CONCLUSIONS

The present studies aimed at evaluation of different properties of carbamate molecules like N-H bond dissociation enthalpies, proton affinities and gas phase acidities (deprotonation affinities). Carbamic acid, which is the parent molecule for the carbamates, has been analyzed first. Carbamic acid and its thio- and seleno- analogs \([\text{NH}_2\text{C(=X)YH; X, Y = O, S, Se}]\) have been predicted to be stable molecules in the gas phase, and they undergo tautomerization with activation barriers ranging from 2.29 to 13.17 kcal/mol in the molecules with different chalcogen at X and Y position. The molecule with higher chalcogen at –ol position is relatively more stable than its isomeric form with exchange of X and Y. As carbamic acid evades isolation, the decomposition pathways have been analyzed. Unimolecular, bimolecular, and a two-step mechanism for decomposition of carbamic acid and its analogs were studied, and out of the three, the two-step hydrogen ion-catalyzed decomposition followed C–N bond rupture is found to be more plausible.

The N-H and C-H BDEs of \(\text{RC(=X)NH}_2\), \(\text{HC(=X)N(H)(R)}\), \(\text{HC(=X)-R}\) and \(\text{CH}_3\text{C(=X)-R} \) [\(X = O, S, Se; R = H, \text{CH}_3, \text{NH}_2, \text{Cl}\)] have been determined at B3LYP/6-31+G*, B3LYP/6-311++G(d,p), MP2/6-31+G*, B3P86/6-31+G*, B3PW91/6-31+G* G2MP2, CBS-Q and CBS-4M theoretical levels. The comparison of the BDE values to the experimental and G2Mp2 values indicated that ROB3LYP/6-311++G(d,p)//B3LYP/6-31+G* theoretical level results are in close agreement with the with only a small loss in accuracy and low computational cost. The C-H BDEs of \(\text{HC(=O)H}\) and \(\text{CH}_3\text{C(=O)H}\) (when radical is formed by C-H cleavage of methyl group) are 16.9 and 10.2 kcal/mol respectively, lower than that of methane but the N-H BDE of \(\text{NH}_2\text{C(=O)H}\) is 7.2 kcal/mol higher than that of \(\text{NH}_3\) at ROB3LYP/6-311++G(d,p)//B3LYP/6-31+G* theoretical level. The analysis of molecular orbital occupancies and energies in ‘C(=X)-R (when H-atom is abstracted from carbonyl carbon) radicals indicates the formation of three electron two-center bond involving C and X atoms. The N-H BDE in the molecules \(\text{NH}_2\text{C(=X)-R}\) decreases in the order of X as O > S > Se. In case X = S or Se the radical is stabilized by the shift of radical center to X-atom as indicated by lone pair occupancies and spin densities but remains at N when X = O.
In order to understand the effect of substituents on N-H bond dissociation enthalpies of amides and carbamates, isodesmic reactions have been studied to evaluate the molecule stabilization effect (ME) and radical stabilization effect (RE). The effect of substituent on N-H BDE is more pronounced when the substituent is present at nitrogen than when at carbon in amines and amides. When the substituents are attached to nitrogen in amides, the ME indicates destabilization. The reason has been assigned to competing interactions of the substituent for the lone pair on nitrogen. For C-substituted amides, stabilization of the molecule results, that can be understood as result of favorable delocalization from nitrogen to carbonyl and/or the substituent interacting with nitrogen lone pair directly through orbital interactions. The ability of substituent to delocalize the radical spin density, hyperconjugative interactions, hydrogen bonding interactions (especially in case of \( R = \text{OH, NH}_2 \)) are the factors that tend to enhance RE value thereby decreasing the N-H BDE in N-substituted amides.

In N-substituted \([(R)(H)NC(=X)YH]\) or Y-substituted \[[NH_2C(=X)Y-R]\] carbamates, the N-H BDE decreases in the order of X as O > S > Se for each value of Y. The variation in N-H BDE with Y though follows the trend O > S > Se but the magnitude of variation is comparatively smaller in comparison to that with X. ME values indicate destabilization for all substituents except –\( \text{CH}_3 \) and \( \text{NH}_2 \) in N-substituted carbamic acid \([(R)(H)NC(=X)YH]\). However, when Y-substituted ME values indicate destabilization of the molecule for oxo-carbamates (X = O) and stabilization for thio- and seleno-carbamates (X = S, Se). The variation in electron delocalization from N, X and Y atoms with substitution in the molecule as well as the radical has been explored and correlated to ME and RE values. In addition, it has been observed that in thiocarbonyl and selenocarbonyl containing molecules there is shift of radical center to the X-atom as indicated by lone pair occupancies and spin densities. N-H BDEs of amides are in general higher than amines. The N-H BDEs for N-substituted amides are lower than C-substituted amides. In N-substituted carbamates the N-H BDE decreases for all substituent but when Y-substituted increases for –F but decreases for –\( \text{CH}_3 \) and -\( \text{NH}_2 \) substituent as compared to carbamic acid.

The proton affinities of chalcogen sites show an edge over the nitrogen site in all the N-substituted and Y-substituted carbamate molecules. The proton affinities for both
chalcogen and nitrogen site decrease in the order of $X$ as $S > Se > O$ with few exceptions. The difference in values of proton affinities of both the N- and Y-substituted molecules when $X = S$ and $X = Se$ is very small. The presence of electronegative substituents (F, Cl) results in considerable decrease in PA of N and X site. The presence of $\sim\text{NH}_2$ substituent at N does not cause large variation in PA values whereas the weak electron donating CH$_3$ causes comparatively larger variation in the proton affinity. The several factors that affect the proton affinity values are change in electron delocalization, change in hybridization, lone pair’s character but the most important factor in deciding the PA values is the variation in electron delocalization of the lone pairs in order to stabilize the positive charge.

The N-H BDEs decrease on protonation as well as deprotonation as compared to neutral molecules but decrease in BDE is larger on protonation than on deprotonation. The results suggest that protonation stabilizes the molecule while deprotonation destabilizes the molecule while the effect is reversed in the radical. The present study also analyzes the effect of cyclization and inclusion of unstauration in the ring on acidities, proton affinities and bond dissociation enthalpies of carbamates. The acidity of cyclic analogs of acyclic carbamate is higher than $S$-conformer due to less stable $A$ conformation that the carbamate group is forced to adopt in the ring structure. The acidity of molecules is decided by the strength of the bond that breaks and stability of the anion formed. The N-H BDEs are lower in cyclic analogs. A larger decrease in the N-H BDEs occurs when double bond is introduced in the ring. The reason has been assigned to the lower stability of $A$-conformation of cyclic molecules and of odd electron delocalization into the ring through double bond. The spin delocalization is higher when the cyclic molecule contains $\pi$-bond.