



Proton Affinities of a Series of α , β Unsaturated Carbonyl Compounds of Type-2-alkene (Acrolein, 4-hydroxy-2-nonenal, Methyl Vinyl Ketone, Acrylamide, Methyl Acrylate, and Ethylmethacrylate), in the Gas and Aqueous Phase in their Low-lying Excited Triplet State: A Density Functional Theory/Polarizable Continuum Model and Self-Consistent Reaction Field Approach

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ABSTRACT

Density functional theory Becke 3-term functional; Lee, Yang, Parr/6-311G(d,p) calculations were performed to quantify triplet state proton affinities (PA) and transition energies of a series of α,β -unsaturated carbonyl compounds and their O-protonated counterparts in gas phase as well as in aqueous phase. To evaluate structural behavior and different quantum mechanical properties in water, we studied our optimization process using polarizable continuum model and Self-consistent reaction field method at the same level of theory of the relevant low-lying excited state. The gas phase O-protonation turns out to be exothermic in each case and the local stereochemical disposition of the proton is found to be almost the same in each case. PA values of the different compounds are affected by substituent present at the carbonyl carbon. Different electrochemical properties (+R, +I, and effect) originate from carbonyl chain are seen to cause change of the PAs. Acrylamide (ACR) shows the highest PA in both phases. In each case, protonation at carbonyl oxygen is observed to be more energetically favorable compared to protonation at other probable binding sites present. Computed PAs of the compounds in gas phase are in the following order $ACR \geq$ ethylmethacrylate $>$ 4-hydroxy-2-nonenal $>$ methyl vinyl ketone $>$ methyl acrylate $>$ acrolein, while in aqueous phase the PA order is ranked differently. Charge density on binding oxygen and on added proton is recorded from both Mulliken population analysis and Natural population analysis. PA values are sought to be correlated with the computed hardness of the unprotonated species in the relevant excited state. The proton induced shifts are in general red shifts for the low-lying excited triplet state. The overall reactivity is explained by distant atom contribution in addition to the contribution from the carbonyl group.

Key words: Density functional theory, Polarizable continuum model, Proton affinity, Low-lying, Unsaturated.

1. INTRODUCTION

Ion-molecule interactions are now a growing interest in the field of both experimental and theoretical research in chemistry. Proton transfer reactions are of considerable importance in chemistry. Excited state proton transfer is very important in biological process [1]. By definition, an acid is an electron acceptor whereas base is an electron donor, so there may have a relationship between charge density distribution and acid-base properties. Acid-base properties of a molecule may change from one electronic state to another due to the extensive molecular charge redistribution in the different electronic state. The basic chemistry of

a carbonyl chromophore in ground state is largely independent of the nature of alkyl or aryl group present at carbonyl carbon. By changing the electronic nature of the low-lying excited state these alkyl or aryl groups markedly influence the chemical and physical nature of the carbonyl chromophore at the lowest excited state. Excited state proton transfer process on guanine and some related species has been investigated theoretically [2,3]. Basicity of some proto-typical carbonyls in the ground and low-lying excited state has been reported earlier [4]. Gas phase methods [5-13] have the advantage for determining inherent acid-base properties in ground state avoiding solvent effect. In

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presence of solvent, excited state acid-base properties of a molecule can be measured utilizing absorption and fluorescence spectral data in conjugation with Forster cycle [14-17]. Different computational studies [18-20] have been performed to investigate gas phase basicities of organic molecules in the excited state. Excited state proton affinities (PAs) and vertical excitation energies of 1,5, and 1,8- diaminonaphthalene were computed with the help of Becke 3-term functional; Lee, Yang, Parr (B3LYP)/6-31G(d,p), and CIS/6-31G(d,p) method of calculations [21]. In last few years the basicities, of a series of substituted aliphatic conjugated carbonyl system (chrotonaldehyde) [22,23] in ground state and their low-lying excited state and PAs of a series of aromatic conjugated carbonyl system (acetophenone) [24] in their lowest excited triplet state has been studied theoretically. In this current work, a series of conjugated α,β -unsaturated carbonyl derivatives of type-2-alkene chemical class has been investigated using density functional theory (DFT)/B3LYP method at most reliable 6-311G(d,p) basis set at relevant low-lying excited triplet state. Compounds investigated in this study are acrolein (ACL), 4-hydroxy-2-nonenal (HNE), methyl vinyl ketone (MVK), acrylamide (ACR), methyl acrylate (MA), and ethylmethacrylate (EMA). A ground state comparative study of proto affinities of the same compounds was previously reported [25]. These unsaturated compounds selected in this work are considered as environmental pollutants. It is also recognized that electrophilic α,β -unsaturated carbonyl derivatives of the Type-2 alkene chemical class cause broad organ system toxicity by forming covalent Michael-type adducts with amino acids [26-28]. The purpose of this work is to deliver comparative data base for PAs and basicities of the carbonyl compounds involved in biomolecular process in their low-lying excited triplet state in both gas and aqueous phase. It was observed that several energetic values obtained in DFT/B3LYP calculation are far better (more nearer to accuracy) than those obtained in *ab initio* Hartree-Fock (H-F) study; therefore, H-F results are not taken into account. Optimized geometry of the protonated complexes tends to suggest that proton (H^+) added to the compound prefers to bind with carbonyl oxygen in all complexes with lowest optimization energy. Both Mulliken population analysis (MPA) and Natural population analysis (NPA) have been applied for evaluating the charge density on carbonyl oxygen of the unprotonated bases and of their protonated complexes and charge on added proton of the protonated complexes. We have analyzed the transition energies (${}^1S_0 \rightarrow T_1$) to understand whether the pre protonation charge distribution local to the chromophore or post protonation relaxation of charge density or both are important in explaining the overall basicity of each compound in a particular state. We have also analyzed the kind and extent of spectral shift caused by protonation. In a particular state, the possibility of correlating the PA values with the global

hardness of the molecules is also explored. Following are the chemical structures (drawn with Chemdraw software) (Figure 1) of investigated unsaturated carbonyl compounds with their proper name and abbreviation.

2. COMPUTATIONAL DETAILS

The geometry of the six α,β -unsaturated carbonyl compounds has been fully optimized with most accurate DFT/B3LYP method [29] at 6-311G(d,p) basis set level of Gaussian "09" program package [30]. To verify geometrical behavior PAs and other computed parameters in solvent, we used self-consistent reaction field and polarizable continuum model [31] for geometry optimization at the same level of theory. Water has been selected as solvent from the solvent list given in Gaussian program. The charge density on atoms (carbonyl oxygen and added proton) of the optimized structures was calculated in both MPA [32] and NPA [33] framework. Basis set superposition error was found to be small therefore results are not included in this work. To obtain the thermodynamic parameters (enthalpies and Gibbs free energies at 298.15 K) frequency calculations were performed for all neutral, protonated complexes at the same level of theory.

3. RESULTS AND DISCUSSION

PA of a base is defined as negative enthalpy change ($-\Delta H^{298.15k}$) of a thermodynamic equilibrium reaction: $B_1 + H^+ \leftrightarrow [B_1H^+]$ and basicity is defined as the negative of the free energy change ($-\Delta G^{298.15k}$) associated with the same reaction. So affinity and basicity can be characterized as,

$$PA (\Delta H) = H^{298.15k} [(B_1H^+) - (B_1)] \quad (1)$$

$$\text{Basicity} (\Delta G) = G^{298.15k} [(B_1H^+) - (B_1)] \quad (2)$$

PA of the compound can be obtain computationally according to Maksic and Kovačević [34,35] that is $PA = [E_{\text{tot}}(B_1H^+) - E_{\text{tot}}(B_1)]$ (3)

Both gas and aqueous phase total energies of six α,β -unsaturated carbonyl compounds and of their O- protonated complexes in low-lying excited triplet state are summarized in Table 1. Evaluated PA values [following equation (3)] of the studied compounds are tabulated in Table 2. It is observed that PA's of different carbonyl compounds have a variation in the range -223.35 – -199.29 kcal/mole in the gas phase, while in aqueous phase the PA's span is increased and it is of -272.61 – -256.11 kcal/mole. It is clear from the obtained values that conjugated double bond effect on PA's are not uniform. The presence of different substituent (B) at the carbonyl carbon and at any other positions (A at α -carbon) of the alkyl chain of the compounds is markedly influence the PAs. It is seen that in both phases ACR exhibits the highest PA values

Table 1: Computed total energies (hartree) of the free bases (B_1) and their protonated complexes (B_1h^+) at the equilibrium geometry of the low-lying excited triplet state.

Compounds	Total energy (hartree)		Total energy (hartree)	
	Gas phase		Aqueous phase	
	B_1	B_1h^+	B_1	B_1h^+
ACL	-191.8663	-192.1839	-191.8695	-192.2786
4HNE	-503.0539	-503.40	-503.0843	-503.4869
MVK	-231.1978	-231.5358	-231.2015	-231.6218
ACR	-247.2466	-247.6035	-247.2580	-247.6934
MA	-306.4280	-306.7630	-306.4378	-306.8725
EMA	-385.1056	-385.4615	-385.1150	-385.5385

ACL=Acrolien, HNE=4-hydroxy-2-nonenal, MVK=Methyl vinyl ketone, ACR=Acrylamide, MA=Methyl acrylate, and EMA=Ethyl methacrylate

Table 2: Evaluated PAs [ΔE_g or $\Delta E_s=(E_{B_1H^+}-E_{B_1})$] for both gas and solvent phase at the equilibrium geometry of the lowest excited triplet state (1 hartree=627.5095 kcal/mole).

Compounds	Gas phase		Aqueous phase	
	PA		PA	
	ΔE_g (in hartree)	ΔE_g (in kcal/mole)	ΔE_g (in hartree)	ΔE_g (in kcal/mole)
ACL	-0.3176	-199.29	-0.4091	-256.11
HNE	-0.3461	-217.18	-0.4026	-252.63
MVK	-0.338	-211.49	-0.4203	-263.14
ACR	-0.3569	-223.35	-0.4354	-272.61
MA	-0.335	-209.61	-0.4347	-272.17
EMA	-0.3559	-222.73	-0.4235	-265.15

ACL=Acrolien, HNE=4-hydroxy-2-nonenal, MVK=Methyl vinyl ketone, ACR=Acrylamide, MA=Methyl acrylate, and EMA=Ethyl methacrylate

(-223.35 and -272.61 kcal/mole in gas and aqueous phase, respectively). The PA value of ACL is predicted to be lowest (-199.29 kcal/mole) in the gas phase. In aqueous phase, HNE exhibits the lowest PA value (-252.563 kcal/mole.) in the series in this particular electronic state. Lone pair electron of nitrogen of $-NH_2$ may increase the electron density on binding oxygen thus the $O-H^+$ interaction in ACR enhanced.

Effect of B (Figure 2) on PA in the low-lying triplet state are in the following increasing order $-H$ (in ACL) < $-CH_3$ < $-OCH_3$ < $-H$ (in HNE) < $-OC_2H_5$ < $-NH_2$. On salvation, this effect on PA's ranked slightly different and it is $-H$ (in HNE) < $-H$ (in ACL) < $-CH_3$ < $-OC_2H_5$ < $-OCH_3$ < $-NH_2$. We observed that gas phase PA value of EMA is comparatively higher than that of MA and MVK. This is may be the cause of double substituent effect ($B=-OC_2H_5$ and $A=-CH_3$). Both +I and +R effects (B) originate from A and B of EMA makes the $O-H^+$ interaction more strong compared to MA and MVK. The enhancement of $-OCH_3$ and $-CH_3$ attached at carbonyl carbon of the unsaturated compounds are less than $-OC_2H_5$ resulted less PA for MVK (-211.49 kcal/mole) and MA (-209.61 kcal/mole). Excited state (low-lying)

PA of HNE compound (-217.18 kcal/mole) obtained little more (approximately 6-8 kcal/mole) compared to MVK and MA. This trend may be explained by the inductive effect (+I) exhibited by the long alkyl group (C_5H_{11}) linked to the carbonyl carbon, contributes by means of bond electron donation to enhance the $O-H^+$ interaction. Computed PA values of the unsaturated compounds are predicted little more in water. PA values in aqueous phase increases in the following order HNE < ACL < MVK < EMA < MA \leq ACR. Different PA order appeared in this phase may be due to electronic relaxation effect in presence of solvation. The change of PA order (with higher values) of the same bases in solution phase is expected, because ions can become modified with the change of phase since the gas phase environment differs from that of the solvent phase. It was already revealed from a previous investigation [36] that, the order of basicity in solution differs from that in the gas phase. Table 2 also clear the fact that, excited (low-lying) state PAs are comparatively higher in gas as well as in the solvent phase compared to that obtained in the ground state. Exceptionally, PA of ACL and HNE in this state is observed little smaller relative to the ground state. This tendency has been

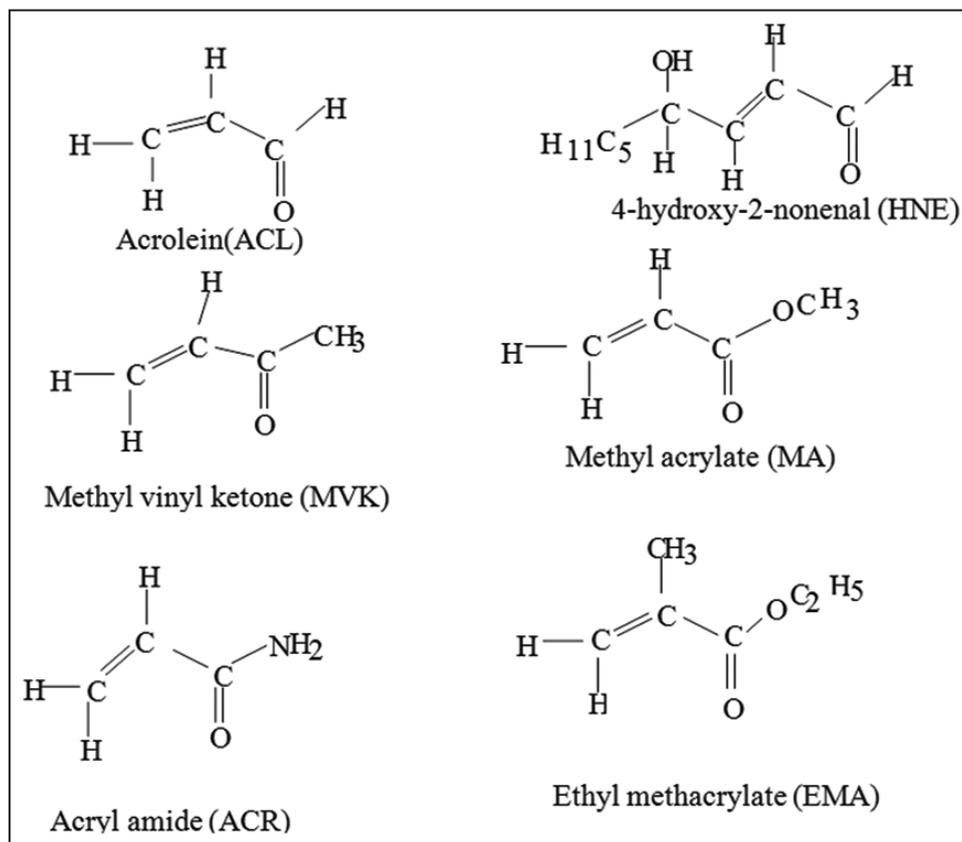


Figure 1: Structure of several conjugated α,β -unsaturated carbonyl compounds.

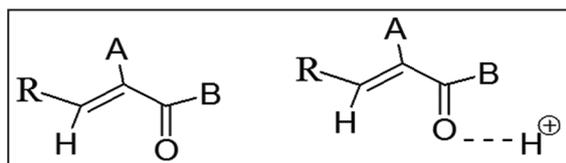


Figure 2: General neutral and protonated structures for conjugated α and β -unsaturated carbonyl compounds of type-2-alkene chemical class ($R=H$ or alkyl group, $A=H$ or $-CH_3$ and $B=H$, $-CH_3$, and $-OCH_3$, $-NH_2$, $-OC_2H_5$).

investigated in an earlier study [37,38] which can be attributed to the phenomenon of redistribution of charges in the excited state in comparison to ground state [38]. Gas phase basicities were evaluated from calculated free energies (G) following above equation (2). The total Gibbs free energies and evaluated basicities of the unsaturated carbonyl compounds in both gas and aqueous phases are collected in Table 3. It was observed that basicity values are closer to corresponding PA in each case, they differs only by ± 4.48 to ± 8.81 kcal/mole in gas phase and ± 4.77 to ± 9.12 kcal/mole in aqueous. The order of the basicities of the compounds is not parallel to their PA's data. Little discrepancy has been found between ACR and EMA in gas phase and between MA and ACR in aqueous phase. Table 4 reports the computed Mulliken net charge on carbonyl oxygen atom of

the free and protonated complexes and also the net charge on added proton of the protonated complexes in both phases in this particular state. Since, MPA is more method sensitive, we have tested another procedure (NPA) for evaluating partial charge on atoms. Table 5 summarized the partial charges on the same atoms obtained in the frame of NPA. From the Q_{CT} and q_{CT} values of Tables 4 and 5 clears that, in both phases, a significant charge transfer from ligand to proton has taken place. One might have expected that transferred charge will be parallel to the PA of the complexes. However this is not the case; both Q_{CT} and q_{CT} gave unexpected order in gas and aqueous phase. Charges obtained from NPA are comparatively higher compared to MPA. MPA charge on proton of the protonated complexes varies in the range of $+0.2961$ - 0.3145 and $+0.3179$ - $+0.3335$ in gas and aqueous phase, respectively, while NPA results shows 0.50 - $0.51e$ natural charges on added proton in the gas phase and it is little bit higher in water ($0.51e$ - $0.52e$). This charge migration is not local and originates from all over the compound. It is observed that there is no direct correlation between NPA or MPA results and complex stability. The Q_{CT} results are given in Table 4. According to the calculated results (Q_{CT}), stability order of the complexes can be written as $HNE \geq MA > ACR > EMA > ACL > MVK$ and $MA \geq ACR > MVK \geq EMA > ACL > HNE$ in the gas and aqueous phaser, respectively.

Table 3: Obtained Gibbs free energies of six α and β -unsaturated carbonyl compounds and basicities (ΔG) in kcal/mol) and entropies (ΔS) in cal/mole by B3LYP/DFT method at 6-311G (d, p) level in gas and aqueous phase at the equilibrium geometry of low-lying excited triplet state.

Compounds	Basicity calculated as: $G(B_1H^+) - G(B_1)$ in kcal/mole			
	Gas phase		Aqueous phase	
	Free energy [G] (in hartree)	ΔG (in kcal/mole)	Free energy [G] (in hartree)	ΔG (in kcal/mole)
ACL	-191.8364	-191.7	-191.8397	-248.74
ACL-H ⁺	-192.1419		-192.2361	
HNE	-502.869	-212.6	-502.89	-247.86
HNE-H ⁺	-503.2078		-503.285	
MVK	-231.1418	-204.37	-231.1456	-255.77
MVK-H ⁺	-231.4675		-231.5532	
ACR	-247.2044	-214.54	-247.2163	-263.49
ACR-H ⁺	-247.5463		-247.6362	
MA	-306.3724	-201.11	-306.3809	-263.8
MA-H ⁺	-306.6929		-306.8013	
EMA	-384.9959	-216.23	-385.0054	-257.52
EMA-H ⁺	-385.3405		-385.4158	

ACL=Acrolien, HNE=4-hydroxy-2-nonenal, MVK=Methyl vinyl ketone, ACR=Acrylamide, MA=Methyl acrylate, and EMA=Ethyl methacrylate

Table 4: Computed mulliken net charge on o-atom (q_o^-) of free bases (B_1) and o-protonated complexes (B_1H^+) and computed mulliken net charge on added proton (q_{H^+}) of the protonated complexes (B_1H^+) and ligand to proton charge transfer (q_{CT}) at the equilibrium geometry of low-lying excited state.

Molecule	(q_o^-)			Q_{CT}	(q_o^-)			Q_{CT}
	Gas phase				Aqueous phase			
	B_1	B_1H^+	q_{H^+}		B_1	B_1H^+	q_{H^+}	
ACL	-0.1335	-0.1438	0.3117	0.6883	-0.1481	-0.1811	0.3316	0.6684
HNE	-0.1986	-0.2556	0.2999	0.7001	-0.2989	-0.3423	0.3335	0.6665
MVK	-0.1581	-0.2148	0.3145	0.6855	-0.1737	-0.2314	0.33	0.670
ACR	-0.3684	-0.2763	0.3082	0.6918	-0.4503	-0.3075	0.3212	0.6788
MA	-0.3044	-0.2023	0.2961	0.7039	-0.3726	-0.2226	0.3179	0.6821
EMA	-0.3157	-0.2539	0.3098	0.6902	-0.3802	-0.2709	0.3232	0.6768

*Charge transfer calculated as $\{[\text{formal charge on proton (+1)}] - [\text{Charge obtained on proton}]\}$ in the complex.

ACL=Acrolien, HNE=4-hydroxy-2-nonenal, MVK=Methyl vinyl ketone, ACR=Acrylamide, MA=Methyl acrylate, and EMA=Ethyl methacrylate

NPA results shows different trend in gas as well as in water, it is $HNE > MA \geq ACL > MVK > EMA$ and $ACR \geq ACL > MA > MVK = HNE > EMA$. This is tending to suggest that NPA results are also method sensitive. Functional sensitivity of NPA results was observed previously [39]. Hence, further exploration

in need to resolve such a major discrepancy. Tables 6 and 7 expose some important geometrical features around the functional carbon in the low-lying excited state. It is obvious from the results tabulated in Tables 6 and 7 that, optimized geometry of the compounds not changed markedly from gas

Table 5: Partial atomic charges on carbonyl oxygen (q_{o^-}) of the free bases (B_1) and their o-protonated complexes (B_1H^+), partial charges on added proton (q_{H^+}) of the protonated complexes (B_1H^+) obtained from NPA and ligand to proton charge transfer (q_{CT}) at the equilibrium geometry of low-lying excited state.

Molecule	(q_{o^-})			q_{CT}	(q_{o^-})			q_{CT}
	Gas phase				Aqueous phase			
	B_1	B_1H^+	q_{H^+}		B_1	B_1H^+	q_{H^+}	
ACL	-0.1770	-0.4692	0.5080	0.492	-0.1912	-0.4961	0.520	0.48
HNE	-0.1870	-0.5774	0.5030	0.497	-0.2050	-0.5529	0.524	0.476
MVK	-0.2004	-0.5428	0.5112	0.4888	-0.2174	-0.5503	0.524	0.476
ACR	-0.595	-0.6032	0.5089	0.4911	-0.6774	-0.6226	0.516	0.484
MA	-0.5109	-0.5573	0.5050	0.495	-0.5856	-0.5726	0.522	0.478
EMA	-0.5546	-0.5905	0.5178	0.4822	-0.6181	-0.5985	0.5268	0.4732

*Charge transfer calculated as a formal charge on proton (+1) – Charge obtained on proton in the complex.

ACL = Acrolin, HNE = 4-hydroxy-2-nonenal, MVK = Methyl vinyl ketone, ACR = Acrylamide, MA = Methyl acrylate, EMA = Ethyl methacrylate, and NPA = Natural population analysis

Table 6: Geometrical features of the free base and O-protonated base (length in Å and angle in degree) in gas phase at equilibrium geometry of the low-lying excited state.

Molecules	Free base		O-protonated base		
	r(C-O)	r(C-O)	R(O-H+)	<C-O-H+	<C-C-O-H+
ACL	1.3106	1.3086	0.9743	114.8519	0.00
HNE	1.33	1.33	0.9766	118.76	-18.761
MVK	1.315	1.319	0.9717	113.0363	179.999
ACR	1.23	1.32	0.9670	113.332	0.00
MA	1.236	1.310	0.9675	113.4913	-13.491
EMA	1.214	1.30	0.9728	110.869	-10.8693

ACL=Acrolin, HNE=4-hydroxy-2-nonenal, MVK=Methyl vinyl ketone, ACR=Acrylamide, MA=Methyl acrylate, and EMA=Ethyl methacrylate

Table 7: Geometrical features of the free base and O-protonated base (length in Å and angle in degree) in aqueous phase

Molecules	Free base		O-protonated base		
	r(C-O)	r(C-O)	R(O-H+)	<C-O-H+	<C-C-O-H+
ACL	1.310	1.308	0.9743	113.77	0.00
HNE	1.296	1.31	0.9706	111.75	178.28
MVK	1.315	1.31	0.9719	112.57	-12.57-
ACR	1.245	1.32	0.9672	111.94	0.00
MA	1.238	1.30	0.9742	111.24	-11.24-
EMA	1.223	1.308	0.9731	110.59	-10.59-

ACL=Acrolin, HNE=4-hydroxy-2-nonenal, MVK=Methyl vinyl ketone, ACR=Acrylamide, MA=Methyl acrylate, and EMA=Ethyl methacrylate

to aqueous phase. C=O bond distance elongated slightly from unprotonated bases to protonated complexes. It is 0.004-0.09 Å in gas and quite similar 0.004-0.085 Å in aqueous phase. The O-H⁺ bond distance has a variation in the range of 0.967-0.9766 Å and 0.9672-0.9743 Å in gas and aqueous phase, respectively. In both phases < C-O H⁺ bond angle of all protonated complexes remain in between 110.869°

and 118.76° in gas phase. The range is reduced on aqueous environment (110.59-113.77°). Among six unsaturated compounds HNE, MVK, and EMA shows planarity in both phases with τ (C-C-O-H⁺) dihedral angle -179.98°, 179.99°, and -179.51° in gas phase, 178.28°, -179.99°, and -179.60° in aqueous. In both phases, optimized geometries of ACL, ACR, and MA provide non-planar structure. The almost invariant

Table 8: Computed adiabatic transition energies ($^1S_0 \rightarrow T_1$) (hartree) and proton-induced shifts (PIS, Hartree) in the low-lying excited triplet state.

Molecule	Gas phase			Aqueous phase		
	Transition energy		PIS	Transition energy		PIS
	B	BH+		B	BH+	
ACL	0.1019	0.105	0.0031	0.1046	0.1481	0.0435
HNE	0.1012	0.0979	-0.0033	0.0801	0.0915	0.0114
MVK	0.1042	0.0998	-0.0044	0.1065	0.0999	-0.0066
ACR	0.1192	0.1106	-0.0086	0.1186	0.1101	-0.0085
MA	0.1134	0.1126	-0.0008	0.1137	0.0894	-0.0243
EMA	0.1083	0.0885	-0.0198	0.1047	0.0838	-0.0209

ACL=Acrolien, HNE=4-hydroxy-2-nonenal, MVK=Methyl vinyl ketone, ACR=Acrylamide, MA=Methyl acrylate, EMA=Ethyl methacrylate, and PIS=Proton induced shifts

Table 9: Estimated dipole moment (μ) of six α and β -unsaturated carbonyl compounds in gas phase as well as in aqueous phase at low-lying excited state (T_1) and ground state.

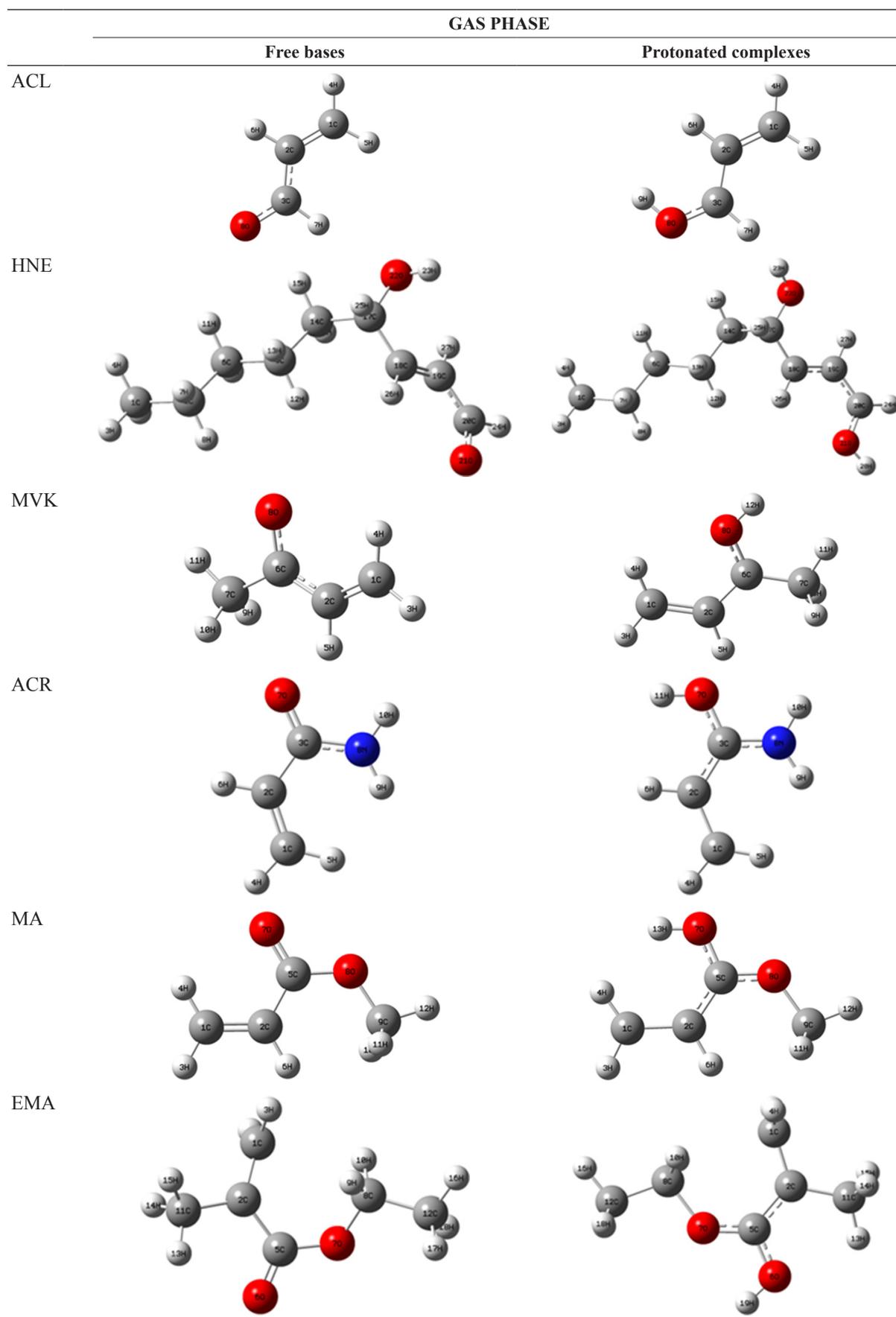
Compounds	Gas phase		Aqueous phase	
	Dipole moment (μ)		Dipole moment (μ)	
	Ground state	Low-lying excited state	Ground state	Low-lying excited state
ACL	3.15	0.833	4.04	0.991
HNE	2.12	1.68	2.83	1.79
MVK	2.7	2.01	3.51	2.60
ACR	3.88	3.97	5.14	5.21
MA	4.32	4.35	5.56	5.71
EMA	1.78	4.22	5.51	5.76

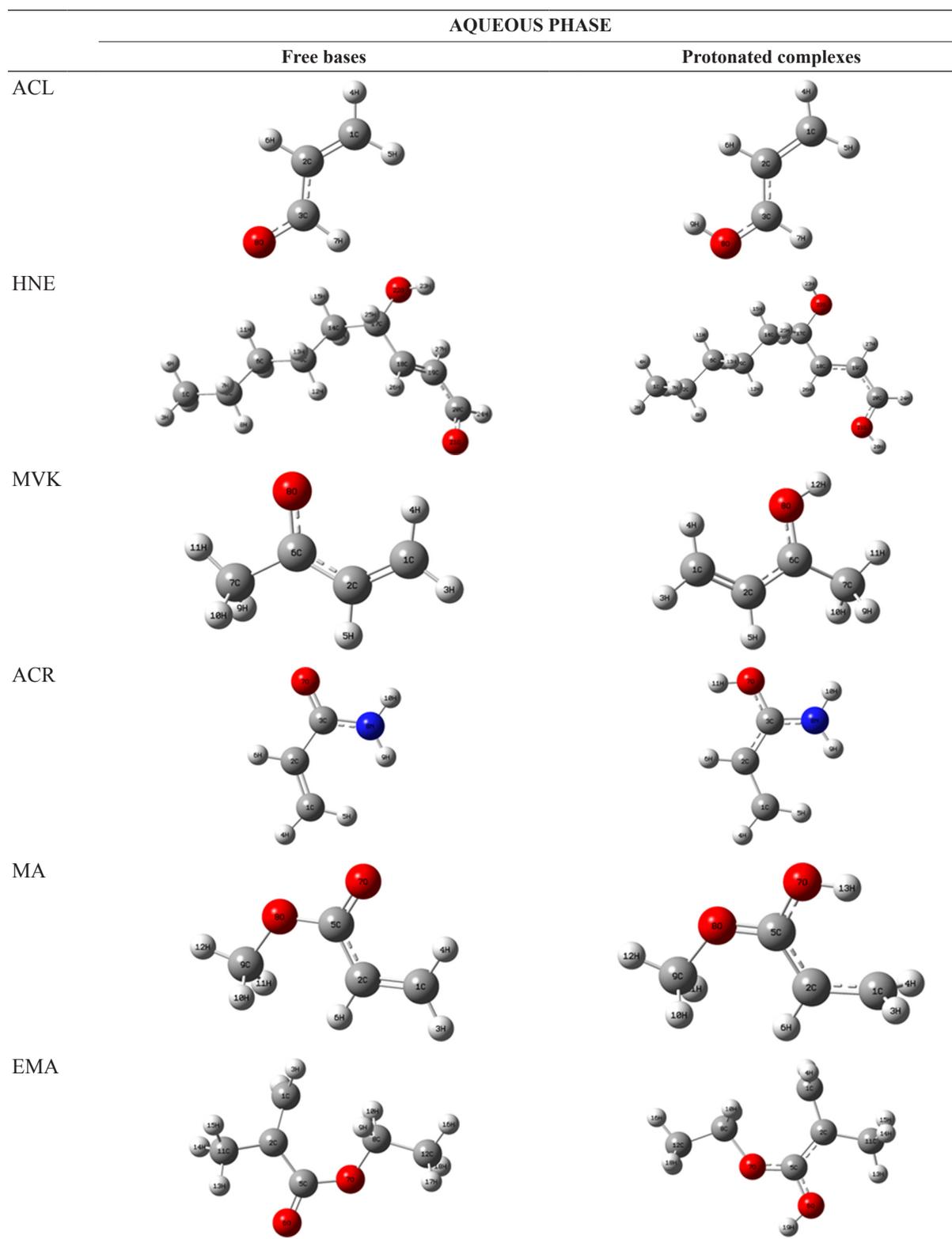
ACL=Acrolien, HNE=4-hydroxy-2-nonenal, MVK=Methyl vinyl ketone, ACR=Acrylamide, MA=Methyl acrylate, and EMA=Ethyl methacrylate

stereochemistry around the binding oxygen site tends to suggest that, PA's of the studied compounds cannot be predicted properly unless considering the contributions from distant atom. Table 8 reports the computed transition energies ($^1S_0 \rightarrow T_1$) as state energies differences and shifts due to protonation. The proton induced shifts (PIS) are red shift in all cases with an exception of ACL, in which it is a blue shift. On aqueous environment, the PIS for ACL and HNE show blue shift whereas other unsaturated carbonyl bases of the series show red shifts. These trends of PIS refer to gas phase protonation of the isolated compounds without any additional effects due to solvation. It is seen from the data recorded in Table 9, low-lying excited state (T_1) dipole moment (μ) of the ACL, HNE, and MVK are reduced relative to that of the ground state in both gas and aqueous phase whereas, it (μ) has been estimated to be higher in ACR, MA, and EMA than that in the ground state. This increase of dipole moment in these three carbonyl compounds may cause by the shifting of electron density from different substituent ($-\text{NH}_2$, $-\text{OCH}_3$ and $-\text{OC}_2\text{H}_5$) to carbonyl chromophore.

4. CONCLUSION

From this theoretical study, it can be concluded that both gas and aqueous phase protonation of the studied α,β -unsaturated carbonyl compounds in low-lying excited state is spontaneous. ACR exhibits the highest PA values (-223.35 kcal/mole and -272.61 kcal/mole in gas and an aqueous phase, respectively). The PA values are little higher in this particular electronic state relative to their ground state in both gas and aqueous phase. The reverse trend also found due to the redistribution of electron density on atoms from one electronic state to another ($S_0 \rightarrow T_1$). Effects of conjugated double on PA's are not uniform. The presence of different substituent (B) at the carbonyl carbon and at any other positions (A at α -carbon) of the alkyl chain of the compounds are influenced the PAs markedly. Dipole moment of several unsaturated compounds is reduced in low-lying excited state compared to their ground state values. PIS are red shifts in general with the exception of ACL in gas phase and both ACL and HNE in aqueous phase. Overall, PA values of the investigated bases cannot be predicted properly without considering the contribution from distant atom along with the contribution from carbonyl moiety.





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