

#ICMolTalks

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Abstract

Experimental and Computational approach towards Chemical Reactivity in the Electronic Ground and Excited states

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Numerous experimental reports have shown that the translational energy distribution profile of NO fragments, following UV photolysis of nitrobenzene, shows bimodal behaviour with slow and fast components.^{1,2} The two components have been ascribed to two distinct nitro-to-nitrite photoisomerization pathways, prior to NO release. The fast and slow components are attributed to a direct elimination channel from the T_1 state featuring an oxaziridine pathway. The slow component, on the other hand, is attributed to NO release through nitro-to-nitrite photoisomerization on the ground electronic state arising either from an oxaziridine ring-type or a NO₂ roaming pathways or both.^{1,2} The NO₂ roaming mechanism originates from the frustrated dissociation of the C–N bond which generates a NO₂ radical that ‘roams’ in the field of phenyl radical and eventually re-orientes and re-combines to form phenyl nitrite (C₆H₅ONO), which subsequently undergoes O–NO bond dissociation to release NO radical with low translational energy.³ In a series of experiments, we have demonstrated intramolecular interaction between the NO₂ group and the rest of the aromatic molecule acts as a pivot to enhance the NO₂ roaming pathway.^{4,5} Additionally, using an appropriate choice of precursors, we have also delineated the oxaziridine and roaming transition pathways. Additionally, the usage of electric field as a descriptor to understand spontaneous proton transfer reactions will also be discussed.⁶

References

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