PHOTODISSOCIATION AND NONADIABATIC DYNAMICS OF SMALL ORGANIC MOLECULES

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The photodissociation dynamics of small saturated and unsaturated hydrocarbons have immense implications in atmospheric[1], interstellar[2], and combustion chemistry.[3] The photofragmentation reactions are important in radical chemistry as well.[4]

To study the photodisscociation and nonadiabatic dynamics we have used the direct dynamics trajectory surface-hopping (TSH) method in conjunction with Tully's fewest switches algorithm[5] as implemented in the NEWTON-X[6] molecular dynamics code. This code is combined with the COLUMBUS[7] suite of programs to obtain potential energy, energy gradients and nonadiabatic couplings, on-the-fly at each integration time step. The MRCIS/6-31++G(d,p) level of theory is used to calculate these parameters for molecules with less number of degrees-of-freedom, like, propane, propyne, methyl hydroperoxide, etc. For the molecules with a large number of normal modes, like, 1-pyrazoline with twenty seven normal modes, the CASSCF(8,8)/6-31G(d) level of theory is used to compute potential energies, energy gradients and nonadiabatic couplings.

Photofragmentation of propyne[8] at 193 nm follows predominantly the adiabatic pathway resulting products in the excited singlet state. We found that H + CH_3CC is the major fragmentation channel which involves dissociation of acetylenic H. Our dynamics results indicate that this dissociation almost exclusively takes place in the first excited singlet state which is in accord with a recent experimental observation reported by Ni *et al.*[9] It is worth pointing out here that our findings contradict with earlier theoretical prediction of Mebel *et al.*[10] where they proposed that fast acetylenic H atom dissociation takes place through a nonadiabatic path along the S_1 and S_2 surfaces followed by the $S_2 \rightarrow S_0$ transition and elimination of the H atom giving H_3CCC in the ground electronic state. One should of course note that this prediction was solely based on electronic structure calculation of the stationary points along the reaction path and looking at the similarity of the excited state potential energy surfaces of propyne with that of acetylene reported by Morokuma and coworkers.[11] We also observed less but significant number of trajectories ended in the CH_3 + CCH products channel. There is, however, no experimental evidence of the formation of these products when propyne is excited at 193 nm.

Our calculations show the evidence of roaming mediated nonadiabatic pathways for the elimination of molecular hydrogen from propane at 157 nm.[12] We found that the 1,2-E and 1,3-E molecular hydrogen elimination channels exclusively follow roaming (of a partially dissociated H atom) mediated nonadiabatic pathway ($S_1 \rightarrow S_0$) via conical intersection to the ground electronic state followed by an atomic hydrogen abstraction from another carbon atom in the ground singlet (S_0) state. This is presumably because of the high barriers to the 1,2- and 1,3-molecular hydrogen elimination processes. In the case of 1,2-elimination of molecular hydrogen, initially a hydrogen atom is partially detached from the middle carbon atom of propane in the first excited singlet state (S_1) and moves up to ~ 4 - 5 Å. Then the system comes back to the ground state via a nonradiative process through an avoided crossing or conical intersection in a roaming (of H atom) mediated path. Once the system comes to the ground state a hydrogen atom from one of the terminal carbon atoms is abstracted by the earlier detached hydrogen atom to form molecular hydrogen and H_3CCHCH_2 fragment. A little different dynamics is followed by 1,3- molecular hydrogen elimination from the photoexcited propane at 157 nm. In this process one of the hydrogen atoms from any one of the terminal carbon atoms of propane is partially dissociated followed by a hydrogen atom migration from the middle carbon atom to the terminal carbon atom. The system then comes to the ground electronic state via avoided crossing (or conical intersection) through H-atom roaming mediated process. Finally, another H atom from the other terminal carbon atom is abstracted by the earlier detached H atom to generate H_2 and CH_2CHCH_3 fragment. One should note that the final products for this particular pathway are the same as that of 1,2-elimination process of molecular hydrogen.

We have observed that the 1,1-E and 2-2-E molecular hydrogen elimination channels proceed through three centre synchronous concerted mechanism either adiabatically in the first excited singlet (S_1) electronic state or through the internal conversion $S_1 \rightarrow S_0$ followed by direct two-body fragmentation in the ground singlet (S_0) state, with equal probability. Our trajectory simulations predicted molecular hydrogen elimination with no site specificity showing equal occurrence of 1,1-E and 2,2-E as major channels.

In our photodissociation dynamics study of propane at 157 nm, approximately one-third of the trajectories those resulted in a triple dissociation channel, $CH_3 + C_2H_4 + H$ completed in the ground singlet state following a nonadiabatic path via the C–C and C–H dissociation coordinate conical intersection S_1/S_0.[13] These trajectories lead to $CH_3(1\ ^2A_2'') + C_2H_4(^1A_g) + H$ products, where ground state methyl radical and ground state ethylene are obtained. On the other hand the trajectories that ended in triple dissociation channel following an adiabatic dynamics in the S_1 state producing $CH_3(1\ ^2A_2'') + C_2H_4\ (1\ ^3B_1) + H$, where methyl radical and triplet ethylene are formed in their lowest electronic state via a spin conserving route.

Approximately 17% of atomic hydrogen eliminations after photoexcitation of propane at 157 nm occur through a direct two body dissociation. From our trajectory propagation we found that the trajectories that lead to direct atomic hydrogen elimination generally follow a nonadiabatic path and completed in the ground electronic state. There would be two different dynamical contributions for the H atom elimination of propane at 157 nm. The terminal-H elimination contributes to slow H atoms peaks at ~1.7 kcal/mol, while the internal-H elimination is responsible for the faster H atom product that corresponds to a maximum at ~10 kcal/mol. The low kinetic energy release of the slow hydrogen atom products from the terminal carbons are presumably because of triple dissociation processes. On the other hand, the faster hydrogen atoms are very likely due to direct two-body dissociation process. Our TSH dynamics simulation shows that about 83% of the atomic hydrogen products are from terminal carbons mainly due to triple dissociation channel $C_3H_8 \rightarrow C_2H_4 + CH_3 + H$, only. This finding corroborates the experimental observation of Tonokura et al.[14] Nonadiabatic dynamics plays an important role in atomic hydrogen elimination processes contributing about ~11% out of ~28% of the overall contribution. While nonadiabatic dynamics dominates for the direct two body atomic hydrogen atom elimination, an adiabatic path is preferred (approximately two-third of the trajectories leading to $C_2H_4 + CH_3 + H$) for the hydrogen atom elimination through triple dissociation channel. Our inspection of the individual trajectories indicates that the H atom formations in the first singlet excited state adiabatically are associated with low kinetic energy release. The H atom products resulted through a nonadiabatic path via conical intersection are, on the other hand, related to high kinetic energy release presumably due to more available energy compared to adiabatic dissociation path in the first singlet excited state.

We have studied the photodissociation dynamics of methyl hydroperoxide (MHP; CH_3OOH) at 193 nm.[15] It is a major reservoir/source of HOx radicals at high altitudes.[4] Our dynamics calculations indicates that the formation of OH along with CH_3O, is the dominating channel contributing ~72.7% of the overall dissociation, while ~27.3% H elimination takes place along with formation of $CH_3OO\ (1\ ^2A')$ or $CH_3OO\ (X\ ^2A'')$. In the case of OH + CH_3O products formation we found that adiabatic dynamics dominates by forming OH exclusively in the excited singlet state S_1 that correlates to the ground state products $CH_3O\ (^2E)$ + OH $(^2\Pi)$. On the other hand, both adiabatic and nonadiabatic dynamics are followed in the formation of H + CH_3OO products. In the adiabatic pathway the trajectories start from the first excited singlet S_1 state and remain on the same electronic state throughout the propagation leading to the products formation in the same state. In the nonadiabatic pathway the molecule starting in the first excited state S_1, quickly hops to the ground S_0 state before products formation via the S_1/S_0 conical intersection. While adiabatic dynamics is more dominant one contributing ~24.42% of the overall products formation in the first excited singlet state, S_1, correlating to products $CH_3OO(1\ ^2A')$ + $H(^2S)$, the nonadiabatic dynamics contributes approximately 2.9% via S_1/S_0 conical intersection leading to the products in the ground state S_0, correlating to the ground state products, $CH_3OO(X\ ^2A'')$ + $H(^2S)$. Inspection of the calculated translational energy distribution reveals that most of the OH products have translational energy in the range 70 to 100 kcal/mole. The high average product translation energy indicates that OH elimination due to O-O bond cleavage is a direct dissociation process on a strongly repulsive potential energy surface and takes place adiabatically in the first excited singlet state, S_1. This is consistent with the experimental observation of Huber and co-workers[16] where they have used a cold molecular beam to study the photofragmentation of MHP at 193 nm.

Our recent photodissociation dynamics study of 1-pyrazoline ($C_3N_2H_6$) at 334 nm indicates that two types of S_1/S_0 conical intersections along one of the C-N bond dissociation coordinates drive its decay fully to the ground state nonradiatively, forming trimethylene diradical in the ground singlet state followed by formation of different hydrocarbons, such as cyclopropane, propene, ethylene and methylene.

In the 1-pyrazoline molecule, soon after excitation to the first excited singlet state S_1 in the Franck –Condon region, in the majority of the trajectories (three-fourths of the total trajectories), one of the C-N bonds scission takes place quickly followed by hopping to the ground singlet state S_0 via S_1/S_0 conical intersection. For another one-third of the total number of trajectories, the first C-N bond dissociation takes place comparatively slowly before hopping. In the ground singlet state, the other C-N bond breaks, forming nitrogen molecule and trimethylene biradical as the primary products.

It is found from our trajectory analysis and conical intersection geometry search in the hopping region that there are two different types of conical intersection geometries for 1-pyrazoline promoting surface hopping from the excited singlet state S_1 to ground singlet state S_0. In one of the conical intersection geometries of 1-pyrazoline the unbroken C-N=N moiety remains out of the plane of the three-carbon skeleton, whereas in the other case, the same undissociated C-N=N moiety remains on the same plane of the three-carbon skeleton. The gradient of the former is much steeper compared to the later. Hence, it is anticipated that the population transfer through the former conical intersection is much faster[17] than through the latter. From our trajectory analysis it is found that among these two types of S_1/S_0 conical intersections, about 76 % of the trajectories are deactivated through the steeper conical intersection, and the remaining 24% go through the less steep one.

The highly reactive nascent trimethylene biradical formed in the ground state, S_0, can either isomerize to cyclopropane or it can yield a variety of products such as propene, ethylene, methylene, etc. as follows:

$$\begin{aligned} \mathrm{CH_2CH_2CH_2} + \mathrm{N_2}(\mathrm{X}^1\Sigma_g^+) &\rightarrow \text{cyclopropane } ({}^1A_1') + \mathrm{N_2}\ (\mathrm{X}^1\Sigma_g^+) \\ &\rightarrow \mathrm{CH_3CHCH_2}\,(\tilde{X}\,{}^1A') + \mathrm{N_2}\ (\mathrm{X}^1\Sigma_g^+) \\ &\rightarrow \mathrm{CH_2}\ ({}^1A_1) + \mathrm{C_2H_4}\ ({}^1A_g) + \mathrm{N_2}\ (\mathrm{X}^1\Sigma_g^+) \end{aligned}$$

The major secondary product channel is the formation of cyclopropane which contributes to ~ 77.8% of the overall product formation. The second major contribution of ~12.5% comes from the generation of propene. The remaining ~9.7% of the total product formation yields methylene radical along with ethylene. The cyclization of trimethylene diradical to form cyclopropane is an isomerization process with no barrier and thus the largest fraction of trajectories (~78 %) ended up in this channel. The formation of propene from trimethylene diradical through a [1,2]-hydrogen shift[18] involves a transition state with a barrier of ~17.0 kcal/mol.[19] Therefore, a comparatively smaller number of trajectories (~12 %) lead to this channel. Formation of ethylene (C_2H_4) with methylene (CH_2) from trimethylene diradical is endoergic by ~30 kcal/mol with respect to trimethylene diradical and hence, is least probable to occur. We found only ~10% of the total trajectories resulting in $C_2H_4 + CH_2 + N_2$ products.

In summary, we have demonstrated that nonadiabatic dynamics plays a crucial role in determining product branching of the photofragmentation of small organic molecules. There is a possibility of the contribution of intersystem crossing in the overall photodissociation processes for these molecules. We have, however, neglected this contribution due to inherent weak spin-orbit coupling interactions in small organic molecules which offer too small effect to have noticeable differences.

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