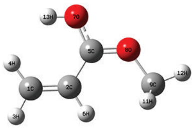
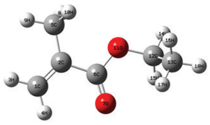
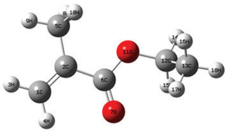
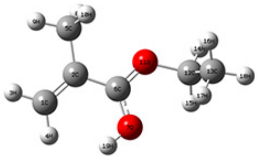
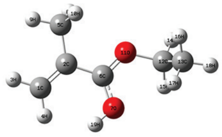
Figure 3: *(Continued)*

Carbonyl compounds	Gas phase	Aqueous phase
ACR (O-H+)		
MA		
MA(O-H+)		
EMA		
EMA(O-H+)		

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